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## Abstracts

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## ABSTRACTS

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Abstract volume includes presentations of the 12th International Platinum Symposium focusing on different aspects of geology, geochemistry, mineralogy and exploration of various platinum-group element (PGE) deposits and occurrences from over a globe. A variety of presentations cover discoveries and evaluations of mineralized areas, descriptions of the host rocks, characterizations of different platinum-group mineral assemblages, and ideas on the processes that form PGE mineralization.

The materials of the volume are of a broad interest for geologists, earth scientists and students.

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# A KEY QUESTION WITH REGARD TO OUR UNDERSTANDING OF PLATINUM-GROUP ELEMENT DEPOSITS

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**ABSTRACT**. Magmatic sulfide deposits fall into two major groups when considered on the basis of the value of their contained metals, one group in which Ni, and, to a lesser extent, Cu, are the most valuable products and a second in which the PGE are the most important. This paper is concerned primarily with the second group. Since Campbell et al. (1983) drew attention to the "R Factor", the most commonly accepted explanation has been to attribute the difference between the two groups to the amount of magma that a given amount of sulfide has reacted with, high magma/sulfide ratios giving rise to PGE-rich deposits, lower ratios to Ni-Cu dominant deposits. Subsequently, it has been appreciated that many deposits have developed in magma conduits in which sulfides have had the opportunity to interact with successive waves of fresh magma, which has increased the effective R factor of the sulfides (Naldrett, 1997, 1999). Kerr & Leitch (2005) have emphasized that this has been achieved not only by the fresh magma contributing Ni, Cu and PGE to the sulfide, but also, if it is unsaturated in sulfide, dissolving FeS from the existing sulfide, thereby increasing the tenor of the sulfides in the more chalcophile elements, Ni, Cu and particularly the PGE.

Experiments on diopside anorthite melts indicate that at appropriate $fO_2$ (QFM), 1-2 ppb Pt can be expected to dissolve (Borisov & Palme, 1997; Ertel et al., 1999), while most mafic volcanic magmas (including most Bushveld chills, Davies & Tredoux, 1985) contain up to 10-20 ppb Pt. Given that the Merensky Reef contains, on average, about 5 ppm Pt over a 1 m thickness, solubilities of 1-2 ppb would require all of the Pt to be scavenged from a 2500 m column of magma, while solubilities of 10-20 ppb would require it to be scavenged from a 250 m column. Naldrett et al. (2009) showed that the distribution of PGE tenors and Cu/Pd ratio over the Merensky Reef indicated fractional segregation of sulfide from a column of magma no more than 12 m thick. This required Pt solubilities of the order of 100's of ppb.

A number of solutions have been proposed with regard to this enigma. Boudreau & Meurer (1999) have suggested that the PGE in the J-M Reef of the Stillwater Complex is the result of scavenging of PGE from rocks underlying the Reef by upward moving chloride-rich volatiles, with their deposition in sulfide-bearing zones at the crystal cumulate-magma interface. While hydrothermal processes seem to have been active at Stillwater, there is much less evidence for them near the Merensky Reef, and it is difficult to understand how underlying PGE-enhance reefs, such as the P1 and P2 Pseudoreefs can be explained in this way. Naldrett et al. (2009) concluded that the Merensky Reef was the result of at least two waves of very PGE-rich magma attaining sulfide saturation and depositing the sulfides at the Reef horizon. The Platreef, which is regarded as the intrusion of pulses of magma carrying PGE-rich sulfides close to the contact of the Bushveld complex, contains zones over 10 m thick carrying sulfide with uniform tenors in the range of 100-200 ppm Pt (Kekana, 2014, Naldrett et al., 2008); this magma must itself have been highly enriched in PGE. The question arises as to how magma so rich in PGE could have originated. Naldrett et al. (2009) suggested that elevated PGE contents were the result of magma interacting with pre-existing sulfides that had achieved very high tenors through the process of enrichment proposed by Ker and Leitch. How such a PGE-rich magma can be envisaged in the light of existing experimental and observational data remains an open question. Helmy et al. (2013) have documented the presence of nano-scale crystalline platelets with a $PtAs_2$ composition and structure in Pt-rich, As-bearing sulfide melts. It is possible that similar nano-scale particles can develop in mafic silicate melts enriched in As, or possibly Sb, Te or Bi, and account for hyper-solubilties that current models of Reef genesis require, a suggestion similar to that made 20 years ago by Tredoux et al. (1995).

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# SESSION 1

# Magma dynamics, cumulates and ore genesis

**Conveners: Rais Latypov & Steve Barnes**

Session focus. Magmatic ore deposits produced by mafic-ultramafic magmatism (e.g. massive sulphide bodies, chromitite and Fe-Ti oxide layers, platinum-group element-rich horizons) are igneous cumulate rocks that are generated by processes of magma differentiation, crystallization and solidification in crustal chambers. Therefore a key to understanding the origin of these deposits and consequently to developing a better strategy for their exploration is the deep knowledge of physico-chemical processes that govern magma evolution in crustal chambers and conduits. This session will emphasize the physical and fluid dynamic aspects of igneous petrology that bear on three major ore-related questions: where are ore deposits located? how did they get there? and how were they produced? The following fundamental aspects of magmatic processes will be addressed by this session: the relative importance of in situ crystallization versus crystal settling in evolving magma chambers and the origin of layering; the role of thermal and compositional convection in magma differentiation; the effects of compaction and post-cumulus melt migration within the cumulate pile on compositional profiles of magmatic bodies; the interactions between resident melt in the chamber and inflowing magma during chamber replenishment events; and the fluid dynamics and emplacement mechanisms of magmas, crystal slurries and emulsions. This session welcomes field, textural, mineralogical, geochemical, isotopic, experimental and numerical examination of igneous intrusions that provide us with new ideas on how magma chambers and conduits work to produce magmatic ore deposits.

# THE SULFIDE COMAGMAT: MODELING R-FACTOR AND Cu-Ni-PGE TENORS IN SULFIDES FOR MULTIPLE-SATURATED MAGMAS

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**ABSTRACT**. Using a "sulfide version" of the COMAGMAT magma crystallization model (Ariskin et al., 2013), modeling of the geochemical effect of sulfide immiscibility on the evolution of an initially sulfide-undersaturated high-Mg magma has been carried out. These results indicate a much less pronounced depletion of the sulfide liquid in chalcophile elements than is predicted by the commonly used R-factor concept.

Since the pioneering work of Campbell & Naldrett (1979), the ratio of the mass of magma to the mass of sulfides has been considered as one important parameter (R-factor) characterizing the evolution of sulfide-saturated systems and defining the Cu-Ni-PGE tenor of sulfides. The basic equation that links the tenor with the R-factor (1) was derived from mass-balance constraints assuming a binary (magmatic melt+sulfide only) system (2):

$$Y_i^{Slf} = X_i^{Magma} D_i^{Sul/Melt} \frac{R+1}{R+D_i^{Sul/Melt}} \qquad (1),$$

$$f_{Melt} + f_{Sul} = 1 \rightarrow f_{Sul} = \frac{1}{R+1} \qquad (2)$$

The general idea was that due to very high distribution coefficients of the base and noble metals between the sulfide liquid and a silicate melt $D_i^{Sul/Sil}$>>100, the established relationship (1) does not depend upon the presence of other mineral phases, e.g. in a closed system producing some amount of internally generated sulfides (Lesher & Burnham, 2001). For several decades, this postulate underlined the use of Eq. (1) to predict Cu-Ni-PGE tenors in sulfides, as well as for estimates of the volume of silicate magma responsible for the highest-tenor mineralization, including PGE-reefs.

More careful consideration of the problem gave us the conclusion that for multiple-saturated crystallizing magmas Eq. (1) is a simplification, as due to the predominance of crystallizing silicate (±oxides) minerals over sulfides (even assuming $D_i^{Min/Sil}=0$), the silicate liquid is predicted to evolve differently from the case of magmatic melt-sulfide binaries. This is because of the mass-balance constraint (3) that gives rise to the final equation (4) that now accurately describes the behavior of multiple-saturated and sulfide-containing magmas:

$$f_{Min} + f_{Melt} + f_{Sul} = 1 \rightarrow f_{Sul} = \frac{1-f_{Min}}{R+1} \quad (3),$$

$$Y_i^{Slf} = X_i^{Magma} D_i^{Sul/Melt} \frac{(R+1)}{(R+D_i^{Sul/Melt})(1-f_{Min})} \quad (4)$$

The major difference between Eq. (1) and (4) is that the first one results in a very fast depletion of the silicate melt in elements with $D_i^{Sul/Sil}$>>100, whereas Eq. (4) predicts a less significant effect of the sulfide immiscibility because of the low proportion of sulfides in the crystallizing material, commonly < 1 wt.% (Ariskin et al., 2009). These differences become even more pronounced when one considers a more realistic situation of an initially sulfide-undersaturated magma that experienced sulfide immiscibility at some stage of its crystallization. It is supported by the results of modeling equilibrium crystallization for a high-Mg magma proposed to be parental for the Yoko-Dovyren massif. Based on the observed S (0.05 wt.%) and Ni contents, this magma approached S-saturation after ~40% crystallization (Fig. 1). Thus, R-factor (as a by-product of the COMAGMAT calculations), new experimental $D_i^{Sul/Sil}$ for Cu, Ag, Re, Pd, and Os (Mungall & Brenan, 2013), and contents of these

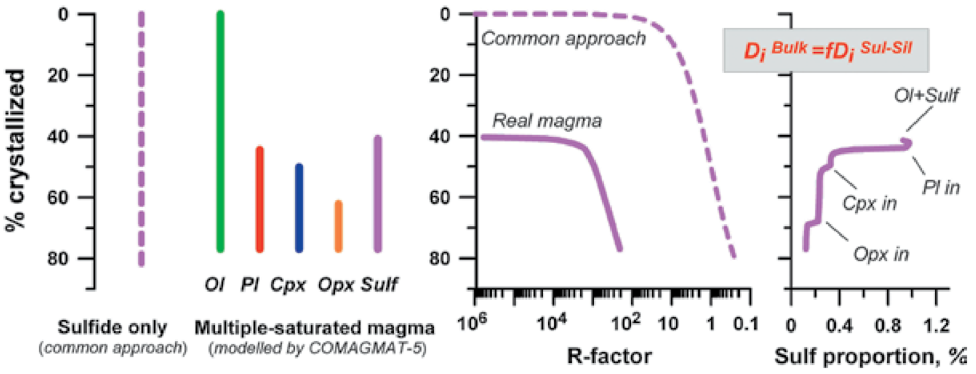

*Fig. 1.* Modeling crystallization sequence, R-factor, and sulfide proportion at crystallization of the Dovyren high-Mg magma. Calculations by Eq. (1) are shown for comparison (see dotted lines)

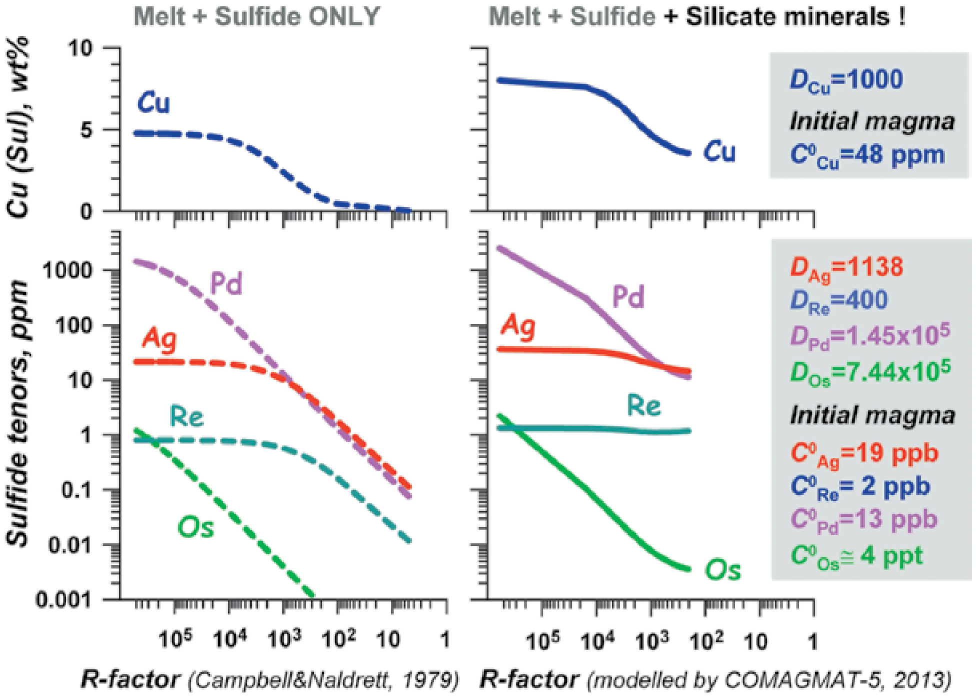

*Fig. 2.* Modeling changes in their tenors of Cu and other chalcophile elements at crystallization of the Dovyren high-Mg magma. Dotted lines are calculations by Eq. (1)

elements in the parent were used to constrain changes in their sulfide tenors as the crystallization proceeds (Fig. 2, plots to the right). Results of similar calculations using Eq. (1) are shown for comparison (Fig. 2, plots to the left).

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# MULTIPLE SULFUR ISOPTOPE INVESTIGATION OF THE STILLWATER COMPLEX: PRELIMINARY RESULTS AND IMPLICATIONS FOR PGE MINERALIZATION

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**ABSTRACT**. Preliminary multiple sulfur isotope studies of rocks from the Stillwater Complex suggest that country rock sulfur was added to magmas that generated the PGE mineralization. $\Delta^{33}S$ values for sulfides from the J-M Reef are anomalous and range from 0.1 to 0.22 ‰. In contrast, low-sulfide anorthosites from the Reef Package show no evidence for contamination by Archean country rock-derived sulfur. Our data are consistent with a process involving the emplacement of isotopically distinct magmatic pulses in the generation of the Reef Package, some of which were sulfide saturated.

The Stillwater Complex in Montana hosts the disseminated-sulfide bearing J-M Reef, located above the Ultramafic Series within what is known as the Lower Banded Series. Proven reserve grades at the Stillwater Mine average 14.4 ppm Pd and 2.8 ppm Pt and those at the East Boulder Mine are slightly lower at 10.3 ppm Pd and 4.1 ppm (SMC, 2013). Specifically, the J-M Reef occurs within the olivine-bearing zone I (OB I) of the Lower Banded Series. Todd et al. (1982) subdivided the olivine-bearing sequence that contains the J-M Reef into four sub-zones and 10 olivine-bearing members. Mine geologists refer to an interval within the first olivine-bearing member (O5b) of Todd et al. (1982) as the “Reef Package” (Corson et al., 2002). Present rock types include dunite, norite, troctolite, and anorthosite, characterized by locally pegmatoidal textures. Models for the genesis of the reef include magma mixing and the attainment of high R-factors to produce PGE-rich immiscible sulfide droplets (e.g., Campbell et al., 1983), leaching of trace sulfides in the Ultramafic Series and concentration at the level of the reef by magmatic fluids (e.g., Boudreau & McCallum, 1992; Boudreau & Meurer, 1999), and the emplacement of PGE-rich magmas that had been upgraded via sulfide dissolution at depth (e.g., Keays & Lightfoot, 2013). The first two models mentioned have not called upon crustal derived sulfur as a component in the genesis of the deposit. The importance of crustal S is well established for the formation of many large sulfide-rich Ni-Cu-PGE deposits, including the PGE-rich deposits at Noril’sk (e.g., Gorbachev & Grinenko, 1973; Grinenko, 1985; Li et al., 2003; Ripley et al., 2010). One of the major reasons that crustal sulfur has not been considered in the genesis of most reef-type deposits is that $\delta^{34}S$ values of sulfide minerals in the Merensky Reef (Li et al., 2004; Penniston-Dorland et al., 2012), the UG2 chromitite (Penniston-Dorland et al., 2012), and the Great Dyke (Li et al., 2008) are close to 0‰ (thought to be indicative of S derived from shallow mantle). In addition, the amount of sulfide in the deposits is relative small and hence large amounts of sulfide have not been proposed (this is true for either the hydromagmatic or magmatic models). The early S isotope work in the Stillwater Complex by Zientek & Ripley (1990) also showed a majority of values close to 0‰, but anomalous values detected as part of that work have re-surfaced in our current work.

In order to better evaluate the possible importance of crustal sulfur in the genesis of sulfide minerals throughout the Stillwater Complex we have initiated a study of multiple sulfur isotopes. Studies of sulfur isotopes in Archean-aged sedimentary rocks have shown that anomalous fractionation between $^{33}S$ and $^{34}S$ that deviated from the relation $\delta^{33}S \approx 0.515\ \delta^{34}S$ may have occurred. The origin of the anomalous fractionation is thought to be a result of photochemical reactions in a low $O_2$ atmosphere (e.g., Farquhar & Wing, 2003), although the precise origin remains a matter of current research. Because there appears to be no process for producing non-zero $\Delta^{33}S$ (deviation from the terrestrial fractionation line with a slope of ~ 0.515) values in high-T magmatic systems, and because the anomalous $\Delta^{33}S$ values cannot be erased (although diluted by mixing), $\Delta^{33}S$ values of igneous rocks provide a means to evaluate possible assimilation of sulfide derived from Archean rocks.

We have measured $\Delta^{33}S$ values for samples of basal zone sulfides and rocks of the Reef Package in the area of the Stillwater Mine. $\Delta^{33}S$ values for massive sulfides in country rocks below the Basal Series range from 0.22 to -0.15‰. Samples with $\delta^{34}S$ values from ~ 4 to 8 ‰ are characterized by negative $\Delta^{33}S$ values. Samples of sulfides from the J-M Reef have $\delta^{34}S$ values from 0 to -1‰. J-M Reef samples, as well as massive sulfides that fall in the 0 to -1‰ range have $\Delta^{33}S$ values from 0.1 to 0.22‰. The $\Delta^{33}S$ values of sulfides from the J-M Reef are significant and indicate that sulfur from Archean country rocks was added to the magmas that generated mineralization. Together with data from country rock-hosted massive sulfides a mixing process is indicated. The relative uniformity of $\Delta^{33}S$ values in the igneous rocks might be taken to indicate that either mixing parameters varied little throughout the emplacement history of the Complex or homogenization was widespread. However, the occurrence of locally elevated, although systematically correlated, $\delta^{33}S$ and $\delta^{34}S$ values in sulfide-enriched layers (massive sulfides, chromitites, J-M Reef with $\delta^{34}S$ values of ~ 4 to 8‰) indicates that isotopically distinct and sulfide-saturated pulses were involved in the mineralization process. Low-sulfide anorthosites from the Reef Package have $\Delta^{33}S$ values of ~ 0.01‰, which suggest little, if any, contamination via Archean country rocks. Although crustal sulfur is detected in many of the Stillwater Complex rocks so far examined, the distribution of values renders it difficult at this time to determine to what extent crustal sulfur was a key for PGE enrichment. Additional analyses of country rocks and intrusive rock types are in progress to complete the stratigraphic sections in both the Stillwater and East Boulder Mine areas and will help to better constrain petrologic interpretations and mixing models.

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# MICROTEXTURAL ASSOCIATIONS OF PRIMARY MAGMATIC Pt PHASES IN Pt-RICH, S-POOR ULTRAMAFIC CUMULATES, AND IMPLICATIONS FOR THE MAGMATIC FRACTIONATION OF Pt FROM Pd

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**ABSTRACT**. Cumulus platinum minerals have been identified in sulfide-poor rocks from two different layered intrusions, using synchrotron-based X-ray fluorescence micro-mapping.

Identifying the mineral hosts of PGEs in silicate rocks and sulfide ores is a challenging process, commonly involving the examination of hundreds of standard petrographic thin sections to identify a handful of grains. X-ray fluorescence micromapping (XFM mapping) using synchrotron radiation (Ryan et al., 2014) has emerged as a powerful technique for rare phase detection, as a result of the penetrating power of the intense x-ray beam and the resulting ability to image small grains within a sample volume, rather than only those much rarer grains that happen to intersect the sample surface.

In this study, we conducted high-resolution mapping using the Maia detector array on the XFM beamline of the Australian Synchrotron at whole thin section scale on a selection of cumulate ultramafic rocks containing anomalous but still low concentrations of Pt, in the range 50-100 ppb. Samples were examined from two localities.

The Mont de Cristal Complex (MdC) is a layered mafic-ultramafic intrusion in Gabon, containing a zone of enriched Pt within heteradcumulate orthopyroxenites (Maier et al., 2012). These orthopyroxenites contain mostly 30-150 ppb Pt, up to 15 ppb Pd, 4 ppb Ir, 9 ppb Ru, 6 ppb Rh, and 3 ppb Au. The highest Pt values occur in a specific layer that can be correlated laterally for several 100 m, having median Pt concentrations around 70 ppb. Platinum and much less abundant Pd show no correlation, there is no associated Ni or Cu anomalism, and only minor traces of magmatic sulfides have been detected within this unit.

The Muang Pha (MP) intrusion in north western Laos (Barnes, 2013) is a recently discovered layered mafic-ultramafic sill, identified on the basis of anomalous Pt concentrations in stream sediment samples. Basal olivine-chromite cumulates consist of variably serpentinised olivine, about 0.5-1% chromite and minor interstitial clinopyroxene. Platinum concentrations in unweathered samples of this unit range from 20 to 100 ppb with a median around 50 ppb.

Maia – XFM mapping revealed approximately 10-25 Pt-rich grains in each of two thin sections of Muang Pha dunite, and five sections of MdC orthopyroxenite. Over 100 grains from the MdC samples were classified according to their immediate geochemical association, and textural relationship to cumulus orthopyroxenes and plagioclase oikocrysts.

The MdC platinum bearing grains occur in the following elemental associations (Fig. 1): as Pt-As rich phases in isolation; (rarely) as Pt-only phases in isolation; as Pt-only phases in close proximity to As-rich phases with no other association; and as Pt-As rich phases in close proximity to Ni-Cu enriched (presumed) sulfides (most abundant). Apparent compositions of Pt-AS phases based on measured peak heights strongly suggest speciation as sperrylite, but other phases cannot be ruled out as S and Te cannot be detected reliably by this method (although Bi can). The great majority of grains, regardless of chemical association, occur at or unresolvably close to the edges of cumulus orthopyroxene grains, regardless of whether these

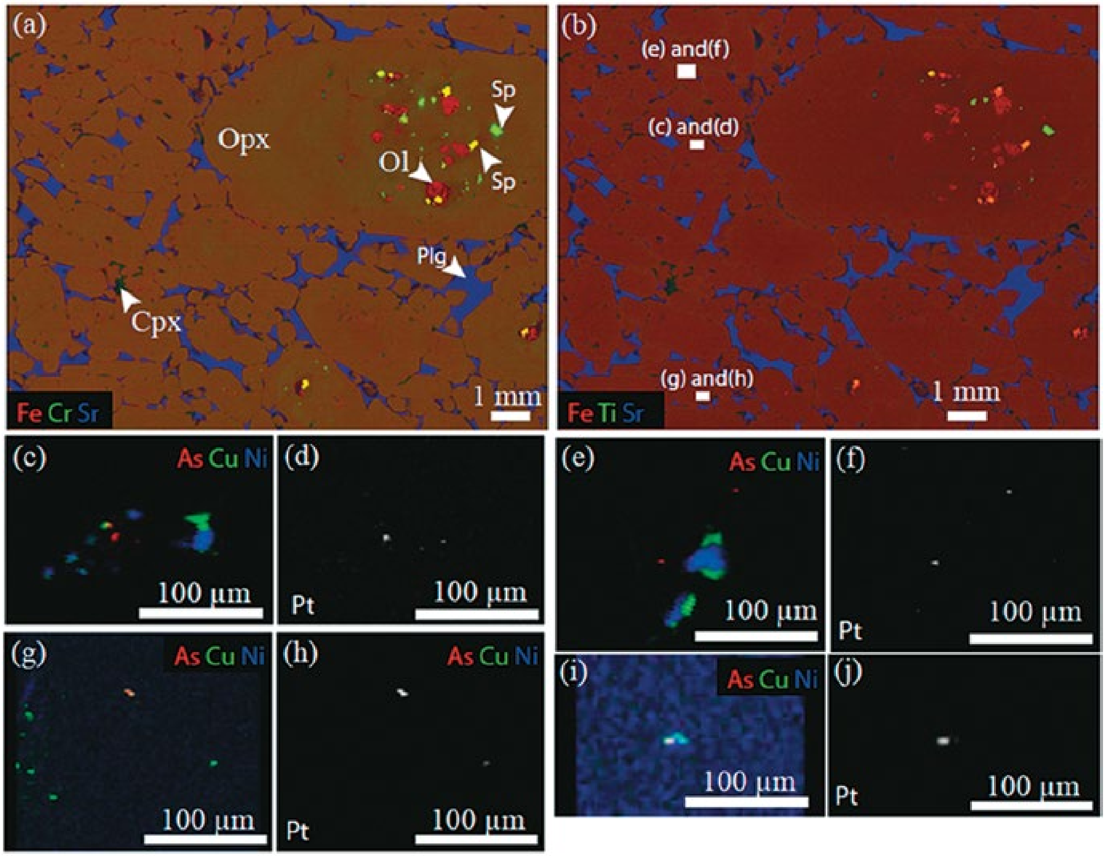

*Fig. 1.* Three element RGB images of MdC sample PX21; indicated elements represented by red, green and blue channels, scaled to maximum values. (a,b) Cr and Ti values are log transformed. Note heteradcumulate texture of plagioclase oikocrysts (blue in both images) interstitial to orthopyroxene. Note subtle complex internal zoning in Cr in some grains (large grain in image a). Light green highlights on (a) are small chromite inclusions, preferentially located in grains showing Cr zoning. White boxes indicate positions of high-detail images (c-h) below. (c-j), three element images for As (red) – Cu (green) and Ni (blue) – light green areas indicate probable presence of Cu-Ni rich sulphide, with corresponding image for Pt (c and d, e and f, g and h, i and j are identical areas). Pt peaks correspond exactly to spatially coincident highs for As, within areas enriched in Cu and Ni, but not exactly matching the Cu-Ni peaks

grains are enclosed in early-formed plagioclase oikocrysts. These grains evidently formed as cumulus phases, probably either arsenide, sulfide or FePt alloy, direct from the magma. The common association with small amounts of sulfide could be due either to subsequent reaction with trapped liquid – unlikely given their presence inside oikocrysts – or due to the precipitation of Pt-As saturated magmatic sulfide droplets that underwent subsequent incongruent dissolution leaving behind a sperrylite enriched residue. Muang Pha Pt grains most commonly occur in the absence of As as micron-scale Pt-only grains on the margins of chromite crystals enclosed in olivine. Mineralogy may have been modified by serpentinisation, but the absence of As or Cu in the association implies precipitation of magmatic FePt alloy directly from the magma.

In both settings, a primary magmatic mechanism for fractionation of Pt from Pd has been caught in the act. At Muang Pha there is no indication of any role of S, while at MdC initial precipitation of extremely Pt-As rich sulfide liquid is implicated.

*Acknowledgments. This research was carried out on the X-ray fluorescence microscopy beam line at the Australian Synchrotron, Victoria, Australia.*

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# CHEMICAL ZONATION IN CHROMITITE DYKES OF THE SOPCHEOZERO DEPOSIT, MONCHEGORSK LAYERED INTRUSION, KOLA PENINSULA, RUSSIA

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**ABSTRACT**. We studied in detail massive chromitite dykes that cut peridotites of the Monchegorsk layered intrusion, Russia. Chromite in these dykes becomes richer in MgO and poorer in FeO from the margins inwards. Individual grains of olivine in host peridotites show a reverse zonation in Fo-content at a distance of at least several cm from the dyke contacts. We interpret the chromitite dykes as accretionary cumulates produced by *in situ* crystallization on microdyke walls from through-flowing chromite-saturated magma. The chemical zonation of massive chromite is most likely due to late postcumulus interaction between chromite in dykes and olivine in adjacent peridotites, mediated through a film of trapped liquid.

We have studied mineralogy and geochemistry of four chromitite dykes that have recently been found in the Sopcheozero deposit. The deposit is located in the south-western part of the so-called Dunite Block that represents the lowermost portion of the Monchegorsk layered intrusion, Kola Peninsula, Russia. The Sopcheozero deposit consists of disseminated to massive chromitite layers interlayered with dunite and peridotite. The chromitite dykes described here are exposed in a quarry in the north-western part of the deposit where they cut a layered sequence of peridotite and chromitite. The dykes are 1.5 cm, 3.5 cm, 11 cm and 18 cm thick and several meters long and are composed of almost monomineralic, cumulate-textured, massive chromitites with less than 5% of interstitial silicate minerals (mostly olivine). The dykes are fresh and show no evidence of late-stage deformation.

Based on about 700 microprobe analyses, chromite in the dykes shows symmetrical inward trends in terms of MgO, FeO and Mg-number ($100^*Mg/[Mg+Fe^{2+}]$), but lack such trends in terms of $Cr_2O_3$, $Al_2O_3$, $Ti_2O$ and Cr-number ($Cr/[Cr+Al]$). From the margins inwards in the 18 cm thick dyke, MgO and Mg-number systematically increase from 8.6 wt.% and 42.7 at.% to 11.1 wt.% and 55.4 at.%, respectively, whereas FeO decreases from 25.8 wt.% to 20.2 wt.% (Fig 1). The characteristic feature of this dyke is the occurrence of a 10 cm wide plateau in its centre in MgO and FeO values (Fig 1). Such a plateau is absent in the smaller chromitite dykes. Individual grains of chromite in dykes are not zoned. Disseminated chromite (1-5 vol.%) in host peridotites has lower Mg-number and Cr-number compared to chromite from the dykes (Fig. 1). This likely reflects a reaction of disseminated chromite with a high amount of intercumulus melt in peridotite (Roeder & Campbell, 1985). It should be noted that olivine (about 600 microprobe analyses) in host peridotite shows a remarkable reverse zonation in Fo-content that is observed at a distance of, at least, 3-4 cm from both contacts of dykes. Fo-content in olivine grains commonly increases from 92.5-93% in the cores towards 95-96% in the rims. The elemental mapping and compositional profiles indicate that a reverse chemical zonation in olivine grains is present regardless of whether they occur in contact with chromite or olivine. Olivine grains have a reverse zonation even if they are completely surrounded by other olivine grains.

We suggest that the chromitite dykes are most likely flow-through channels for chromite-saturated magma that have been periodically refilling the overlying reservoir of the evolving magma chamber. The through-flowing magma crystallized chromite along sidewalls of channels forming *in situ* accretionary cumulates (a similar mechanism is proposed for the formation of dunite dykes in ophiolite complexes, e.g. Maaløe, 2005). The chemical zonation of chromite in massive chromitite dykes (in terms of MgO and FeO) and reverse zonation of olivine in host peridotites (in terms of Fo-content) appears to be most consistent with a late-stage interaction between

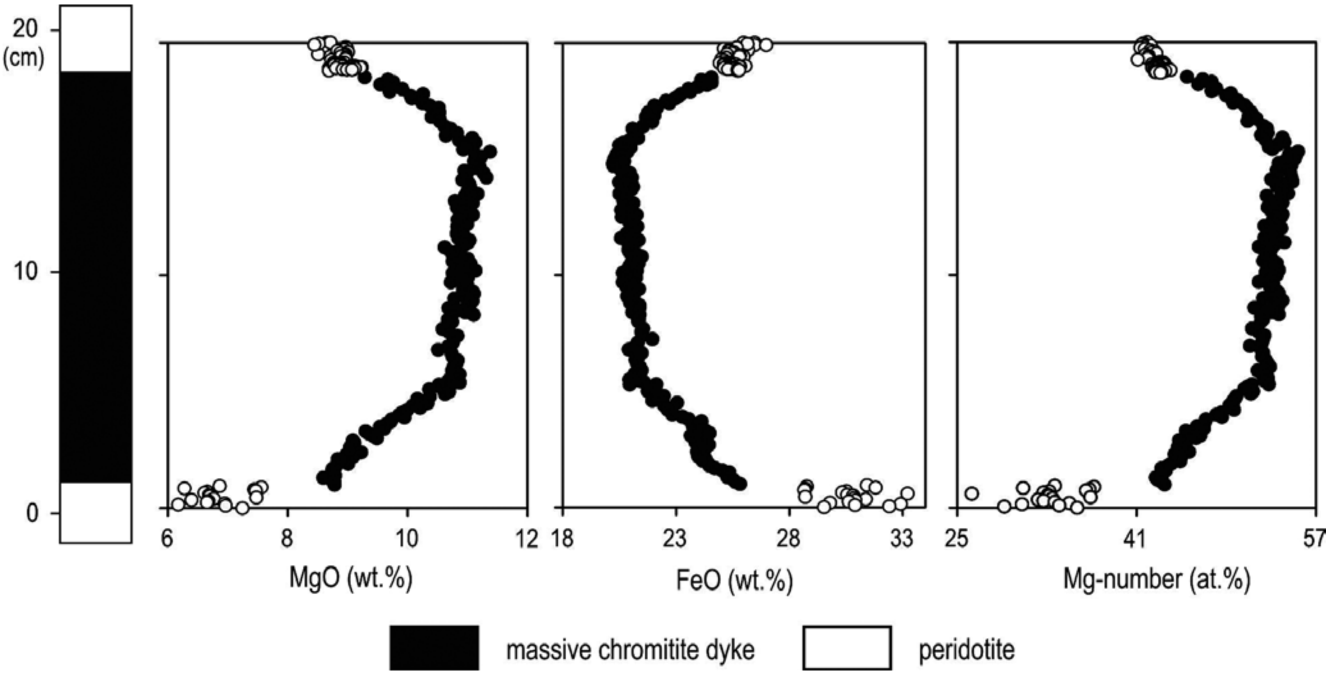

*Fig. 1.* Microprobe data for chromite across a 18 cm thick massive chromitite dyke. Solid circles – chromite in a chromitite dyke, open circles – disseminated chromite in host peridotite

chromite and olivine (Roeder et al., 1979). The problem, however, is that a solid state re-equilibration is a very slow process that operates at micro- to millimetre scale and only directly at olivine-chromite contacts. In contrast, in our case the marginal portions of dykes showing a chemical zonation in chromite are up to 5 cm thick (Fig. 1) and the adjacent parts of peridotite revealing a reverse zonation in olivine are, at least, 3-4 cm thick. Most likely we are dealing here with a distant chemical exchange between marginal parts of massive chromitite dykes (that supply MgO and consume FeO) and olivine in adjacent peridotite (that consumes MgO and supplies FeO). The exchange reaction could probably be accomplished via thin films of fluid-rich trapped liquid during a postcumulus stage. The driving force for this reaction is likely a change of thermodynamic properties of the spinel and olivine solid solutions with falling temperature (Irvine, 1965; Roeder et al., 1979; Barnes & Jones, 2013).

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# DYNAMICS OF INTRUSIVE Ni-Cu-PGE DEPOSITS: ENTRAINMENT, ASCENT AND BACKFLOW OF SULFIDE LIQUIDS

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**ABSTRACT**. We discuss how sulfide liquids formed at deeper levels of crustal-scale mafic-ultramafic magma flow networks are transported, concentrated and re-mobilized at high crustal levels to form intrusion-hosted Ni–Cu–PGE sulfide deposits.

Sulfide liquids that precipitate from silicate magmas after sulfide saturation represent a volumetrically small portion of mafic-ultramafic magmatic systems, yet they are responsible for the formation of intrusive Ni–Cu–PGE sulfide deposits. Compared to silicate melts, immiscible magmatic sulfide liquids have lower viscosities (by 1 to 3 orders of magnitude), higher densities (>1500 kg/m$^3$ higher) and lower solidus temperatures (~150°C lower, depending on their composition). These properties hinder the withdrawal of sulfide liquid from magma staging chambers and its ascent to higher structural levels, and allow for late-stage mobility and downward movement through existing magma conduits and into country rocks by percolation along grain boundaries and fractures.

Prior to emplacement towards higher crustal levels, sulfide liquid will have a tendency to accumulate and pond at the bottom of staging chambers. Later mobilization and upward or lateral withdrawal of sulfide can occur by viscous entrainment within relatively buoyant (mafic-ultramafic) magma. Analytical solutions and laboratory experiments applied to the low viscosities, high densities and relatively high volumetric flow rates expected within mafic melt-sulfide liquid systems predict that significant vertical draw up of sulfide liquid can occur within ascending mafic magmas at high, yet realistic flow rates (10-1000 m$^3$/s), under transitional to turbulent flow regimes. At lower flow rates and within non-inertial regimes draw up is hindered by interfacial tension. There are several possible fates for sulfide liquid after it is entrained:

1) it can be pulled back down by gravity into the lower staging chamber;

2) it can break down into filaments and droplets that are carried to higher levels of the system and re-aggregate in structural traps to form massive sulfide bodies;

3) it can be transported to higher levels as a coherent mass where it will occur as late-stage injections of sulfide cutting across older silicate magma phases.

There is evidence that both (2) and (3) have occurred in Ni–Cu–PGE deposits such as Voisey's Bay (Labrador, Canada), Eagle (Michigan, USA), and Sudbury's offset dykes. However, in these systems there are also strong indications both within magma conduits and in country rocks that sulfide liquids have migrated downwards after aggregating or being emplaced at higher levels. The dynamics of such backflow and sulfide percolation are analogous to the behavior of dense non-aqueous phase liquids (DNAPL) in near-surface environments. In fractured systems, sulfide backflow is strongly controlled by the column height of the dense liquid. Because dense fluids flow downwards, this column generates a higher vertical body force when the down-flowing liquid network remains interconnected. The fluid must overcome the capillary pressure to enter a fracture, and because this is inversely proportional to fracture width, progressively thinner fractures can be intruded as a body of dense fluid percolates downwards. This process, along with late stage backflow of sulfide liquid into mushy silicate magma hosted within intrusions, can explain the presence of thin (cm to m sized) massive sulfide injections into wall rocks as well as larger bodies associated with structural complexities in conduits as observed in some deposits.

# DISTRIBUTION OF PGE THROUGHOUT THE MIRABELA COMPLEX, BRAZIL: CONSTRAINTS FOR THE ORIGIN OF THE Ni-Cu-PGE MINERALIZATION

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**ABSTRACT**. Three distinct PGE-enriched zones occur in specific stratigraphic positions of the Mirabela Complex (MC). Stratigraphic, petrological and geochemical results of the layered rocks and PGE-rich intervals suggest that these zones originated from a single parental magma during emplacement and fractionation of the mafic-ultramafic intrusion. Distinct PGE tenors and Pt/Pd and Cu/Pd ratios are interpreted as the result of fractionation processes within the layered intrusion.

The MC (~ 8 km$^2$) is part of a cluster of tardi-orogenic Paleoproterozoic mafic-ultramafic intrusions located in the southern portion on the Itabuna-Salvador-Curaçá mobile belt. The MC has an ellipsoidal shape with a NW trending major axis. Steep dipping layering throughout the intrusion is interpreted as the result of post crystallization tectonism. The stratigraphy of the MC (Fig. 1) consists of a Lower Border Group (LBG), an Ultramafic Zone (UZ), a Mafic Zone (MZ) and an Upper Border Group (UBG). Similar rock types occur throughout the stratigraphy, such that stratigraphic subdivisions are based on fractionation trends (Fig. 1).

The world-class Santa Rita Ni-Cu-PGE deposit consists of disseminated sulfides hosted within the cumulate pile of the MC. Economic deposits of Ni-Cu sulfide located within the stratigraphy of layered intrusions are uncommon, a feature emphasized in papers describing the Ni-Cu ore (Barnes et al., 2011) and PGE minerals (Knight et al., 2012) of the Santa Rita deposit.

Apart from PGE associated with the Santa Rita deposit, two additional PGE-enriched zones occur in specific stratigraphic positions of the MC (Fig. 1). The lowermost PGE enriched zone, denominated footwall zone, consists of sulfide-poor dunite located dozens of meters below the Santa Rita ore. This zone is characterized by low S contents (<100 ppm), high Pd/Pt ratio (>1) and distinctively low Cu/Pd ratio (<1000). The footwall zone has highly variable Pt+Pd contents, which reach few ppm in thin and discontinuous intervals, but average 300 ppm in an interval up to 70 meters thick in the central portion of the MC. Olivine composition in dunite and harzburgite of the upper portion of the UZ show progressive upward fractionation ($Fo_{86}$ to $Fo_{88}$).

PGE contents associated with the Santa Rita Ni-Cu sulfide ore (Fig. 1) is characterized by high sulfide contents (usually >0.5 wt.%), irregular but systematic positive correlation of Pt+Pd and S contents, low Pd/Pt ratios (< 1) and higher Cu/Pd ratio ($10^4$-$10^6$). Pt and Pd tenors decrease and Pd/Cu ratios increase irregularly but progressively from the base to the top of the Santa Rita ore zone. The Santa Rita ore has highly variable Pt+Pd contents (up to few ppm) and average of about 200 ppm for the total mineral resources of the open pit. The ore zone is located within the progressive transition from dunite, harzburgite, orthopyroxenite and wesbsterite, a characteristic feature of the upper portion of the UZ. Opx compositions within the upper portion of the UZ and lower portion of the MZ indicate a progressive upward fractionation ($En_{87}$ to $En_{77}$) with minor reversals.

The PGE interval associated with base metal sulfides of the Peri-Peri zone is located in the UBG (Fig. 1). This Ni-Cu sulfide ore zone is located close to the upper intrusive contact of the MC. PGE contents associated with the Peri-Peri zone (Fig. 1) are characterized by high sulfide contents (usually >0.5 wt. %), irregular but systematic positive correlation of Pt+Pd and S contents, intermediate Pd/Pt ratios (~ 1) and Cu/Pd ratio ($10^3$-$10^5$). Pt and Pd tenors decrease and the Pd/Cu ratios increase

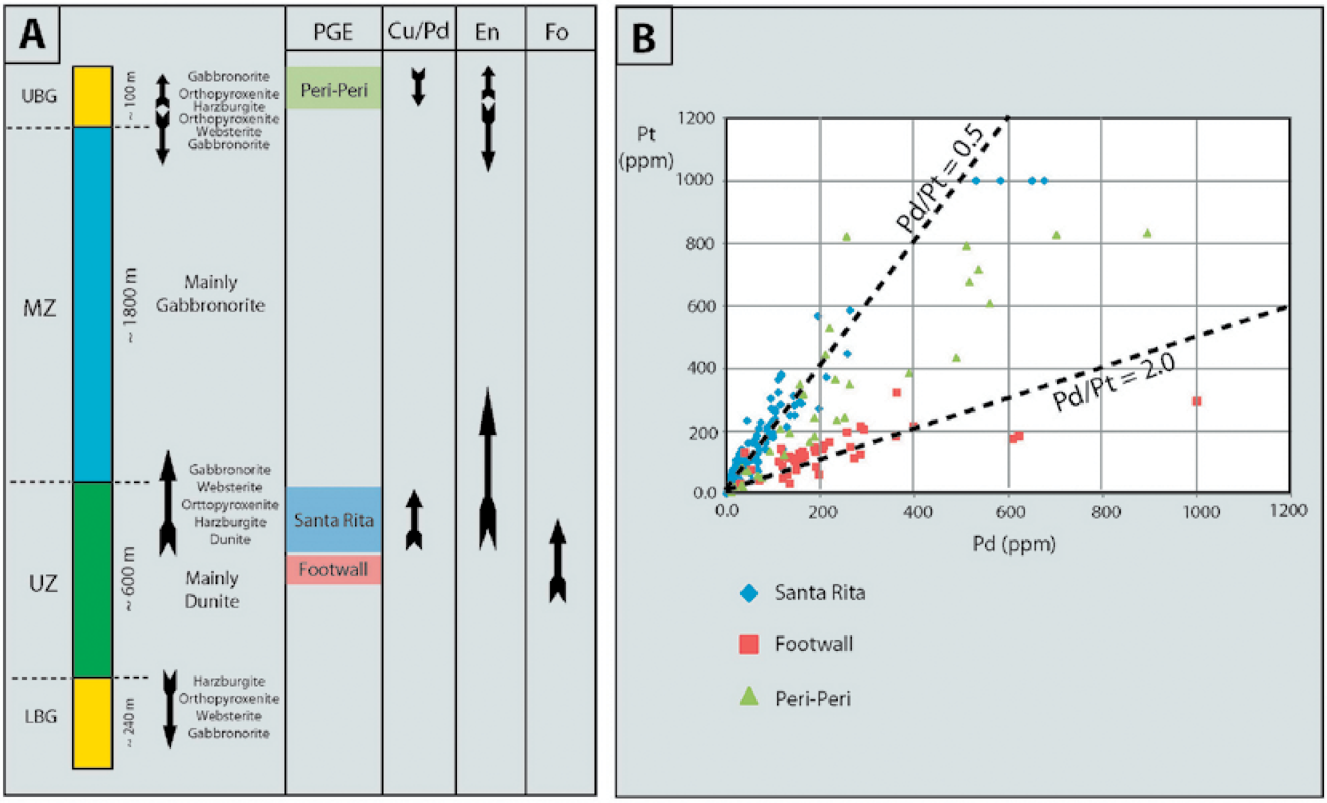

*Fig. 1.* A) Schematic stratigraphy of the Mirabela Complex. B) Pd-Pt plot for representative drill cores. See text for explanation

irregularly but progressively from the upper contact toward the inner portion of the intrusion. The Peri-Peri zone ore has highly variable Pt+Pd contents (up to few ppm) and average of about 150-200 ppm for the total ore resources. Opx compositions within the UBG indicate a sharp reversal adjacent to the upper contact ($En_{74}$ to $En_{87}$) followed by progressive fractionation ($En_{87}$ to $En_{68}$) toward the inner portions of the layered intrusion.

Sulfide-poor PGE mineralization are described in sections of variably fractionated layered intrusions (MC, Great Dyke, Serra da Onça, Skaergaard). Some of these examples of sulfide-poor PGE mineralization are followed upwards by sulfide-bearing PGE mineralization and display significant vertical zoning of metals. These features have been interpreted as the result of different processes, which usually includes the combined effect of early segregated sulfides (characterized by extremely high PGE tenors) together with the ease with which the PGE concentrated within segregating sulfide droplets. In the MC, a significant amount of PGE with higher Pd/Pt ratio (> 1) was originated in the footwall zone. The lower Pd/ Pt ratio observed in the sulfide-bearing Santa Rita ore is therefore likely to result from an early depletion of Pd (relative to Pt) in the fractionated magma. The Peri-Peri zone located in the UBZ is characterized by intermediate Pd/ Pt ratios (~ 1). This zone is interpreted to represent a sulfide liquid segregated from a silicate liquid close to the composition of the parental magma. Distinct PGE tenors and Pt/Pd and Cu/Pd ratios throughout the stratigraphy of the MC are interpreted as the result of fractionation processes within the layered intrusion.

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# SLUMPING SLURRIES AND KINETIC SIEVING: AN EXPERIMENTAL STUDY ON THE CHROMITE CUMULATE FORMATION

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**ABSTRACT**. A series of analogue experiments was conducted to simulate the slumping of semi-consolidated cumulates in an unstable magmatic chamber. The starting material was a mixture of particles with different size and density immersed in a box fully filled with glycerin. Experiments were conducted at different inclination angles with two different proportions of particles. During the run, particles became segregated with larger less dense particles at the top of the flow and smaller denser ones at the bottom. Moreover, levees and flow fronts typically found in granular flows are observed in deposits and a particle velocity gradient is observable. The morphology of deposits was then compared to several naturally occurring analogues found in layered intrusions.

Processes leading to the layered intrusions have been extensively debated for many decades but are still poorly understood. Numerous models proposed over the years have focussed on geochemical or physical anomalies associated with fractional crystallization in the magma chamber to form chromitite layers (Irvine, 1975, 1977; Murck & Campbell, 1986; Lipin, 1993). However, recurrences of such anomalies to form chromite-rich horizons at regular intervals, in very large magma chambers such as the Bushveld Complex, are still problematic. Maier et al. (2013) proposed a model based on a physical process in which magmatic layering forms through the slumping of semi-consolidated cumulate pile forming crystal slurries leading to sorting of crystals based on density and/or size differences. Using analogue modelling, we have identified the required conditions leading to the sorting of particles from a homogeneous mixture.

For our experiments we use a perplex box fixed on an inclinable apparatus. In order to accurately model crystals in a magmatic chamber, the box is completely filled with an ambient fluid (glycerine) representative of tholeiitic basaltic magma with 1.8% water at a temperature of 1282 °C (Irvine, 1975). Crystals within the melt are simulated with a mixture of particles with three different sizes and densities: silicone balls, polyacetal balls and glass beads. These particles are selected to replicate plagioclase, pyroxene and chromite crystals, respectively. Two series of experiments with different proportions of glass beads (also the smaller particles) are conducted: 1) seven experiments with 5 vol.% black silicone balls, 5 vol.% white polyacetal balls and 0.5 vol.% red glass beads; and 2) four additional experiments with 5 vol.% black silicone balls, 5 vol.% white polyacetal balls and 10 vol.% red glass beads to better visualize the glass bead deposits in the box.

Following the downslope flow of particles in glycerine (Fig. 1), the morphology of the deposits is studied. Four principal results are observed:

1) Flow begins once the angle of repose is reached. The deposits show a segregation of particles: red smaller denser ones (representing chromite) comprise the base and are then overlain by white medium size particles (representing pyroxene), which are then in turn overlain by black larger lighter particles (representing plagioclase) on the top. The segregation mechanism is fast and effective but dependent on the inclination angle.

2) In all experiments, final deposits are characterized by three regions that evolve with time, slope and the amount of smaller particles:

  a) the front flow contains the greatest concentration of larger particles;

  b) the body of the flow directly behind the flow front is thicker than the rest of the flow;

  c) particle concentration decreases significantly in the tail of the flow. Additionally, in certain experiments we observe the formation of levees composed of larger particles.

3) The length of the final deposit and the front flow are directly related to the angle of inclination.

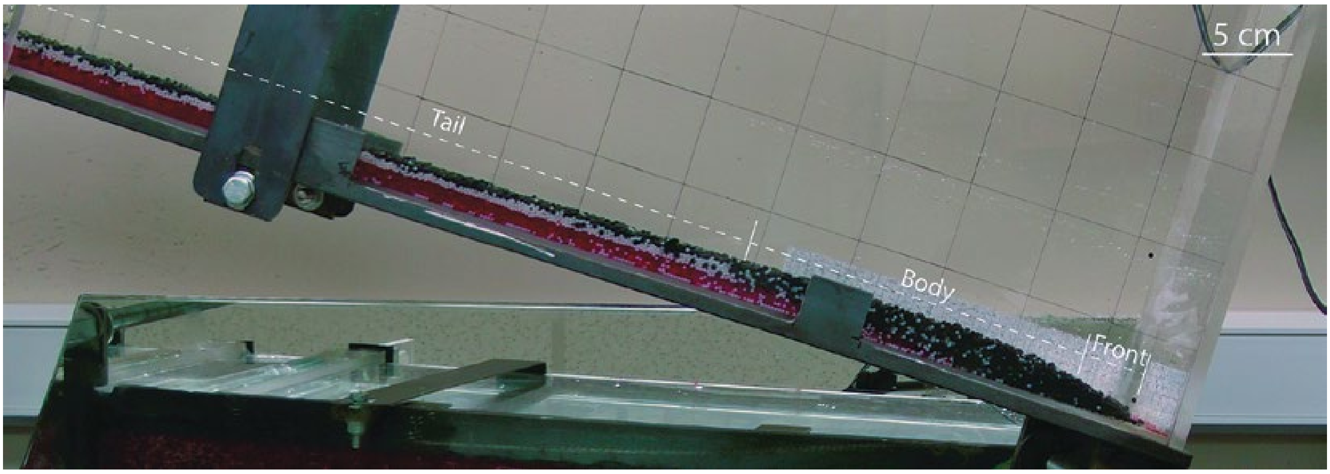

*Fig. 1*. Final deposit of experiments MB026 with 10 vol.% of red smaller denser particles

At smaller angles, the deposit is very thin but very elongated. When the slope is increased, the relative size of the front flow increases and the length of the final deposit decreases.

4) The larger particles move downslope more quickly than smaller ones. The proportion of the smaller particles affects the velocity of larger particles.

During flow, the smaller particles percolate through the voids between the larger particles in a process known as kinetic sieving. Through these experiments, we observe that the efficiency of this mechanism depends on the angle of inclination, the proportion of smaller particles (i.e. the speed and thickness of the flow) and the relative size and shape of particles (e.g., Makse et al. 1997; Kleinhans 2004; 2005). The morphology of the final deposits observed in experiments compare favorably to some natural examples. In the case of relatively flat-lying magma chambers (small inclination angles), the deposits would be consistently very thin over a long distance – similar to the observed morphology of the Bushveld Complex in South Africa. For a magma chamber with inclined walls, deposits would be thinner in proximity to the walls and would become thicker toward the centre of the chamber. This geometry is observed within intrusions such as the Great Dyke in Zimbabwe (Wilson & Prendergast, 1989) or in the Kemi Complex in Finland.

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# COMPOSITION OF Fe-Ti-OXIDES FROM THE JURASSIC DUFEK LAYERED MAFIC INTRUSION, ANTARCTICA: FIRST RESULTS OF MICROPROBE ANALYSIS

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**ABSTRACT**. The mainly gabbroic Dufek intrusion, Antarctica, is characterised by an association of platinum-group element (PGE) enrichment (up to ~ 800 ppb) with Fe-Ti oxide-rich cumulates in the upper part of the 8-9 km thick cumulate pile. Our first results of microprobe analysis of Ti-magnetite indicate positive correlations between Ti, V, Cr, Ni, Mg and Al that mainly follow differentiation trends with upward decreasing element abundances. Deviations from the observed trends are shown by individual cumulates from the cyclic sequence of the Stephens Anorthosite Member that hosts the majority of the PGE-enriched gabbros and Ti-magnetitites. The deduced changes in redox conditions and the significant changes in magma composition due to extensive oxide crystallisation are proposed to have partly triggered sulphur saturation and thus, the fractionation of the PGE from the highly evolved residual melt.

## INTRODUCTION

Despite the increasing knowledge about magmatic ore deposits related to layered mafic-ultramafic intrusions, it is still a matter of debate which physico-chemical processes are crucial for the formation of cumulate rock sequences within crustal magma chambers and thus, for the generation of stratiform ore deposits. A large number of well-known reef-type PGE occurrences are found within the lower third of layered complexes where the oxide mineral associated with the PGE enrichment is chromite. In contrast, there is a smaller number of intrusions with enrichment of PGE related to late-stage Fe-Ti oxide cumulates in the upper part of the cumulate sequences. Among the latter, one of the less-known examples is the Jurassic Dufek intrusion in Antarctica. The 8 – 9 km thick stratiform sequence consists mainly of layered gabbroic cumulates with minor interlayers of anorthosites, pyroxenites and magnetitites. This sequence has been proposed to be generated by a single major intrusive event forming a mainly *in situ* differentiated cumulate series with systematically changing compositions of the cumulus minerals pyroxene and plagioclase. As shown in our previous study, significant enrichment of PGE up to ~ 800 ppb is indicated in the lower part of the upper third of the entire cumulate profile. This so-called Stephens Anorthosite Member is composed of a cyclic sequence of Ti-magnetite-bearing gabbros and anorthosites that contains thin layers, laminae and lenses of Ti-magnetitites. It comprises the most prominent accumulation of Fe-Ti oxide minerals observed in the whole intrusion so far. However, the PGE do not vary systematically with the stratigraphy, and the degree of PGE enrichment in oxide-bearing gabbros and oxide layers varies considerably. Due to the overall rareness of sulphides, the PGE-enriched cumulates are difficult to distinguish from the PGE-poor host rocks. Hence, understanding the formation of the cumulus layering, especially the origin of rhythmical layering including repetitive oxide layers is important to understand the fractionation behaviour of the PGE and their enrichment associated with oxide accumulation at advanced stages of differentiation of the tholeiitic Dufek intrusion.

## RESULTS

We have analysed the trace element composition of Fe-Ti oxides in selected oxide-bearing samples from different stratigraphic levels of the exposed upper part of the Dufek intrusion. These samples were previously studied for their PGE chemistry and mineralogy. Their modes of cumulus oxide minerals range from 5 vol.% in gabbros to nearly 100 vol.% in thin layers of pure magnetitite. The oxides present are mainly Ti-magnetite accompanied by varying but generally low portions of co-existing, homogeneous ilmenite. Ti-magnetite is largely characterised by exsolutions of ilmenite; the abundance, thickness and patterns of the ilmenite lamellae vary strongly between different samples. Analyses of the composition of the different oxides present were performed on polished rock sections using a JEOL JXA 8230 electron microprobe equipped with five wavelength-dispersive spectrometers. Operating conditions were 15 kV acceleration voltage, 100 nA sample current, 10 μm beam size and 20 to 30 seconds measurements on peak and 10 seconds on background. Calibration and monitoring the data quality was done using a range of natural and synthetic standards. Our first results show largely homogeneous compositions of oxides within individual samples without noticeable core to rim zonation of individual oxides. For Ti-magnetite from different samples, we observe largely positive correlations between Ti, V, Cr, Ni, Mg and Al concentrations (max. concentrations: 18 wt.%, 1.8 wt.%, 0.6 wt.%, 0.08 wt.%, 1.14 wt.% and 2.1 wt.%, respectively) that mainly tend to decrease upward with stratigraphic height. However, deviations from the overall trends are observed for individual but not all elements analysed for cumulates within the rhythmically layered succession of the Stephens Anorthosite Member that contains the oxide-bearing cumulates with the most enriched PGE concentrations found so far. Within this sequence, compositional differences exist for Ti-magnetite from oxide-bearing gabbros and from nearly pure oxide layers from similar stratigraphic positions indicated by higher Ti, V, Mg and Al contents in the Ti-magnetitite.

## DISCUSSION AND OUTLOOK

The trends of composition of Ti-magnetite from gabbro cumulates and oxide layers from different stratigraphic units within the upper part of the Dufek intrusion can be largely attributed to magmatic differentiation by both gravity driven crystal settling and *in situ* crystallisation. Deviations of individual samples from the observed trends as well as differences in Ti-magnetite composition of pure oxide layers and of the hosting oxide-rich gabbros may indicate changed distribution coefficients of trace elements sensitive to oxygen fugacity due to changes in the redox conditions during the crystallisation of increased amounts of oxides. Changing redox conditions and considerably changing magma composition in the course of oxide fractionation can be considered as being crucial in triggering the sulphur saturation of the evolved residual Dufek magma. This underlines the interpretation that the PGE are enriched during an extensive differentiation history within the crustal Dufek magma chamber under mainly S-undersaturated conditions until the onset of significant oxide fractionation. Further analyses of Fe-Ti oxide composition from additional cumulate rocks, especially of those with elevated PGE-contents, will be performed to verify the compositional variations observed so far. The results will be evaluated considering further magmatic processes to understand further phenomena, e.g. the small compositional reversals reported for cumulus silicates, the repetitive occurrence of cumulates with elevated PGE in different stratigraphic levels or the formation of cyclic cumulate sequences.

# THE ORIGIN OF IMMISCIBLE SULPHIDE INCLUSIONS IN THE CONTAMINATED AND Ni-Cu DEPLETED LAVAS FROM DISKO AND NUUSSUAQ (WEST GREENLAND)

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**ABSTRACT**. The West Greenland Igneous Province consists approximately of 3 km thick sequence of picrites and variably crustally contaminated lavas. The contaminated lavas are Ni and Cu depleted and carry sub mm-sized sulphide inclusions. This indicates that sulphur saturation occurred in response to increased $SiO_2$ due to crustal contamination, which led to the scavenging of Cu and Ni by magmatic sulphides. The West Greenland Tertiary Igneous Province is thus a possible analogue to the Siberian Traps and Noril'sk, because of its geological setting and potential for hosting massive Cu-Ni, and PGE sulphide deposits (e.g., Lightfoot & Haqkesworth, 1997, Lightfoot et al., 1997, Keays & Lightfoot, 2007).

These lavas erupted through and into the sedimentary Nuussuaq Basin approximately 62-60 Ma ago during the opening of the Davis Strait and the arrival and early melting of the proto-Icelandic mantle plume. On Disko and Nuussuaq the lower volcanic sequence (Vaigat Formation) is characterized by a high proportion of Mg-rich picrites with a significant volume of crustally contaminated, Ni-Cu-PGE depleted lavas (Larsen & Pedersen, 2009). The most strongly contaminated units within the Vaigat Formation are the Asuk and the Kûgánguaq members. Relative to the uncontaminated picritic lavas, the contaminated lavas have high $SiO_2$ and $K_2O$ combined with low MgO, FeO and CaO in addition to being Ni-Cu-PGE depleted (Larsen & Pedersen, 2009).

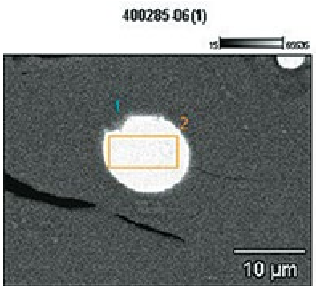

*Fig. 1.* Spherical sulphide inclusion

The presence of immiscible sulphide droplets in contaminated lavas (Pedersen, 1985 and this study); an occurrence of massive Ni sulphide mineralization within the Igdlukngauaq dyke (Pauly, 1958); and the reports by Ulff-Møller (1985, 1990, 1991) of a number of gabbrodoleritic to picritic intrusions located in the Disko and Nuussuaq area with Ni, Cu and PGE mineralisation, demonstrate that sulphide segregation played a major role in the genesis of the Ni-Cu-PGE depleted lavas.

We have initiated a study of sulphide inclusions in the crustally contaminated Ni-Cu-PGE depleted lavas from the Asuk, Kûgánguaq, and Tunoqqu Members to characterize their chemical compositions and in turn to understand sulphide melt saturation and segregation processes and their implications for the formation of economic sulphide deposits in the volcanic conduits. The sulphide inclusions are analyzed by scanning electron microscope and electron microprobe.

Two morphologies of sulphide inclusions are indentified. Spherical sulphide inclusions are present in lavas of all of the major contaminated lava units, namely the Asuk, Kûgánguaq, and Tunoqqu members (Fig. 1). These range in size from 5 to 20 µm, but are typically around 10 µm. Clusters of multiple spherical sulphides of 20 to 100 µm in size are documented from andesite glass of Asuk member on Nuussuaq (Fig. 2). Based on compositional variations in sulphide inclusions, their segregation history will be constrained and lines to the ongoing exploration for Ni-Cu-PGE sulphide deposits will be drawn.

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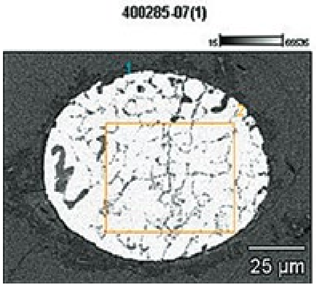

*Fig. 2.* Cluster of multiple spherical sulphides

# THE EFFECT OF MAGMA-SEDIMENT INTERACTIONS ON THE REDOX STATE AND VOLATILE CONTENT OF THE MAGMA AND THEIR IMPLICATIONS FOR ORE GENESIS

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**ABSTRACT**. We show by gas-melt thermodynamic modeling how the interaction of mafic and ultramafic magmas with volatile-rich sedimentary rocks (e.g. evaporitic or organic matter-bearing rocks) can substantially (i) modify the redox state of the magma, (ii) increase its volatile content, and consequently (iii) impact ore genesis. The assimilation of carbonaceous sediments induces a strong reduction of the magma redox state and can eventually trigger graphite and native iron saturation in a primitive magma. The incorporation of sulfates oxidizes the magma and increases its sulfur content. Extreme assimilations (> 5 wt.% $CaSO_4$) can eventually lead to sulfate saturation in the magma. Combined assimilation of sulfates and then carbonaceous sediments, can trigger massive sulfide production as a consequence of S incorporation into the magma, followed by a substantial reduction of the magma redox state. Applications of our modeling to some natural cases (e.g. the native iron ores of the Siberian Platform, and the Noril'sk-Talnakh district) will be presented.

Redox conditions in magma are widely interpreted as internally buffered and closely related to that of their mantle source regions. We use thermodynamic calculations to show that high-temperature interactions between magma and volatile-rich sedimentary rocks can lead to a dramatic change in the magma redox state, and significant departure from that of the original source. We show how this change can crucially impact ore forming processes associated to the emplacement of mafic and ultramafic magmas in the crust.

Our modeling is based on gas-melt thermodynamic calculations that take into account S-H-O-C gaseous species at temperatures and pressures in equilibrium with mafic liquids (Iacono-Marziano et al., 2012). Both homogeneous (gas-gas, and melt-melt), and heterogeneous (gas-melt) equilibria are considered. The assimilation of sulfates by the magma is simulated by addition of $SO_3$, while the assimilation of carbonaceous material by addition of CH or $CH_2$.

The assimilation of carbonaceous sediments induces a strong reduction of the magma redox state (Iacono-Marziano et al., 2012). Addition of very low amounts of organic matter (0.2 wt.% CH) can decrease the $fO_2$ of the magma of more than 3 log units, and trigger graphite saturation at pressures > 40 MPa in a primitive magma. Lower pressures and higher amounts of assimilation are required to saturate the magma in native iron, in addition to graphite. The application of our modeling to the case of the native iron ores of the Siberian Platform (Ryabov & Lapkovsky, 2010) suggests that these ores formed at pressures lower than 10 MPa as a consequence of the assimilation of > 0.5 wt.% CH. The assimilation decreased the $fO_2$ of the magma of > 5 log units and led to graphite and native iron saturation (Iacono-Marziano et al., 2012).

Figure 1 shows how the incorporation of sulfates oxidizes the magma (a) and increases its sulfur content (b). The pressure at which the calculation is performed (and therefore the depth at which the assimilation of sulfates ocuurs) controls the partitioning of S between the magma and the fluid phase, and therefore the amount of S that is dissolved in the melt, but has a very slight influence on the $fO_2$ of the magma. The assimilation of 1.4 wt.% $CaSO_4$ increases the $fO_2$ of the magma of ~1 log unit, but more than 2 wt.% $CaSO_4$ is necessary to increase the S content of the magma. Extreme assimilations (> 5 wt.% $CaSO_4$) increase the $fO_2$ of the magma of >4 log units, the S content up to > 1 wt.%, and can eventually lead to sulfate saturation in the magma.

If the assimilation of sulfates is followed by assimilation of carbonaceous sediments, massive sulfide production can be predicted as a consequence of S incorporation into the magma, followed by a substantial reduction of the magma redox state. This scenario has already been proposed for the Noril'sk-Talnakh district (Naldrett, 2004; Arndt et al., 2005). We quantitatively constrain the amount of wall-rock assimilated and the variation in involved parameters such as $fO_2$, sulfide saturation and S speciation in the melt.

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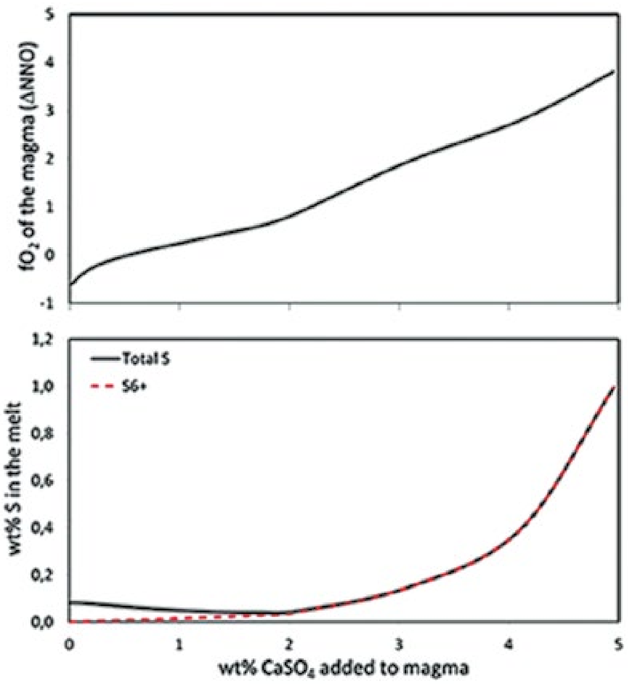

*Fig. 1.* Oxygen fugacity of the magma, expressed as logarithmic units relative to the Nickel-Nickel oxide buffer (a), and sulfur content of the melt, expressed as both total sulfur and $S^{6+}$(b) as a function of the amount of assimilated sulfate. Calculations are performed at 1200°C, and pressures of 50 MPa. The considered mafic melt has a total iron content of 10 wt.% FeO, and an initial sulfur content of 0.1 wt.% S

# GEOLOGICAL CONSTRAINTS ON THE ORIGIN OF THE MERENSKY REEF, BUSHVELD COMPLEX

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**ABSTRACT**. We discuss geological observations that are indicative of the formation of the Merensky Reef of the Bushveld Complex from a basally-emplaced layer of new magma, in which formation of chromite and sulphides and concomitant scavenging of PGE from the magma took place essentially *in situ*, i.e., directly at crystal-liquid interface.

The Merensky Reef of the Bushveld Complex has been interpreted in the context of the classic "downers" model, i.e., as a result of a large scale mixing of new and resident magma followed by downward settling of chromite crystals and sulphide droplets through a magma column several km thick (e.g., Naldrett, 1989). New geochemical data on the platinum group element (PGE) distribution across the Merensky Reef resulted, however, in a realization that PGE deposition must have occurred from a restricted volume of magma close to base of the chamber (Naldrett et al., 2011). The revised version of the "downers" model therefore suggested that the Merensky Reef was produced by fractional crystallization and gravity settling of chromite and sulphide droplets from a basally-emplaced layer of magma only about 16 meters thick (Naldrett et al., 2011). Although this revised model provides a better explanation of many compositional features of the Merensky Reef, there are two fundamental geological observations that still remain unexplained. Firstly, many sections of Merensky Unit with extensive development of regional 'potholes' show 1-2 cm thick chromitite seams of the Merensky Reef that occur along vertical to overhanging pothole sidewalls (e.g., Ballhaus, 1988; Ballhaus and Ryan, 1995; Ballhaus and Sylvester, 2000; Latypov et al., 2013). Clearly, gravity settling cannot produce chromitite seams on overhanging sidewalls of depressions suggesting that the Merensky reef is more likely a result of magma crystallization in situ, i.e., directly at the crystal-liquid interface. Secondly, there are examples of sulphide-bearing dykes of the Merensky Reef that cross-cut the footwall stratigraphy and occur 10-25 m below the normal Merensky Reef elevation on the margins of large potholes (e.g., Carr et al., 1994, 1999). The dykes often show 1-2 cm thick chromitite seams along both margins and are commonly enveloped by anorthosite rims that are formed via reconstitution of adjacent noritic rocks. It is hard to envision the Merensky Reef dykes resulting from crystal settling from 'above' onto the magma chamber floor. The textural and compositional features of the dykes are not compatible with late-stage remobilization of the semi-consolidated crystal mush of the Merensky Reef and are, again, better explained by in situ sidewall crystallization from through-flowing magma in a conduit. The simplest way to reconcile these two observations with the revised "downers" model of Naldrett et al., 2011 is to suggest that nucleation and crystallization of chromite and sulphides took place heterogeneously at the crystal-liquid interface rather than within the magma layer during its emplacement at the base of the chamber. For kinetic reasons the heterogeneous nucleation of any phases, including chromite and sulphides, on pre-existing crystals in the mush pile is a much more viable option than homogeneous nucleation within the magma itself (e.g., Campbell, 1996). We believe that the aforementioned geological features of the Merensky Reef provide strong support to our recently developed model that implies the in situ origin of PGE reefs, in which sulphide droplets form directly at the crystal-liquid interface and extract noble metals from fresh magma delivered towards the base by flow/convection in the magma chamber (Latypov et al., 2013).

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# GENESIS OF CHROMITE DEPOSITS BY PARTIAL MELTING, PHYSICAL TRANSPORT, AND DYNAMIC UPGRADING OF SILICATE-MAGNETITE FACIES IRON FORMATION

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**ABSTRACT**. Thick chromite deposits form by melting of the silicate component of silicate-magnetite facies iron formation and the physical transport and dynamic upgrading of the magnetite component with Cr-rich magma.

A fundamental problem in the genesis of chromite deposits in layered mafic-ultramafic intrusions is how to generate layers of massive to semi-massive chromite that are commonly up to 0.2-1 m thick (e.g., Bushveld, South Africa; Stillwater, USA) less commonly up to 2-10 m thick (e.g., Inyala and Railway Block, Zimbabwe; Ipueira-Medrado, Brazil; Sukinda, India) but sometimes up to 100 m thick (e.g., Kemi, Finland; Black Thor, Ontario) from magmas that contain only a few hundred to a few thousand ppm Cr and that normally crystallize chromite in very small amounts. Many models have been suggested, including 1) oxidation (Ulmer, 1969), 2) silica addition (Irvine, 1975), 3) magma mixing (Irvine, 1977), 4) pressure increase (Lipin, 1993), 5) assimilation of iron-formation (Rollinson, 1997), and 6) hydration (Prendergast, 2008; Azar, 2010), with or without 7) physical transport (Eales 2000) and/or 8) slumping (Maier et al., 2013). Magma mixing, contamination, oxidation, hydration, and pressure changes require the amount of magma to exceed the thickness of the magma chamber. A dynamic (open) system requires the modification process to operate continuously, a balance difficult to maintain. Wholesale assimilation of iron formation will not work if the host magma is already saturated in oxide and would increase the Fe content of the magma to a point where it will not crystallize observed olivine and orthopyroxene compositions (Azar, 2010). Mechanically transporting very fine grained (0.1-0.2 mm) chromite, requires that it be extracted from another location and simply relocates the mass balance problem.

The solution is for the parental magma to partially melt and to assimilate the silicate component (chert/quartz and iron-rich silicates) of silicate-magnetite iron-formation – a lithology that is common in most areas or that can be reasonably expected to occur in most areas – but not the oxide component. Addition of silica would account for the presence of orthopyroxene in magmas that would not normally crystallize orthopyroxene. Undissolved fine-grained magnetite would be easily transported in the magma (Fig. 1) and upgraded through interaction with the magma (Fig. 2). This process is analogous to the model now favoured for many magmatic Ni-Cu-PGE deposits. Using conservative abundances of Cr in the magma and partition coefficients, magma:chromite ratios as low as 100 (at the low end estimated for many magmatic Ni-Cu-PGE deposits) can produce Cr-rich chromites (Fig. 2). Such a model explains why the thickest chromitites (and richest Ni-Cu-PGE deposits) are interpreted to occur in dynamic systems such as feeder sills and magma conduits.

This model is particularly well suited to explain the very thick chromitites in the Black Thor–Black Label–Black Creek–Big Daddy–Black Horse–Blackbird segment of the 2.7-2.8 Ga McFaulds Lake greenstone belt in the Oxford-Stull domain of the northern Superior Province (Metsaranta & Houlé, 2012). An association of ultramafic intrusions with country rocks containing magnetite-silicate iron formation across the Bird River–Uchi–Oxford–Stull–La Grande–Eastmain 'superdomain' could explain the greater abundance of chromite deposits in this metallotect relative to other areas (Houlé et al., 2013).

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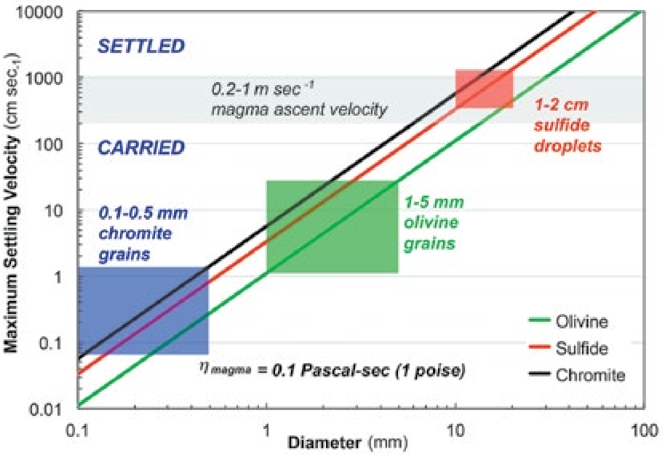

*Fig. 1.* Calculated maximum settling velocity (using Stokes' Law) versus diameter

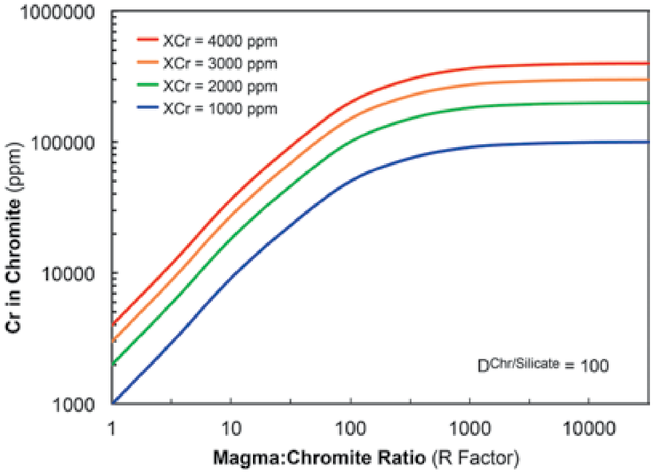

*Fig. 2.* Calculated chromite compositions (using method of Lesher & Burnham, 2001) versus magma:chromite mass ratio for various magma compositions.

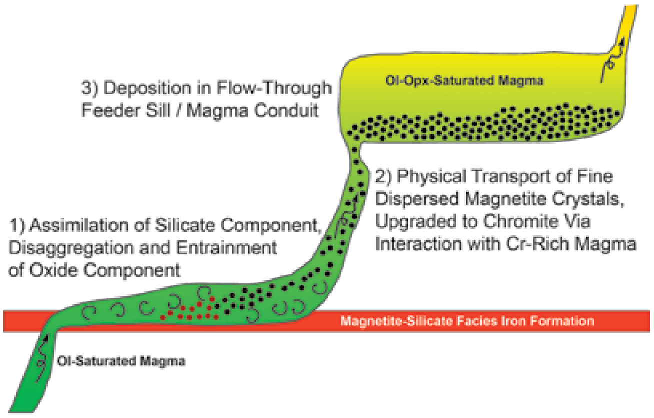

*Fig. 3.* Proposed model for partial melting, physical transport, and dynamic upgrading of magnetite to form thick stratiform chromitite deposits

# THE RELATIONSHIP BETWEEN LITHOLOGY AND PGE-RICH SULFIDE MINERALIZATION OF THE JM-REEF, STILLWATER COMPLEX, MONTANA

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**ABSTRACT**. Recent subsurface drilling at the Stillwater Mine, Montana, confirms that PGE-rich sulfide mineralization is not confined to any particular lithologic or stratigraphic position within what is known as the Reef Package. The downward extent of sulfide mineralization is defined by the presence of sulfide minerals and not by variations in host lithologies. Models to explain the transgressive nature of the PGE mineralization must address the episodic emplacement of sulfide saturated magmas, the presence of similar PGE-rich assemblages in different rock types, and potentially the strong oxygen isotope anomalies that occur in the Reef Package and indicate localized interaction with post magmatic fluids.

The Stillwater Complex of Montana hosts one of the world's premier PGE deposits; the J-M Reef averages 1 to 3 m in thickness and occurs over 40 km of strike length (Todd et al., 1982). The Complex has been divided into a Basal Series, an Ultramafic Series, and Lower, Middle, and Upper Banded Series. The J-M Reef is found in what is known as olivine-bearing zone I (OB I) of the Lower Banded Series. Todd et al. (1982) subdivided the olivine-bearing sequence that contains the J-M Reef into four sub-zones and 10 olivine-bearing members. The mine geologists refer to an interval within the first olivine-bearing member (O5b) of Todd et al. (1982) as the "Reef Package" (Corson et al., 2002). Rock types present include dunite, norite, troctolite, and anorthosite, characterized by pegmatoidal textures locally. PGE concentrations strongly correlate with sulfide abundance. Proven reserve grades average 14.4 ppm Pd and 2.8 ppm Pt at the Stillwater Mine and 10.3 ppm Pd and 4.1 ppm Pt at the East Boulder Mine (SMC, 2013). The origin of the Reef remains controversial, and theories are broadly divided between those which favor downward collection of PGE-bearing immiscible sulfide liquids and those that favor an upward accumulation of PGEs controlled by magmatic hydrothermal fluids. We are in the midst of a study that focuses on detailed examination of interfaces between sulfide- and PGE-bearing units of the Reef and sulfide- and PGE-poor rock types. Of particular importance are the transgressive relations found associated with the Reef Package. There is an angular discordance between rocks of the O5b members and underlying rocks in the area of the Stillwater Mine (e.g., Dahy et al., 2002). Wolfgram (2002) has suggested that the Reef Package is related to channel features that may be analogous to thermal erosion features in extrusive rocks. Boudreau (1999) proposed that the regional unconformity between the J-M Reef and the Troctolite and Anorthosite subzones of OB I result from slumping of over-steepened volatile-rich cumulates. Recent subsurface drilling at the Stillwater Mine confirms that sulfide mineralization is not confined to any particular lithologic or stratigraphic position in the Reef Package (Fig. 1). In particular, there is a vertical separation of sulfide-rich lenses as well as horizontal discontinuities. Sulfide mineralization may also occur within the Reef Package and its footwall up to 20 m down dip. The sulfide minerals in these occurrences are also not stratabound, and the zones of significant production are termed "ballrooms" because of the large rooms that may be mined (Childs et al., 2002). Sulfides within the ballrooms may be either in sub-horizontal pods or in zones that are strongly discordant relative to the magmatic stratigraphy.

Our work with respect to the ballrooms is in agreement with that of Cooper (2009). The downward extent of the mineralization is defined by the presence of sulfide minerals and not by variations in host lithologies. The association between PGE-rich sulfide mineralization and a variety of rock types in the J-M Reef is a perplexing problem that is difficult to explain by a purely magmatic (downward accumulation of immiscible sulfide liquid) process. For primary sulfides to transgress lithologic boundaries sulfide saturation must have been maintained throughout a fractionation/differentiation sequence;

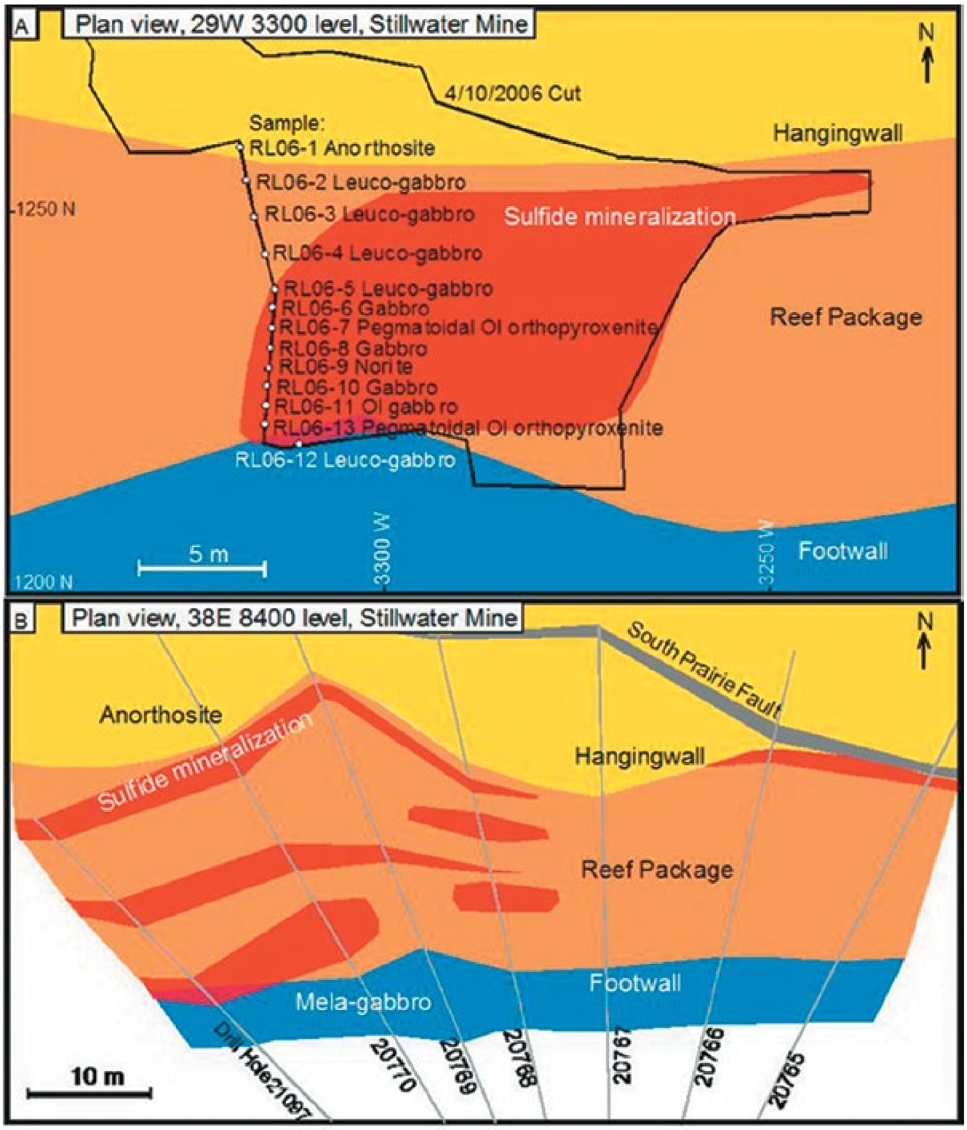

*Fig. 1.* Relationships between "ballroom" Pt-Pd-bearing sulfide mineralization and lithology in the J-M Reef of the Stillwater Complex, Stillwater Mine. New features revealed by recent underground adits and fan-drill holes include (1) downward offset of sulfide mineralization with respect to the reef lithology, (2) horizontal discontinuity of sulfide mineralization, and (3) vertical separation of sulfide lenses

in the Reef and particularly in the ballrooms this would have to have occurred on a local scale. Some of the distribution of sulfide minerals in the Reef and associated ballrooms may be a function of low-T hydrothermal fluid mobilization. Oxygen and hydrogen isotopic studies show that the J-M Reef behaved as a horizon of relatively high permeability. $\delta^{18}O$ values of plagioclase as low as 4.4 ‰ are indicative of kinetically controlled oxygen isotopic exchange with a low-temperature and low-$^{18}O$ fluid.

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# PLATINUM-GROUP ELEMENTS WITHIN THE MERENSKY REEF, WESTERN LIMB, BUSHVELD COMPLEX: RESULTS OF A HIGH RESOLUTION MINERALOGICAL AND GEOCHEMICAL STUDY

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**ABSTRACT**. Variation occurring within the thickness of the Merensky reef and mineralogical and geochemical studies show a close relationship between chromium and PGE enrichment.

A study of the Merensky reef was undertaken in the south-western portion of the Western Limb of the Bushveld complex. Variation occur in the thickness of the Merensky reef (pegmatoidal and a non-pegmatoidal reef), with the term "Merensky reef" referring to that part of the Merensky unit that is economically exploitable (Leeb-du Toit, 1986). The mineralogy and geochemistry were described on core sections across both reef types (pegmatoidal and non-pegmatoidal) from the area. All three sets of core studied, corresponds to the normal Merensky 'A' type reef (Leeb-du Toit, 1986).

The core were analysed in 2 cm intervals. Samples were analysed by optical microscopy. Quantitative analysis was done using scanning electron microprobe and electron microprobe analysis. Major elements were determined by using x-ray fluorescence and trace elements by using ICP-MS (inductively coupled plasma mass spectrometry). Platinum-group elements (PGE) were determined by Ni-S fire assay with an ICP-MS finish and sulphur by an Eltra Infrared Analyser.

Microscope analysis showed sulphide inclusions visible in chromite grains (Fig. 1). These inclusions display negative crystal shapes imposed by the crystal structure of the host chromite. Similar trapped sulphide inclusions have been described from chromites in the Platreef by (Holwell & McDonald, 2011).

Results indicated that there is a close relationship between chromium and PGE enrichment (Fig. 2). Chondrite normalized patterns showed a relative increase in Pd in the footwall with a significant decrease in the hangingwall. The opposite can be seen for Pt. REE plots suggest a small amount of local differentiation with respect to La.

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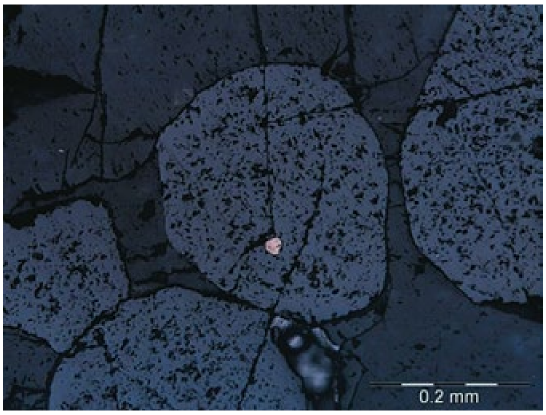

*Fig. 1*. Microscope analysis of non-pegmatoidal Merensky reef sulphide inclusion visible in chromite grain. Chr, chromite; Sul, sulphide; dark, plagioclase

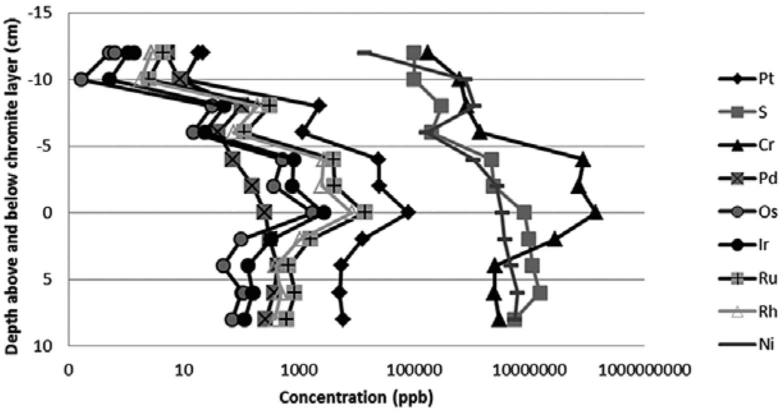

*Fig. 2*. PGE, Cr, S and Ni concentrations vs depth of the non-pegmatoidal Merensky reef . The PGE concentrations, except for Pd, correlate with the chromite enrichment with depth, whereas Pd tend to show a better correlation with S enrichment

# THE HISTORY OF A MERENSKYITE: FROM CRYSTALIZATION TO HIGH GRADE METAMORPHISM AND HYDROTHERMALISM

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**ABSTRACT**. Merenskyite [(Pd,Pt,Ni)(Te,Bi)2] accounts for 72% in area of the platinum-group minerals (PGM) in the Limoeiro Ni-Cu(-PGE) sulfide deposit and reveal a complex history after magmatic formation by exsolution from base metal sulfides (BMS). Recrystallization during granulite-facies metamorphism has produced distinctive metamorphic textures in the merenskyite, while later hydrothermal alteration formed an assemblage of Bi-rich merenskyite and hessite in remobilized sulfide stringers.

The Limoeiro deposit consists of thick (up to 150 m) and elongated (up to 1 km) masses of disseminated sulfides (2-10 vol.%) with a few thin massive sulfide layers (up to 500 x 300 x 1 m). It is hosted within a concentrically zoned tube-like (chonolithic) subhorizontal orthopyroxenite-harzburgite intrusion, interpreted as formed in a dynamic multi-pulse mafic magma conduit (Mota-e-Silva et al., 2013). In the area of the deposit the magma flowed from the west to the east, as the Cu/Pd ratio raises from 6492 to 8225 in concordance with the drop of Ni, Cu and PGE tenors to the east (Fig. 1). The intrusion and its country rocks are metamorphosed and partly deformed. Peak metamorphic paragenesis indicates an upper amphibolite to granulite facies grade (~750 °C) of metamorphism which is represented by the crystallization of anthophyllite, hornblende, phlogopite, chlorite, spinel and sub-grains of olivine and orthopyroxene (Mota-e-Silva et al., 2013). Experimental evidence indicates that merenskyite melts congruently at 740°C and that it is unstable at temperatures above 500° to 540°C (Hoffman & MacLean, 1976). The merenskyite in the Limoeiro deposit is most frequently found included by and on the margins of base metal sulfide aggregates (BMS). Among the BMS there is a preference for pyrrhotite, followed by fewer associations with chalcopyrite and pentlandite. This spatial relationship is compatible with merenskyite exsolving from BMS as the magmatic system cooled. The merenskyite grains in the Limoeiro massive sulfide ore are relatively coarse (grain size median of 10 µm with a maximum of 70 µm), euhedral to subhedral grains, occasionally with conspicuous cleavage parallel to the longer crystal axis. When included in the BMS they are commonly attached to spherical silicate aggregates (Fig. 2A). These silicates are metamorphic serpentine, hornblende, carbonate and chlorite as single minerals or as a assemblages in individual

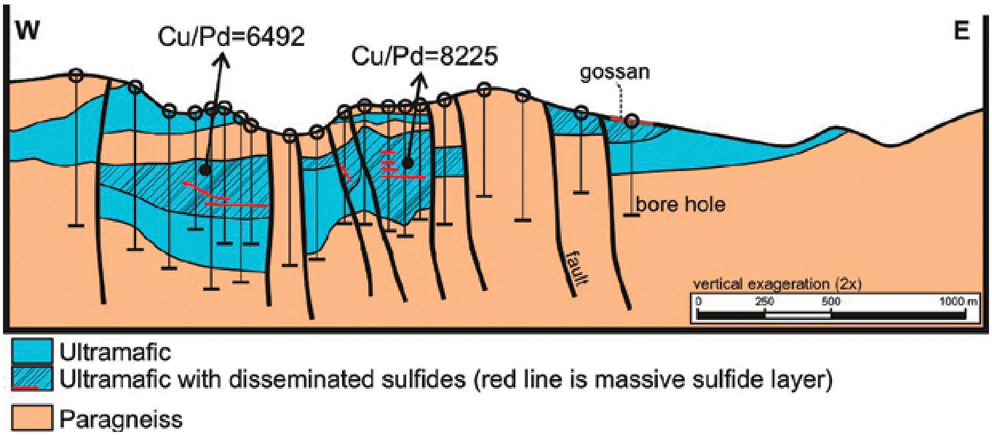

*Fig. 1.* Longitudinal section of Limoeiro Ni-Cu(-PGE) sulfide deposit

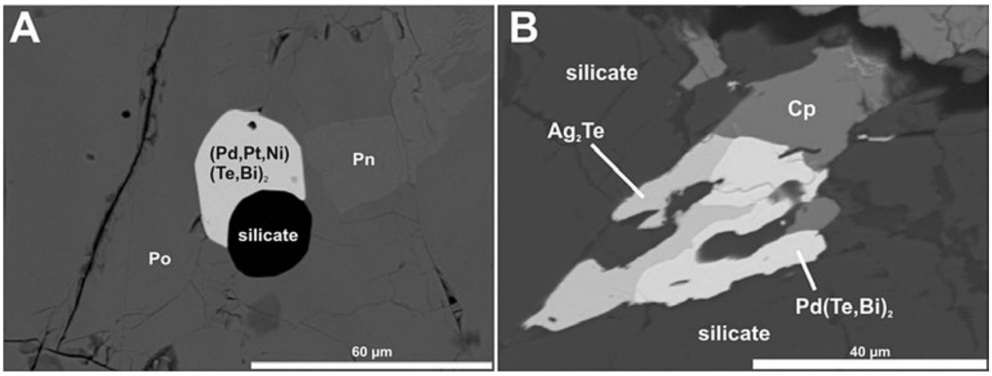

*Fig. 2.* BSE images of: A) Merenskyite attached to a spherical silicate included in pyrrhotite (Po); B) Bi-rich merenskyite with hessite in hydrothermal assemblage

inclusions. The association of PGM with spherical silicates may be characteristic of PGM that exsolved during upper amphibolite to granulite facies metamorphism. Additionally the high grade metamorphism is probably responsible for the very low partitioning of Pd into solid solution in BMS (12-16%) compared to Pd in the PGM (88-84%). The slow cooling rate of the metamorphism (compared to a magmatic cooling) optimized the diffusion of the PGE in the MSS (see Barnes et al., 2008) permitting a homogeneous and slow exsolution of large PGM grains in conditions of equilibrium within the buffered massive sulfide orebody.

The cryptic variation in composition of the merenskyite along the magma conduit reflects the magmatic sulfide geochemistry, which is more evolved to the east. Merenskyite becomes Ni- and Pt-poor towards eastern parts of the chonolith (Fig. 3). The lower Ni content is expected as the sulfide liquid segregated from a more fractionated S-saturated magma should contain lower base metals (e.g. Ni) tenors. The lower Pt-content may be the result of loss of Pt relative to Pd in the sulfide melt in the eastern parts. As the magma flowed through the narrower conduit eastwards mafic magma has probably assimilated considerable amounts of As-rich country rock triggering the directly crystallization of sperrylite ($PtAs_2$) from the suspended sulfide blebs, causing the accumulation of Pt-depleted sulfide liquid to the east.

During the low grade metamorphism, localized hydrothermal alteration promoted a heterogeneous removal of BMS, Pd, Te and Bi from the outer parts of the chonolith. These fluids reprecipitated the metals as a BMS, Bi-rich merenskyite and hessite assemblage in remobilized sulfide stringers (Fig. 2B). These sulfide stringers have whole rock Pt/Pd ratio of ~0.06 which contrasts with the deposit average Pt/Pd ratio of ~0.35.

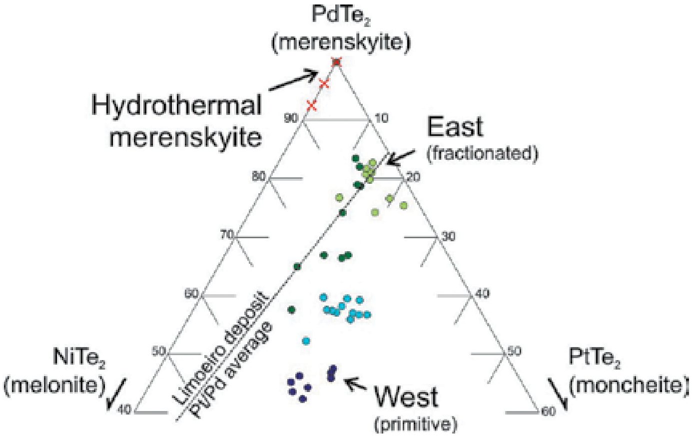

*Fig. 3.* Compositional variation of PGM in the melonite-merenskyite-moncheite system

The merenskyite in Limoeiro Ni-Cu-PGE deposit reveals a complex history of crystallization within a conduit system, followed by high grade metamorphism recrystallization and partial remobilization in the later hydrothermal event.

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# MODELING SPINEL – MELT EQUILIBRIA UP TO 15 KBAR: SPINMELT-2 PROGRAM AND ITS PETROLOGICAL APPLICATIONS

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**ABSTRACT**. A new version of the SPINMELT program (Ariskin & Nikolaev, 1996) has been developed. It allows for modeling chromian spinel compositions at variable $T$-$f_{O2}$-conditions in a wide range of mafic to ultramafic melts at pressures up to 15 kbar. Results of detailed testing of the new spinel model on experimental data are given. Topology of the modelled chromite-silicate liquid system with application example for a parental magma of the Burakovo-Aganozero layered massif is considered.

Previously, three models had been developed to calculate spinel-melt equilibrium in mafic to ultramafic magmas at 1 atm (SPINMELT: Ariskin & Nikolaev, 1996) and elevated pressures, including the MELT-CHROMITE calculator by Pustovetov & Roeder (2001) and the Sack's model adjusted to MELTS/pMELTS (1982-2002). Both previous and new experimental data obtained since that time allow for detailed testing of the spinel models proposed. To perform such test, we compiled a representative dataset of 350 spinel-glass compositions from 33 experimental studies available in the INFOREX-2014 database. These data represent anhydrous conditions and $fO_2 \leq$ QFM+2, with glass compositions of low to moderate alkalinity. The selected array includes 221 runs carried out at $P$=1 atm, 105 runs at 10 kbar, and 24 runs at 15 kbar. To challenge the problem of unknown $fO_2$ for the high-P experiments, we used an updated version of the Ol-Sp oxybarometer similar to that proposed by Ballhaus et al. (1991). Results of testing on the "1 atm"-array evidence for all three models are accurate to predict the spinels crystallization temperatures and their compositions. However, for high-P runs both the MELT-CHROMITE calculator and pMELTS-spinel model are inadequate, particularly in predicting Cr/Al ratios in the modelled spinels (Fig. 1). As a result, we stated the problem of recalibration of the SPINMELT model to make it applicable to elevated pressures.

The calibration carried out by multiple linear regressions for five spinel-melt expressions of a general formula:

$$\ln K = \frac{A}{T} + B * P + C * \Delta \lg QFM + \sum_i D_i * R_i + Const$$

where $K$ is an equilibrium constant (describing Sp-melt partitioning for Cr, Al, $Fe^{3+}$, $Fe^{2+}$, and Mg) and $R_i$ is a variable melt structure-chemical parameter. The finally calibrated equations were combined into a single program (SPINMELT-2), which now is capable to accurately calculate the low to high aluminous spinel crystallization temperature and compositions in the pressure range 1 atm – 15 kbar (Fig. 1).

The new model was used to determine constraints on the stability and compositions of chromian spinels that could crystallize in a range of pressures from high-Mg magmas with otherwise similar major element compositions, but with variable $Cr_2O_3$ contents.

Further, the spinel-melt modeling approach was applied to the parental magma of the Burakovo-Aganozero layered massif in Northern Karelia, Russia (Nikolaev & Ariskin, 2005) to estimate $T$-$fO_2$ conditions at which the observed high-Cr spinel could crystallize after olivine. This is because the Ol (Fo88) has been shown to be the only mineral phase to be stable at the initial magma temperature ~1330°C, assumed $P$=6 kbar, and WM buffer conditions. Finally, it is shown that the calculated chromite solubility isopleth (0.14 wt.% $Cr_2O_3$ in the melt) in the $T$-$fO_2$ coordinates, intersects the line of the WM buffer ~30°C below the original olivine liquidus. This is consistent with the initial magma parameters given above.

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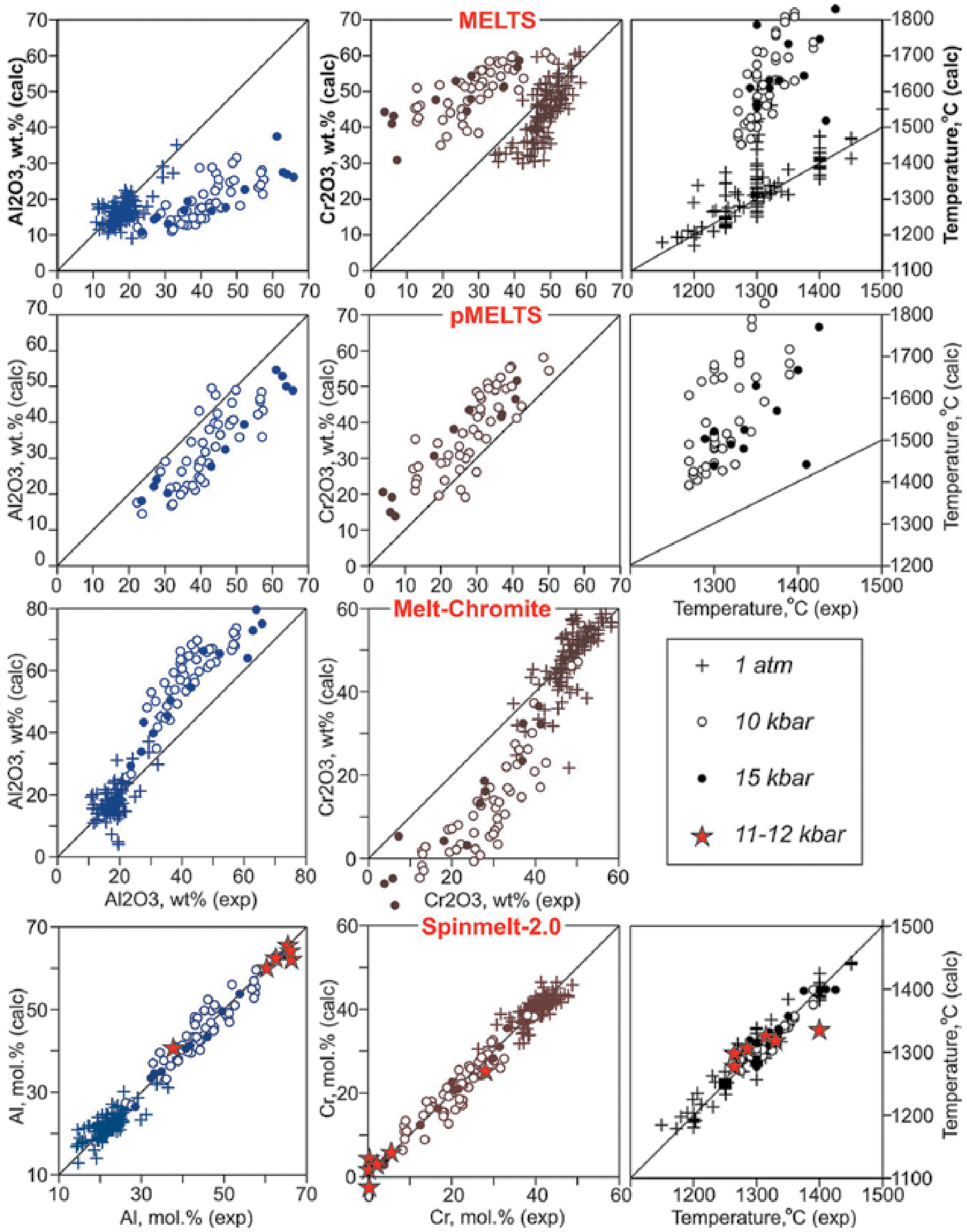

*Fig. 1.* Comparison of experimental spinel saturation temperatures and compositions with those calculated by different models. The red stars represent independent experiments used to test the SPINMELT-2 model

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# A CYCLIC DIFFUSION-ACCUMULATION MODEL FOR RHYTHMIC LAYERING IN BASIC MAGMAS

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**ABSTRACT**. Crystallization differentiation is one of the most important processes in the evolution of magmatic systems, and it controls their ore-forming potential. There are different models for basic magma differentiation to explain the formation of rhythmically layered intrusions that are characterized by layers of varying mineralogical composition and cryptic layering (e.g., Wager & Brown, 1967, Sharkov, 1980, Frenkel et al., 1989). The author offers his own cyclic diffusion-accumulation model for rhythmic layering in basic magmas. The proposed model is, in general, similar to the convection-accumulation model for stratified intrusions (Frenkel et al., 1989), but the author has introduced here the concept of "cyclic oscillatory movements of the residual liquid composition along the above the the liquidus path".

Crystallization of a basic melt in a tabular magma chamber is considered (Fig. 1).The presence of early-formed minerals (phenocrysts) in the chilled zones of layered intrusions is indicative of a subliquidus temperature ($T_0$) for the melts. As magma gradually looses its heat into cold host rocks, the crystallization front of the early-formed olivine ($Ol_1$) begins to move parallel to the roof and base of the intrusion. At the crystallization front, growth of $Ol_1$ nuclei is due to the diffusion of infusible components from the melt into the growing crystalline phase. This leads to the formation of easily fusible aureoles around the olivine crystals. The thickness of the aureoles is comparable to the size of the growing crystals. Upon gravity settling, $Ol_1$ sinks into the lower levels of the equilibrium melt and continues growing there. This causes the depletion of magnesia in the layer above the crystallization front, while olivine crystallizing there, under the lower temperature conditions ($T_1$), becomes richer in Fe. The latent heat of olivine crystallization compensates for the heat loss, and the composition of the residual liquid ($L_1$), enriched in easily fusible components, gradually moves along the above the liquidus path toward the anorthite crystallization field (point 2 in Fig. 1 A, B, C). As a result, crystallization of the first generation of plagioclase ($An_1$) from the melt, localized at the upper margin of the intrusion, begins at a lower temperature ($T_2$). Space and temperature gaps exist between the olivine and plagioclase crystallization fronts and there is also a difference between chemical compositions of the initial magma and the upper layer of the residual melt. This gradient is due to diffusive accumulation of infusible components in the early subliquidus phase and its further gravity settling, i.e. it has a diffusion-accumulation nature. Subsequent cyclic movements of the magma crystallization front, along the above the liquidus path, from the anorthite field back to the olivine field ($T_3$), result in rhythmic layering of magma. Once the excess olivine is used up, cyclic alternation of the anorthite (An) and pyroxene (Py=Di or En) crystallization occurs, in a similar way.

The crystallization trend depends on the initial composition of magma. Specifically, the crystallization trend in layered intrusions of the gabbro-clinopyroxenite-dunite series may be traced on the Di-An-Fo diagram (Fig. 1A) while that of the anorthosite-norite-orthopyroxenite-harzburgite-dunite series is traced on the Fo-An-$SiO_2$ diagram (Fig. 1C). The structure of rhythmic layers is schematically shown in correlation with the reversed pseudobinary join Fo(Py)-An (Fig. 1B). As the crystallization front moves downward, the composition of the residual melt in the upper part of the intrusive body approaches the eutectic composition, and solidification of the intrusion begins ($T_E$). Frequent cyclic movements of the crystallization trend from one mineral field into another cause the formation, near the cotectic line, of fine alternating melanocratic and leucocratic layers, which gradually change their high-T initial composition to the low-T eutectic one.

In the lower part of the intrusion the heat is lost only downward, and a high temperature is maintained there due to the latent heat of crystallization of excess $Ol_1$ from the higher levels and its accumulation in the near-bottom zone of the

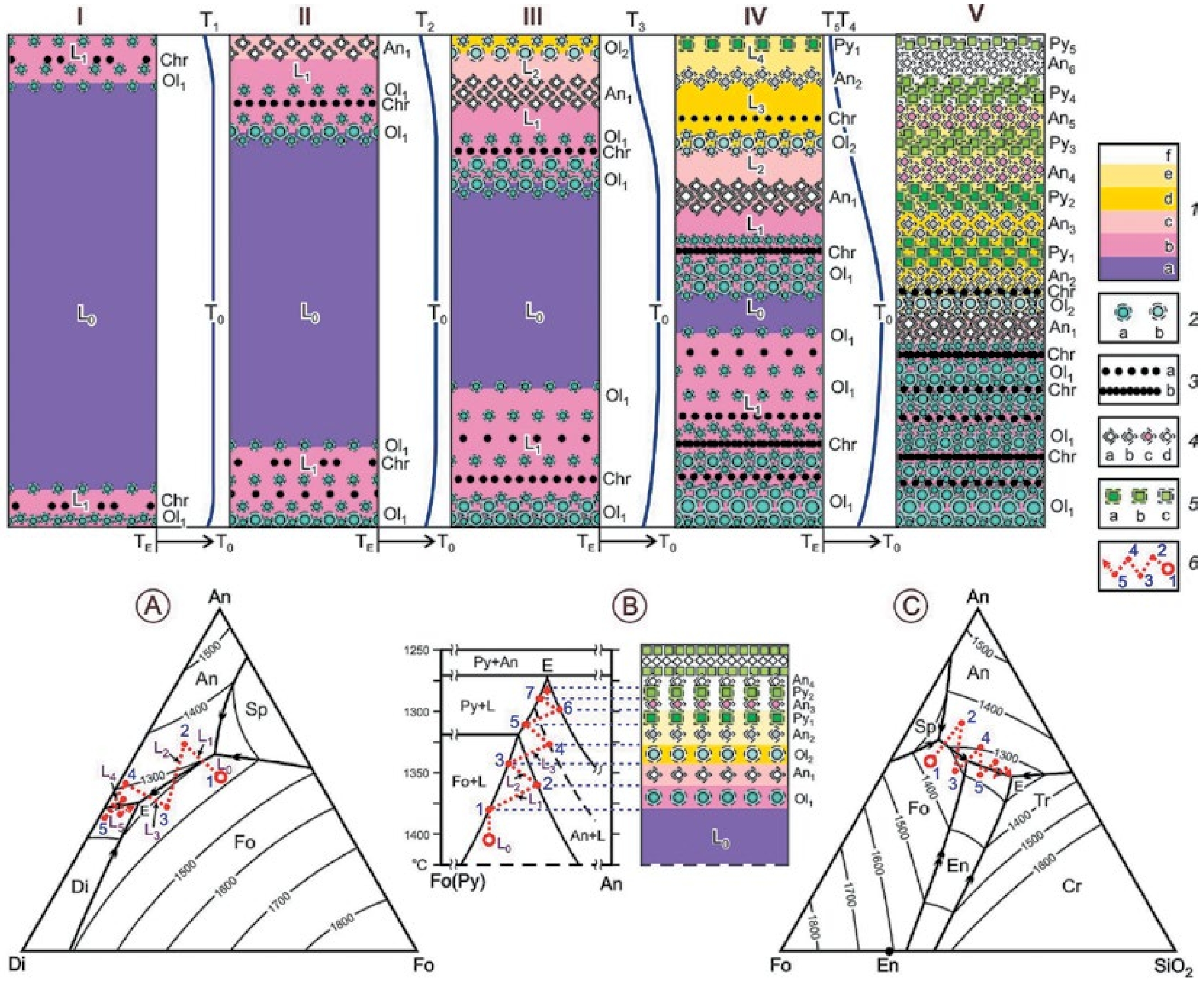

*Fig. 1*. Schematic representation of the cyclic diffusion-accumulation model for rhythmic layering in basic magmas. 1 – initial (a) and subsequent (b-f) residual liquids; 2 – cumulate olivine of the first (a) and second (b) cycles, diffusive aureoles of mineral growth are shown by a dashed line; 3 – accessory (a) and segregation (b) Cr-spinels; 4 – plagioclase of successive cycles; 5 – pyroxenes; 6 – oscillatory movements of the residual melt composition along the above the liquidus line. Temperature curves are schematically shown on the sides of the cross-section columns (I-IV). A – phase diagram of the system Di-An-Fo after Osborn & Tait (1952), B – schematic structure of rhythmic layers in correlation with the reversed pseudobinary join Fo(Py)-An, C – system Fo-An-$SiO_2$ after Andersen (1915)

intrusion, which leads to the formation of thick dunite-cumulative layers here. Chromitite (Chr) layers make their appearance here, and with a sufficient concentration of $Cr_2O_3$ in the residual melt, separation occurs of the PGE-chromitite ore, as an immiscible liquid from the silicate magma (Okrugin, 2011). The final subsolidus solidification of the intrusion begins with the merging of the upper and lower crystallization fronts. Thus, oscillatory movements of the residual melt composition, along the above the liquidus line and across the cotectic line, from the crystallization field of one mineral to that of another mineral, cause the formation of rhythmically layered anchimonomineralic rocks.

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# CHAOTIC ENTRAINMENT CAN DRIVE SULFIDE REMOBILIZATION AT LOW MAGMA FLOW RATES

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**ABSTRACT**. There has been a recent vogue for ore formation models that attribute the initial segregation and accumulation of sulfide liquid to deep seated processes, occurring in the deep crust well below the eventual level of formation of the actual deposits. These accumulations are held to have been remobilized, transported upward and redeposited at the eventual site of ore formation (e.g., Lightfoot et al., 2012). However the physical mechanisms controlling this remobilization remain enigmatic. Does the high density and low viscosity of the sulfide liquid make it difficult for sulfide to be entrained by the host magma? How fast does the magma need to flow in order to entrain and transport sulfide liquid upward through the crust?

Using computational fluid dynamic (CFD) simulations we have examined the role of mixing in time-dependent multiphase viscous flows with large density and viscosity contrasts. We consider a simplified case of sulfide sitting beneath a periodically driven channel flow (Fig. 1). The simulations are laminar flows at low Reynolds numbers. Under steady flow conditions there is no mixing between the cavity and the channel flow. However a pulsing flow generates complementary lobes of magma and sulfide which drive chaotic mixing across the cavity interface and mobilization of the sulfide into the channel flow.

By varying the viscosity and density contrasts between the sulfide and magma we find that realistic viscosity and density contrasts improve the mixing rate as larger magma lobes are generated and secondary gravitational instabilities force more sulfide out of the cavity and into the host magma (Fig. 2). As the maximum flow rate increases, the shear flow at the cavity surface becomes increasingly unstable and Kelvin-Helmholtz billows take over from the lobes as the primary mechanism for sulfide mobilization. Mobilized sulfide lobes undergo rapid stretching and filament formation after entrainment, and break up into droplets with power-law size distributions similar to those seen in natural disseminated sulfide ore deposits. The resulting droplet populations can potentially be transported over trans-crustal distances at typical magma flow rates.

These results show that remobilization can occur under much lower magma flow rates than previously assumed. This suggests that sulfides could potentially be mobilized and deposited repeatedly during the formation of an ore deposit.

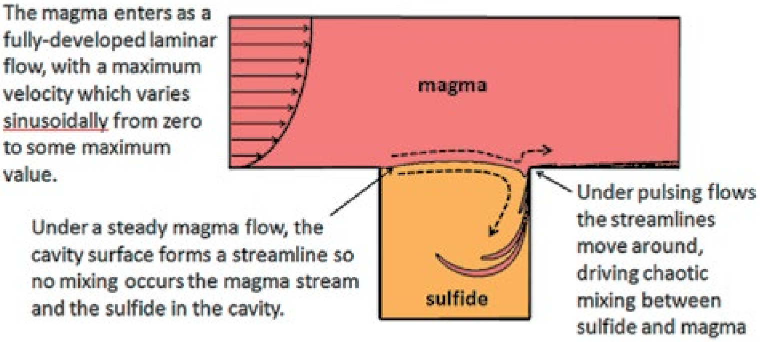

*Fig. 1.* Schematic diagram showing the features of the periodically-driven coupled channel and cavity flow

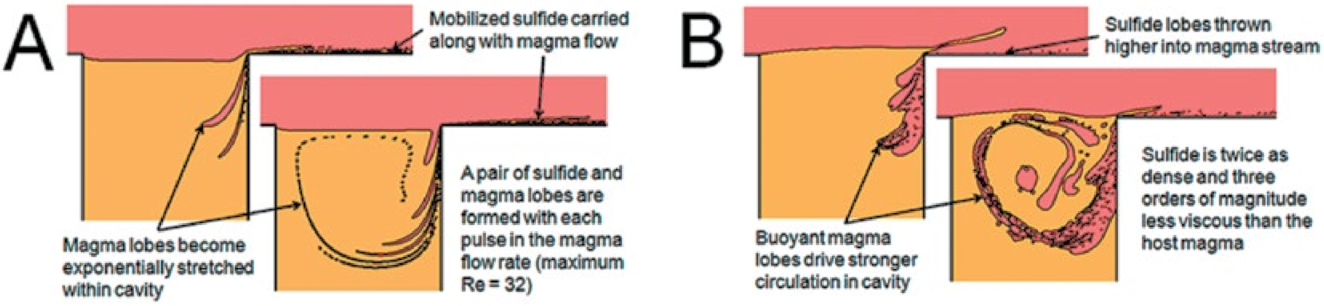

*Fig. 2.* Snapshots of two simulations, showing the effects of a realistic viscosity and density contrast between the sulfide and the magma. Diagram A shows a simulation where both the sulfide and magma have the same viscosity and density, while B shows a simulation with properties similar to real sulfide-magma systems. Both simulations have a maximum Reynolds number (using the width of the cavity as a length-scale) of 32

Conversely, it highlights the importance of considering preservation mechanisms when targeting – if it is easy to mobilize sulfide at low magma flow rates, then how do massive deposits get preserved?

*Acknowledgments. This work was supported by iVEC (www.ivec.org) through the use of advanced computing resources located at iVEC@Murdoch. JCR is supported by the CSIRO Office of the Chief Executive Postdoctoral Fellowship Scheme with additional support from the CSIRO Minerals Down Under Flagship.*

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# ISOTOPICALLY HETEROGENOUS PLAGIOCLASE POPULATIONS IN THE MAIN ZONE OF THE BUSHVELD COMPLEX SUGGEST THE INTRUSION OF CRUSTALLY CONTAMINATED CRYSTAL MUSHES

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**ABSTRACT**. A variety of models have been proposed to explain isotopic disequilibrium in layered intrusions. Here we show the presence of multiple, isotopically heterogeneous populations of plagioclase from the Main and Upper zones of the Rustenburg Layered Suite of the Bushveld Complex. The results are consistent with a model in which contamination of mantle-derived magma took place in a sub-compartmentalized, sub-Bushveld staging chamber prior to the intrusion of crystal-laden magmas into the presently exposed part of the Rustenburg Layered Suite. We also show that the results cannot be satisfactorily explained with reference to previously developed models to account for isotopic disequilibrium in the Bushveld Complex and other layered intrusions.

Recent work on the Bushveld Complex and other layered intrusions has shown the presence of locally significant isotopic heterogeneity, both between and within co-existing cumulate minerals. Various processes have been proposed to account for this, including the intrusion of variably contaminated crystal mushes from deeper staging chambers (Roelofse & Ashwal, 2012), the mixing of semi-consolidated crystal mushes as a result of subsidence during cooling (Yang et al., 2013), the infiltration of contaminants into a partially solidified crystal mush (Chutas et al., 2012), the density-driven mixing of minerals from isotopically distinct magma pulses (Prevec et al., 2005), contamination of crystals at the roof of an intrusion and mechanical incorporation of such contaminated crystals into the lower crystallisation front as a result of gravitational instability at the upper crystallisation front (Tepley & Davidson, 2003), and late-stage metasomatic processes (McBirney & Creaser, 2003). Here we present precise Sr-isotopic compositions for rim and core domains of plagioclase from the Main and Upper zones of the Bushveld Complex, which show the presence of multiple, isotopically heterogenous populations of feldspars occurring within the same rocks. We propose that the data are best explained through the intrusion of variably contaminated crystal mushes derived from a sub-compartmentalized, sub-Bushveld staging chamber that underwent different degrees of contamination with crustal rocks of the Kaapvaal craton.

The presence of intracrystalline isotopic disequilibrium and multiple isotopic populations of the same mineral suggest the inadequacy of studying mineral separates (even using sequential leaching experiments) in deciphering the petrogenesis of layered mafic intrusions. The model that we have developed to explain our data is a striking testament to the fact that layered intrusions do not necessarily represent simple systems undergoing differentiation in-situ, but rather intricately complex products of mantle melting followed by varying degrees of crustal contamination within multi-level staging chambers prior to final emplacement.

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# INTERCUMULUS CRYSTALLIZATION AND CHEMICAL DIFFUSION IN THE UPPER CRITICAL ZONE OF THE BUSHVELD IGNEOUS COMPLEX, SOUTH AFRICA

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**ABSTRACT**. The study presents the first results of laser ablation trace-element analyses of cumulus and intercumulus minerals in the Upper Critical Zone of the Bushveld Igneous Complex in the stratigraphic interval between the UG2 chromitite layer and the Merensky reef. The data imply high mobility of alkalis through intercumulus melt during post-cumulus crystallization and generation of significant redox gradients at contacts of chromitite layers with silicate cumulates.

The Upper Critical Zone (UCZ) of the Bushveld Igneous Complex displays spectacular layering in the form of cyclic units comprising a basal chromitite layer overlain by a sequence of silicate cumulates in the order, from bottom to top, pyroxentite-norite-anorthosite. Our electron microprobe and laser ablation ICP-MS studies of chromite and silicate minerals in the cyclic units between the UG2 chromitite and the Merensky reef revealed variations in major and trace element compositions of pyroxene, plagioclase and Cr-spinel that imply significant mobility of alkalis and changes of the ferrous-ferric ratio in the intercumulus melt. The variations are best developed at sharp contacts of chromitites with adjacent anorthosite and pyroxenitic cumulates (Figs. 1 & 2). There, chromite compositions change abruptly from high and constant $Mg/(Mg+Fe^{2+})$ and $Fe^{2+}/Fe^{3+}$ratios in chromitite layers to variable and generally lower values in chromite disseminated in silicate layers. Major and trace element composition of disseminated chromites also varies depending on the host silicate assemblage. Importantly, the abrupt change in chromite composition across the chromitite-silicate layer contacts is independent of the thickness of the chromitite layer and the estimated mass proportions of chromite to intercumulus liquid. Chemical variations in plagioclase are also abrupt and some of the features demand a major rethink of conventional models of reequilibration with intercumulus liquid. Among those features is the decoupling of alkalis from other incompatible lithophile elements. In comparison with cumulus plagioclase, intercumulus poikilitic plagioclase cementing chromitite layers is enriched in REE but strongly depleted in equally incompatible Li, K and Rb. Strong alkali depletion is also observed in intercumulus pyroxene.

Combining previous results with the trace element data from this study, we propose a new model of post-cumulus re-crystallisation which intensifies the modal layering in the crystal-liquid mush producing the observed sequence of nearly monomineral layers of chromitites, pyroxenites and anorthosites that define the cyclic units. The crucial element of this model is the establishment of redox potential gradients at contacts between chromite-rich cumulates and adjacent silicate layers due to peritectic reactions between the crystals and intercumulus melt. Since basaltic melts are ionic electrolytes with $Na^+$as the main charge carrier, the redox potential gradient will induce electrochemical migration of $Na^+$and other alkali ions. Selective mobility of alkalis can explain the enigmatic features of plagioclase composition in the cyclic units. Sodium migration is also expected to cause re-melting of previously-formed cumulates and major changes in modal mineral proportions, which result in the formation of sharply-divided monomineral layers. The observed variations in ferric-ferrous iron ratios in chromite from the cyclic units and variations in the total Fe content of plagioclase imply a redox gradient on the order of 0.9 log-units $fO_2$, equivalent to a potential gradient of 60 mV. More reducing conditions

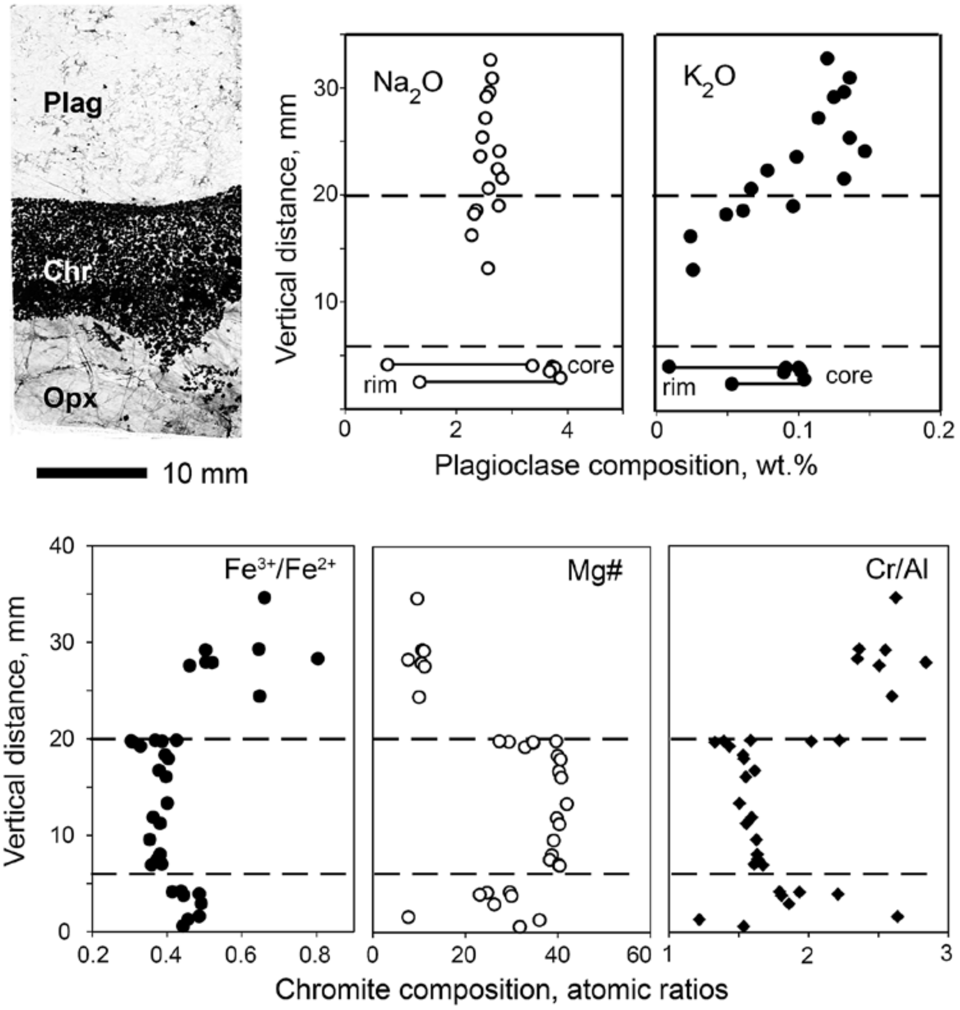

*Fig. 1.* Variations of chromite and plagioclase compositions across a thin chromitite seam between anorthosite and feldspathic pyroxenites within a single petrographic thin section. Western Bushveld.

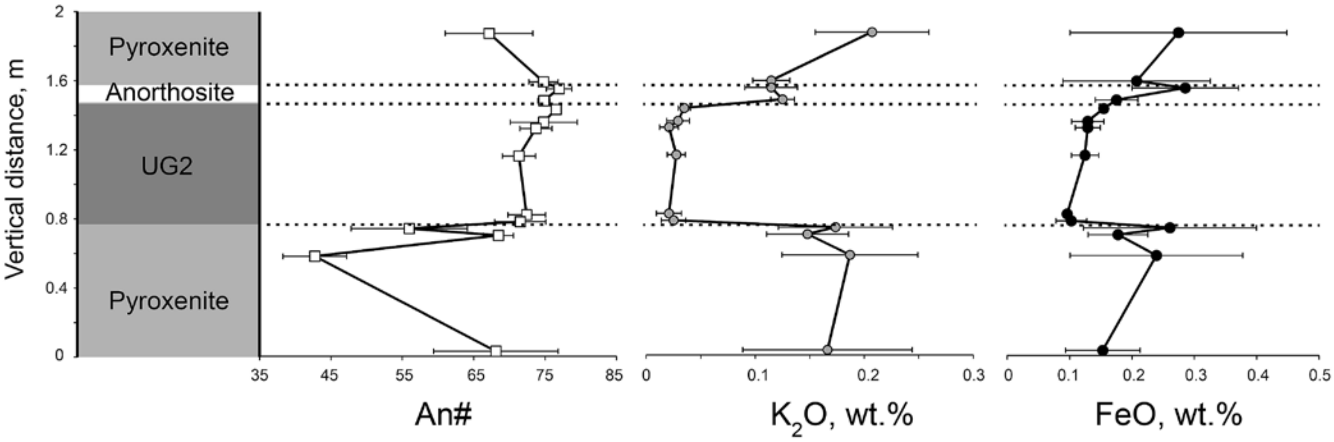

*Fig. 2.* Variations of cumulus and intercumulus plagioclase compositions across the UG2 chromitite layer, hanging wall pyroxenite, thin anorthosite stringer and footwall pyroxenite. Eastern Bushveld. Points represent average compositions; horizontal bars – standard deviations

are generated in chromitite layers and alkalis are expected to migrate out of chromitite layers into silicate cumulates. Preliminary estimates suggest that the resulting electrochemical flux of Na$^+$ions is sufficient to mobilize about one-third of the total Na content of a metre-thick mush layer within 10 years. The proposed electrochemical effect of post-cumulus crystallisation is enhanced by the presence of cumulus chromite but, in principle, it can operate in any type of cumulates where ferrous and ferric iron species are distributed unequally between crystalline and liquid phases.

# EXSOLUTION AND GENESIS OF Ti-Fe-Al METALLIC OXIDE IN GIANT MAGNETITE OF THE QIEGANBULAKE COMPLEX, XINJIANG PROVINCE

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**ABSTRACT**. The Qieganbulake deposit is the only ultrabasic-carbonate complex which contains superlarge vermiculite-apatite deposits in China. It is located at the southwest margin of the Kuluketage block. One kind of Na- and Zn bearing spinel and Mg-rich ilmenite occurring as exsolution minerals were discovered within the magnetite. We also found that there are some zircons / baddeleyites surrounding the ilmenite, possibly produced by exsolution from ilmenite. We found many tiny minerals (nanoscale) 1-4 um in length and 40-60 nm in width both in the magnetite and ilmenite.

Exsolution microstructures in orogenic rocks not only can be the indicators of ultra-high-pressure metamorphism, but also play an important role in deciphering the subduction depth as well as the related geodynamics (Green, 2000; Chopin, 2003). However, previous studies focused mainly on the non-opaque minerals. In this paper, we present observations on exsolution microstructures in Fe-Ti oxides, which may indicate one ultra-high temperature event in the Kuluketage block, NW China.

The spinel is about 6~80 µm in length and 5~70 µm in width (Fig. 1), composed of MgO 19.8%~20.8%, $Al_2O_3$ 61.51%~64.05%, FeO 5.94%~10.37%, ZnO 4.35%~6.53%, $Na_2O$ 0.52%~0.66%, where the content of $Na_2O$ and ZnO are very stable and positively in different grains. The Mg-rich ilmenite occurred as exsolution lamella in three groups in magnetite, with the length of 3~6 mm and 15~30 um. Continuous EMPA profiles across ilmenite grains show that the first and second group have the same regular composition: with the increase of the Ti content, the content of Mg decrease from the edges to the core; while the third group ilmenite show the opposite relationship. Combined with the differences in their form, position and the EDS analysis of aluminum, it is likely that the third group of ilmenites was formed at different stages from the first and second group ilmenites. By means of high magnification SEM (>7000), we found many tiny minerals 1-4um in length and 40-60 nm in width both in the magnetite and ilmenite (Fig. 2).

Based on presence the higher temperature exsolution of acicular hematite, and the EDS analysis of Al, Na within the quartz-calcite and the baddeleyite associated with metasomatic ilmenite, we infer a late high-temperature metasomatic event. This produced the third group ilmenite, hematite and Zn-Na spinel located between the ilmenite grains.

Considering all evidence, we interpret the Qieganbulake complex as having experienced the collisional tectonics associated with the breakup of the Rodinia supercontinent. Metallic oxides were formed in this process and contain possible indications of detailed P–T–t history.

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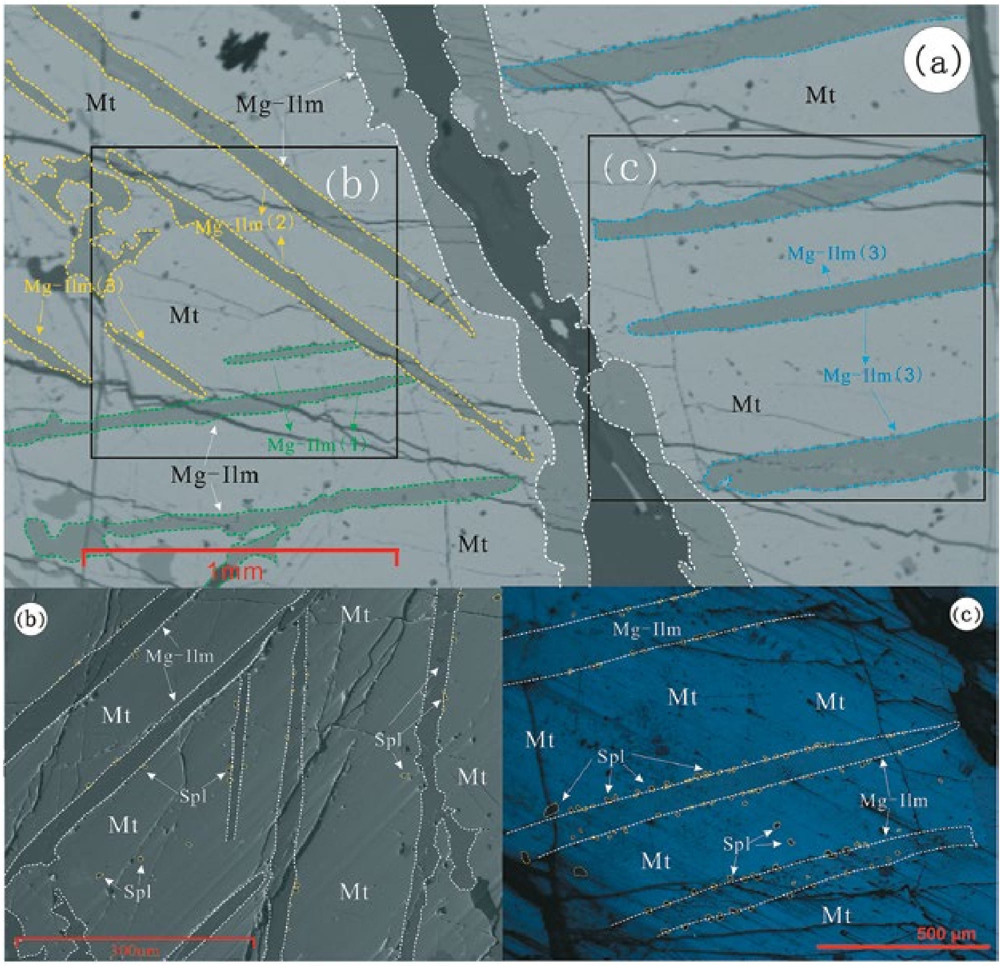

*Fig. 1.* Magnetite-ilmenite-spinel exsolution: photomicrograph and BSE image

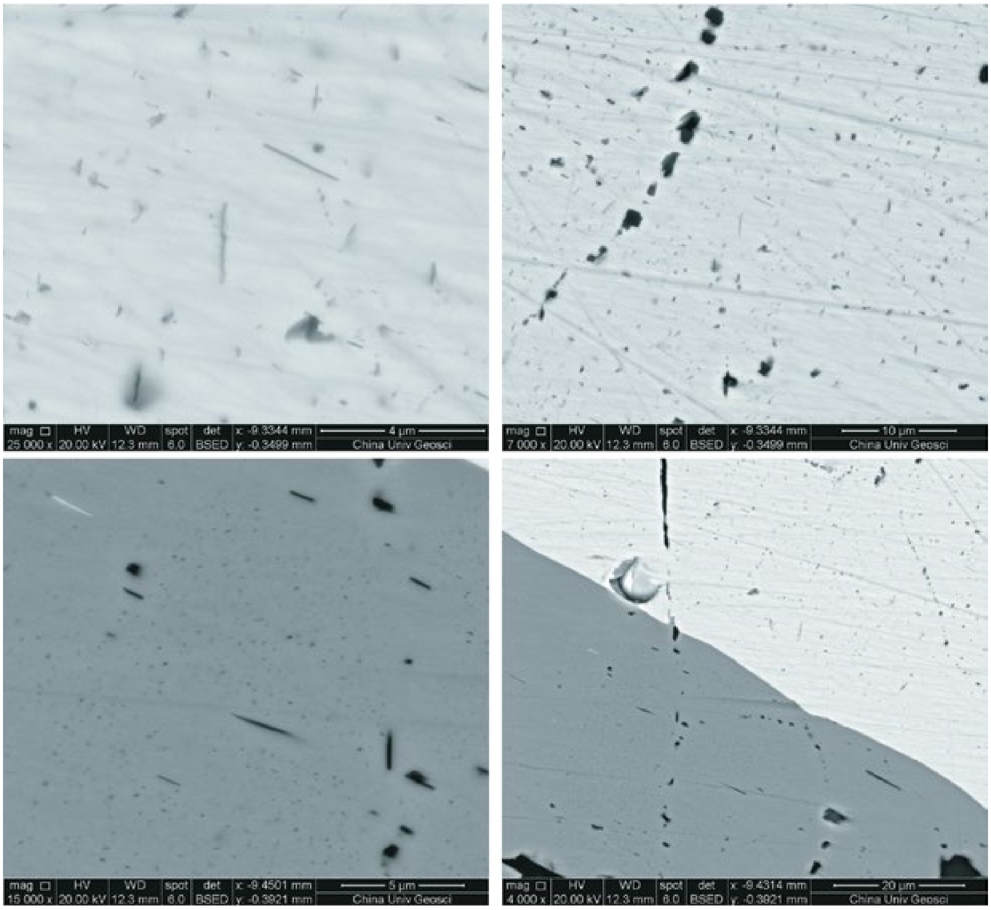

*Fig. 2.* BSE image of needle-like exsolutions in magnetite and ilmenite.

# SESSION 2

## PGE mineralization in mafic–ultramafic intrusions of Russia: geology and petrogenesis

**Conveners: Alexey Ariskin & Wolfgang Maier**

The session will focus on PGE mineralized mafic to ultramafic intrusive complexes of Russia. We invite presentations that provide information on their geology, petrology, mineralogy, and geochemistry and that help to constrain the petrogenesis of the intrusions and their different styles of PGE mineralization. Contributions dealing with sulfide and chromite transport in the parental magmas, and percolation of sulfides and volatiles through the cumulate pile are particularly welcome, as are talks and posters that have implications for exploration targeting, using a variety of techniques and vectors.

# GEOCHEMICAL EVOLUTION OF Cu-Ni-PGE TENORS IN DISSEMINATED SULFIDES FROM THE YOKO-DOVYREN MASSIF, RUSSIA

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**ABSTRACT**. Po/Pn/Cpy/Cub proportions in disseminated sulfides have been determined for poorly-mineralized rocks (0.05-0.5 wt.% S) from the Yoko-Dovyren massif. Two distinct mineralogical trends between sulfides from the main PGE-reef and the bottom dunite unit have been observed. Combing mineral proportions with the compositions of sulfides from dunites (LA-ICPMS), Cu-Ni-PGE tenors for the bulk sulfides have been estimated. Spatial variations in bulk sulfide compositions display a systematic pattern consistent with the results of modelling sulfide crystallization using COMAGMAT-5.

The Yoko-Dovyren massif (YDM) forms a 26 km long ridge located ~60 km NE of Lake Baikal. It is a lens-shaped body up to 3.5 thick which, together with associated peridotite sills and overlying basalts, represents a Riphean (728 ± 3.4 Ma) volcanic-plutonic complex. The modal layering of the YDM is represented by the basal unit of plagioclase lherzolite overlaid by a succession of cumulate rocks (Fig. 1A):
Ol+Chr → Ol+Pl+Chr → Pl+Ol±Cpx±Chr → Pl+Cpx±Opx±Pig.

The YDM contains massive sulfide ores near its bottom and PGE-rich ("reef") anorthosites within olivine gabbro in the upper part of the sequence (Konnikov et al., 2000). In addition, three other horizons of disseminated sulfides exist within the bottom Pl-dunites, carbonate contaminated dunites, and upper marginal rocks (Fig. 1A).

To estimate Cu-Ni-PGE contents in the "average sulfide composition" for a particular rock, we used the relative proportions of Po, Pn, Cpy, and Cub determined by Mineral Liberation Analysis

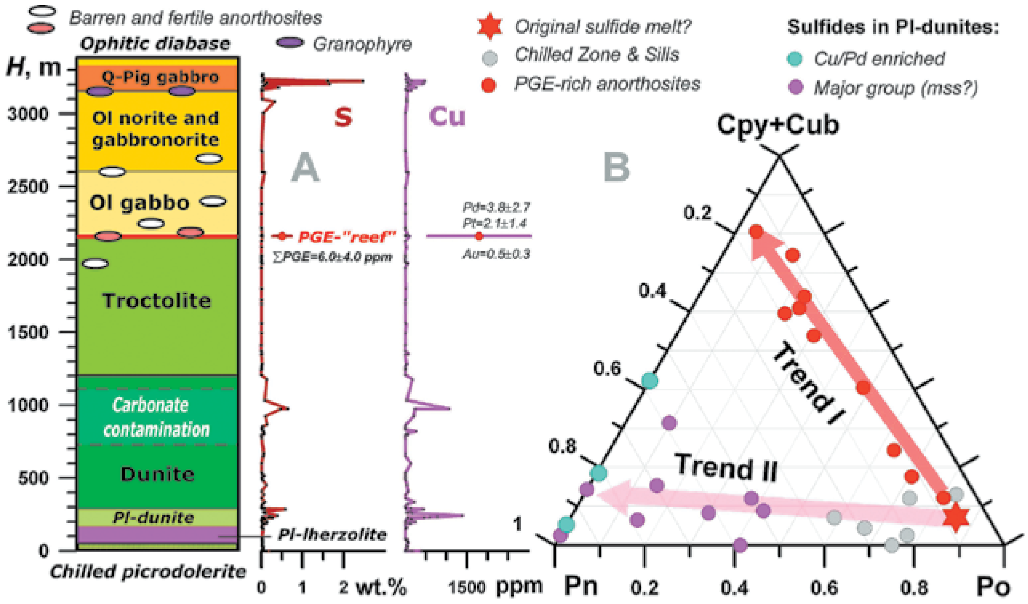

*Fig. 1.* The structure of the Yoko-Dovyren massif vs. main horizons of disseminated sulfides (A) and two trends of average sulfide mineral compositions in the S-poor rocks (B)

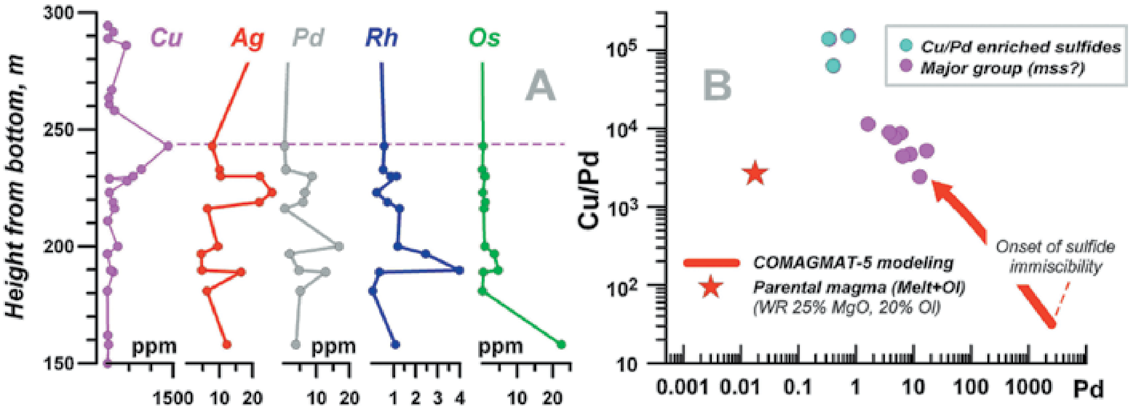

*Fig. 2.* The average weighted tenors of sulfides from Pl-dunites demonstrating the offset-like behavior of Ag and PGE (A) and Cu/Pd vs. Pd plot for the observed sulfides and those modeled by COMAGMAT-5 (B)

(MLA, using FEI Quanta 600 SEM fitted with EDS) and the compositional data on individual sulfide phases obtained by LA-ICPMS at the University of Tasmania (Gilbert et al., 2013). We found two mineralogical trends distinguishing sulfides from the main PGE-reef (trend I) and the bottom dunites (trend II) (Fig. 1B). Trend II was interpreted to represent the base metal evolution in evolving mss liquids which crystallisation record is represented by the observed sulfide mineral proportions. The bulk PGE (+Re, Ag, Au) contents calculated for the sulfides disseminated in dunites, display an enrichment of the mss in Rh, Ru and Os at the base of the sulfide horizon, whereas Pd and Ag (Fig. 2A) are enriched at higher levels, and Cu is enriched at the top of the horizon. This "chromatographic" (offset-like) pattern of PGE and noble metal distribution was previously observed in the whole-rock compositions from the Great Dike and Munni-Munni intrusions (Naldrett & Wilson, 1990; Barnes, 1993), where it was explained by fractional sulfide segregation. To test this hypothesis, we compared the observed patterns with calculations based on the new experimental data on $D_i$ sulfide – silicate melt (Mungall & Brenan, 2014). To do this, we combined the results of COMAGMAT modeling of sulfide immiscibility in the Dovyren parental magma (see Fig. 1 in Ariskin & Danyushevsky, this volume) with calculations of the PGE and noble metal contents in sulfide and silicate melts as crystallization proceeds. Some of the results are summarized on Fig. 2B as a comparison of the modeled and observed Cu/Pd vs Pd trends for the average sulfide compositions. The results for Pd display remarkable consistency of the modeled and observed compositions. The latter reflect ~80 wt.% magma crystallization, which leads to formation of 0.11 wt.% sulfide. Similar results are obtained for Ag. This emphasizes both the high quality of the used experimental $D_i$ for Cu, Pd, Ag, and the ability of COMAGMAT-5 to model accurately sulfide immiscibility. However, the calculated Cu/Pd vs Pt trends deviate significantly from the observed Pt contents. This may indicate either an incorrect (too high) experimental $D_{Pt}$ or the presence of additional Pt in a finely dispersed native form in the dunites.

*This research was supported by the AMIRA project P962 (2007-2010) and the Russian Foundation for Basic Research (projects 11-05-00268a, 14-05-00216a).*

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# PROCESSES LEADING TO CONCENTRATION OF PLATINUM-GROUP ELEMENTS IN CHROMITE RICH ROCKS

**Barnes, S-J.[1], Pagé, P.[1], Prichard, H.M[2]., Zientek, M.L.[3] & Fisher, P.C.[2]**

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**ABSTRACT**. Platinum-group elements are enriched in the ultramafic parts of the Stillwater, Bushveld and Great Dyke Complexes. Processes whereby this enrichment may occur are considered.

It is well established that the ultramafic portions, and in particular the chromite layers, of many layered intrusions are enriched in platinum-group elements (PGE) relative to the amount that can be accounted for by a silicate trapped liquid fraction. Furthermore, the IPGE (Os, Ir, Ru) and Rh show a greater degree of enrichment than Pt and Pd. Two models are currently used to explain these enrichments. The first proposes that chromite crystallization leads to the saturation of the magma in laurite ($RuS_2$) resulting in the enrichment of Ru (and to a lesser extent Os and Ir, which occur as minor elements in laurite), in chromite layers. Platinum and Pd are added after laurite crystallization by addition of a small amount of base metal sulfide liquid to the chromite layers. The second model proposes that all of the PGE were originally collected on the cumulate pile by a base metal sulfide liquid, with the higher concentration of sulfide liquid in the chromite layers being due to the high density of chromite and sulfide liquid. Later, a hydro-magmatic fluid partly dissolved the base metal sulfides and Pt+Pd, leaving a cumulate enriched in IPGE and Rh. In order to consider these models more closely we have carried out a petrological, mineralogical and geochemical study of the Ultramafic series of the Stillwater Complex.

Based on the following observations the rocks appear to have lost S. The S content of the rocks is too low (<100 ppm) for them to contain cumulate sulfides. Many of the tiny (0.01-0.05 mm) base metal sulfide grains show disequilibrium textures and are rimmed by magnetite. The average S/Se ratio of the rocks is low (~1500). Given that S has been lost we will use Se as a proxy for S. If base metal sulfides collected the PGE then there should be a positive correlation between the PGE and Se. There are correlations between Pd, Cu and Se as illustrated for Pd (Fig. 1a) suggesting sulfide liquid collected these elements. There is no correlation between the IPGE or Rh and Se, as illustrated by Ru vs Se (Fig. 1b). The IPGE and Rh correlate with Cr, illustrated by Ru vs Cr (Fig. 1c). These observations and the platinum-group mineral study which shows that laurite is the most common PGM in the rocks tend to favor model 1.

However, the Rh and Pt data are not consistent with model 1; Neither laurite nor a base metal sulfide liquid has the correct ratios to be the carrier of these elements. The mantle normalized patterns of the chromite layers (G chromite layer illustrated in Fig. 1d) peak at Ru and Rh. The pattern for laurite does not match that of the chromite layers. The laurite does not contain enough Rh. The addition of a base metal sulfide liquid would add more Pt than Rh, therefore simply adding base metal sulfide liquid will not solve the problem. Model 2 might work, but the lack of correlation between IPGE, Rh and Se requires that Se was mobilized. Furthermore to have a correlation between Pd, Cu and Se it requires that they precipitate together which seems rather fortuitous.

We propose a new model based on recent results from lasering chromites from volcanic rocks. Chromites in volcanic rocks appear to contain the IPGE AND Rh within the structure.

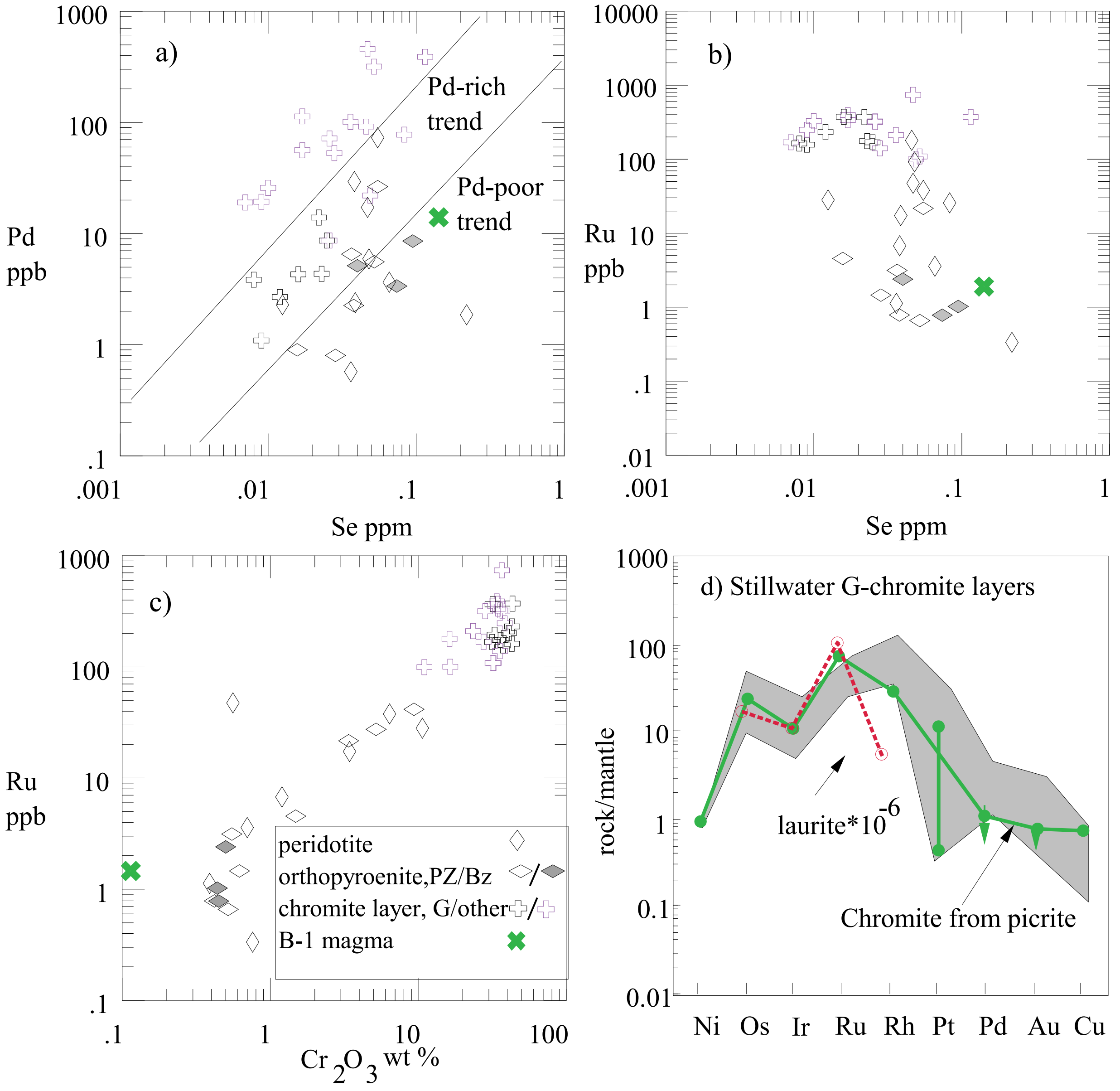

*Fig. 1.* a) Pd vs Se showing that Pd and Se correlate suggesting collection of Pd and Se by a sulfide liquid; b) Ru vs Se showing that Ru does not correlate with Se suggesting that Ru was not collected by a sulfide liquid; c) Ru vs $Cr_2O_3$ showing a good correlation suggesting the phase collecting Ru was concentrated in the chromite layers; d) Mantle normalized patterns of the chromite layers, laurite and chromite from picrite (Page et al., 2013) showing that the whole patterns from Stillwater chromite layers most closely resemble the patterns from chromite grains from picrite

The mantle normalized pattern for chromite from a continental picrite (Fig. 1d) is similar to that of the G chromite layer, which is the layer with the greatest enrichment of IPGE and Rh. This model proposes that the IPGE and Rh partitioned into the G chromites at high temperature. The chromite grains underwent grain boundary migration during cooling. Small amounts of base metal sulfide crystallized from the trapped liquid and were incorporated in the chromites during this process. As cooling continued the Fe and Ni in the sulfide diffused into the chromite and the IPGE and Rh in the chromite diffused into the sulfide transforming the base metal sulfide into laurite with remnant sulfides and a few PGM grains. Laurite is the main PGM produced because Ru is the most abundant PGE in the chromite. If this model is correct it would apply to the Bushveld and Great Dyke because the chromite layers in these intrusions show the same types of patterns.

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# INSIGHT INTO THE GENESIS OF PGE-Ni-Cu MAGMATIC SULFIDE DEPOSITS OF THE MONCHEGORSK IGNEOUS COMPLEX: EVIDENCE FROM MASS-INDEPENDENT SULFUR ISOTOPE FRACTIONATION

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**ABSTRACT**. We present the first multiple sulfur isotope data for the Ni-Cu-PGE sulfide mineralization of the ~2.5 Ga Monchegorsk Igneous Complex (MIC). Base Metal Sulfide (BMS) composition, PGE distribution and PGM assemblages were also studied for different types of Ni-Cu-PGE mineralization. Small, negative Δ33S values for sulfides in both MIC ore mineralization and hosting rocks indicate that sulfur required for mantle melt to exsolve sulfide melt was assimilated from hosting Archean gneisses and that it underwent mass-independent fractionation (MIF) in the oxygen-poor Archean atmosphere before it was incorporated into protoliths of the host rocks. Interestingly, the Δ33S values decrease from the center to the margin of the MIC, indicating that both local assimilation and S homogenization occurred in the central part of the large intrusion.

## INTRODUCTION

Investigation of sulfur sources for the ~2.5-2.4 Ga PGE-bearing Fennoscandian mafic-ultramafic intrusions has significant value in understanding the genesis of Cu-Ni-PGE sulfide mineralization. Sulfur isotope data for Russian, Kola-Karelian layered intrusions are extremely scarce. According to L.N. Grynenko et al. (1967), $\delta^{34}S$ variations in BMS from the disseminated and veined Fe-Ni sulfide ores of the Monchepluton range from+0.02 to +0.16 ‰ CDT, consistent with the mantle source of sulfur. However, it has been recently emphasized that Archean sedimentary sulfides show a small range of $\delta^{34}S$ values similar to that of the mantle S, but can exhibit a large range of $\Delta^{33}S$ values

$$\Delta^{33}S = \delta\Delta^{33}S\left[\left(\overline{\frac{\delta^{34}S}{1000}}\right)^{\lambda_{RFL}} - 1\right] \text{ x } 1000,$$

$$\text{where } \lambda_{RFL}=0.515,$$

acquired in Archean, oxygen-free atmosphere via UV-mediated photochemical reactions. The $\Delta^{33}S$ signature thus represents an excellent new tool for differentiating mantle and crustal sources of sulfur, and for quantifying how much crustal material was assimilated (Bekker et al., 2009; Penniston-Dorland et al., 2008 and references therein). This is particularly relevant to mantle-derived mafic to ultramafic intrusions that host economic, Ni-Cu-PGE sulfide mineralization, since partial melting of the mantle generates a sulfur-undersaturated magma as it ascends through the crust due to increased solubility of sulfur in mafic to ultramafic melts as pressure decreases.

## GEOLOGICAL BACKGROUND

The late Neoarchean to early Paleoproterozoic layered intrusions of the MIC, i.e. Monchetundra, Monchepluton, Vuruchuaivench, and few small intrusions of the same age, are located within the southern inner part of the Pasvik-Pechenga-Imandra-Varzuga greenstone belt. The MIC intrudes Archean gneisses of the Kola-Belomorian complex and in turn is unconformably overlain by volcanosedimentary rocks of the Paleoproterozoic Imandra-Varzuga Series. The Monchepluton is well known for previously mined-out Cu-Ni sulfide ore mineralization (hosted in veins) of the NKT intrusion, and is currently being explored for disseminated Fe-Ni sulfides of "Peridotite layer 330". Low-sulfide, high-grade PGE deposits were recently discovered in the Monchetundra and Vuruchuaivench intrusions.

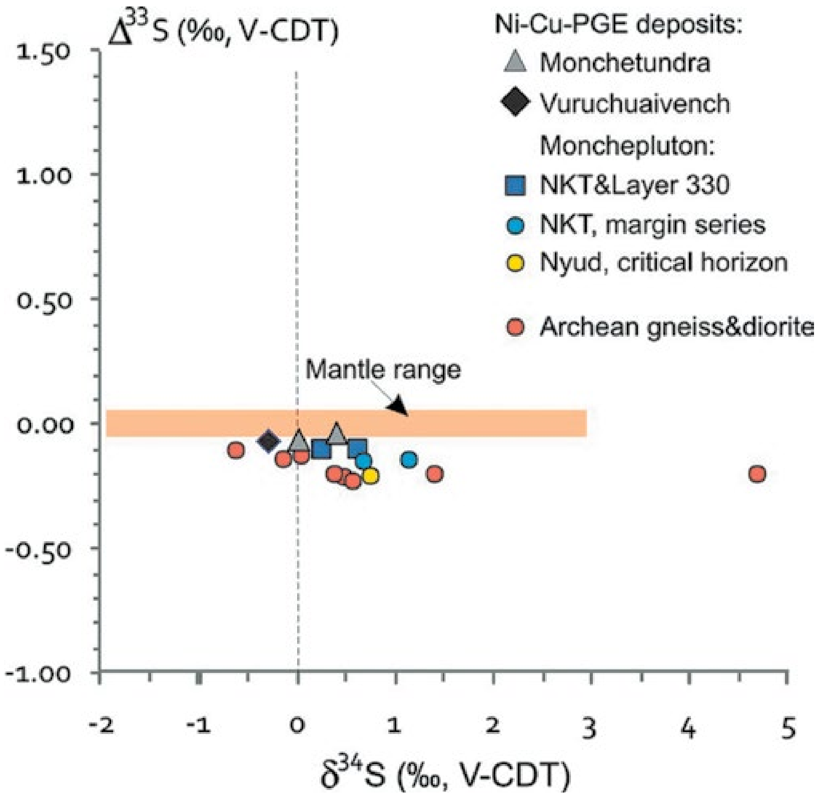

*Fig. 1.* $\Delta^{33}S$ vs. $\delta^{34}S$ data for the studied samples from the MIC PGE-Cu-Ni deposits and Archean exocontact gneiss and hypersthene diorite. Mantle field values are from Bekker et al. (2009)

## RESULTS

We characterized different types of PGE-Ni-Cu mineralization in different positions within the intrusions. All ore types are represented by the chalcopyrite-pentlandite-pyrrhotite assemblage, which in varying degrees is replaced by millerite, pyrite and other minor mineral species. Primary PGM are represented by Pt- and Pd-sulfides, arsenides and bismutotellurides, and may be replaced by secondary PGM, which were formed via hydrothermal alteration of primary sulfide and silicate minerals by magmatically-derived fluids.

The studied samples from all MIC deposits have a small range of $\delta^{34}S$ values similar to that of the mantle. The $\delta^{34}S$ values in the country rocks on the contact of the pyrite-pyrrhotite-(rarely) chalcopyrite-bearing gneiss and diorite range from -0.64 to +4.68 ‰ V-CDT, while the $\Delta^{33}S$ values range from -0.21 to -0.10 ‰ (Fig. 1). Notably, there is a trend in $\Delta^{33}S$ values; disseminated and veined BMS in the layered series of the central part of the intrusions have close to the mantle $\Delta^{33}S$ values, whereas sulfides from the peripheral part of NKT and Nyud have $\Delta^{33}S$ values almost comparable to those of the hosting gneisses (Fig. 1). We infer that sulfur in the country rocks underwent MIF as indicated by its negative $\Delta^{33}S$ values, and was then incorporated into the ore mineralization. These values are all outside the accepted $\Delta^{33}S$ range of the mantle, ruling out mantle sulfur as the dominant source. Based on small, negative $\Delta^{33}S$ values, the sulfur source was likely Archean VMS or massive, base-metal barren sulfide lenses, which were incorporated in the host rocks and then assimilated by primitive mantle magmas, generating ore mineralization in layered mafic to ultramafic intrusions.

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# THE MINERAL ASSEMBLAGE OF Au-PGE-Cu-V-Ti-Fe ORES IN THE VIKSHOZERO ORE OCCURENCE (KOYKAR SILL, SOUTH KARELIA, RUSSIA)

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**ABSTRACT**. Both mineral and major element composition of Fe-rich gabbros from the ore zone of the Koykar intrusion (Southern Karelia, Russia) is presented. These data allowed for the distinguishing five stages of the formation of the observed mineral assemblages. The noble metal mineralization in these rocks includes at least 23 minerals, with Pd and Pt arsenides being the most abundant.

The Koykar intrusion was emplaced at (1983±6 Ma) into upper Yatuly igneous-sedimentary rocks. It forms a 50 m thick, flat-dipping sill of quartz gabbro-dolerites. In the lower part of the sill vanadium titanomagnetite ores were delineated within a poor quality sulfide deposit (0.2-0.4 wt. %) containing Cu, Au, Pd, Pt mineralization (Philippov et al., 2007, Mineral deposits.., 2012).

The rocks of the ore zone are represented by metamorphosed and variably altered magnetite gabbro-dolerites. Major minerals present are: plagioclase (35-60%), amphibole (30-45%), magnetite and ilmenite (total 10-30%), minor minerals are epidote (3-6%), biotite (1-3%), chlorite (2-3%), quartz (1-2%), feldspar (0.5-1%), sericite (up to 1-2%), titanite (up to 2%) and apatite (up to 1%). Of note is the presence of characteristic granophyric textures (graphic intergrowths of quartz with microcline or oligoclase). Almost all the minor minerals in these rocks are secondary, i.e. they result from epigenetic replacement processes of early phases. This is also the case with one of the major minerals – amphibole, whose aggregates are pseudomorphing protolite pyroxene. Zoisite, epidote, chlorite and sericite are epigenetic minerals. They either form on early plagioclase as microveins or partially or fully replace plagioclase.

XRF analysis shows that the ore bearing rocks of the Koykar sill complex are Fe-rich gabbros: $SiO_2$ (25.6–44.7 wt. %), $Fe_2O_3$ (20–47.9 %), $Al_2O_3$ (8.6–15 %), $TiO_2$ (3.7-8.1 %), $V_2O_5$ (0.13-1 %).

These rocks contain elevated concentrations of copper (1053±517 ppm, ICP-MS) There is a positive correlation of copper with Au, Te, Re, P, REE, Be, Zr, Hf, Th and a negative correlation with Fe and Ni. Noble metals have strong correlations with each other, particularly Pt and Pd ($r=0.91$). There is a slightly weaker correlation between Pt-Au ($r=0.77$) and Pd-Au ($r=0.60$). The total concentration of noble metals is about 1-1.5 ppm. Relative to primitive mantle, all samples are enriched in Cs, Rb, K, Mo, Pb and Ti. Some samples are also enriched in U. The rocks are relatively depleted in Nb, Sr, and P.

In the Koykar sill complex ores, five sequential stages of ore paragenesis are emphasized:

a) Paragenesis 1 is represented by magnetite-1 and ilmenite-1, which resulted from titanomagnetite disintegration;

b) Ilmenite-2 formed by recrystallization of ilmenite-1;

c) Formation of the polysulfides is preceded by tectonic deformation, which is followed by recrystallization of early minerals, accompanied by introduction and release of PGE and chalcophile elements;

d) Replacement of minerals that formed in stages a, b, and c;

e) Hypergenetic mineral paragenesis.

The major ore paragenesis is represented by magnetite-2, pyrite, cobaltite, sphalerite, pyrrhotite, chalcopyrite, bornite, linnaeite, carrollite, galena and clausthalite**.** Noble metal minerals crystallized at a final stage of the paragenesis formation.

Nine noble metal minerals were identified in thin section: naumannite**,** isomertieite**,** mertieite II, sperrylite, vincentite**,** kotulskite, merenskyite**,** moncheite**,** paolovite and native gold. Software MLA3.1 (method SPL-GXMAP) was used to search noble metal minerals in flotation concentrates. This research significantly expanded the list of minerals and determined their relationship. It was found that the most abundant minerals are palladium and platinum arsenides, namely arsenopalladinite, palladoarsenide, palarstanide and sperrylite. Noble metals sulfides are less common, including braggite, cooperite and vysotskite, and a new, unnamed phase $(Pt,Cu,Co)_4S_5$. The least prevalent are kotulskite and native gold and grains of mertieite I, atokite, merenskyite, hessite, hollingworthite and other minerals. Thus, the noble metal mineralization of these ores is quite diverse, comprising at least 23 minerals, but consisting of tiny grains which vary in size from 100-200 nanometers to 10-15 micrometers.

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# CONCENTRATIONS OF TRACE ELEMENTS IN ROCKS OF THE LOWER LAYERED HORIZON OF THE WEST-PANA INTRUSION

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**ABSTRACT**. The Lower Layered Horizon (LLH) of the West-Pana intrusion and associated horizons of PGE mineralization were formed as a result of one or several additional magma injections (Korchagin & Mitrofanov, 2010). Its composition was essentially similar to the saturated tholeiite basalt assumed to be a parental magma for the West-Pana layered intrusion in the Kola Peninsula (Latypov & Chistyakova, 2000). In the present study, whole-rock (GI KSC RAS) and ICP-MS trace-element data (IGG UB RAS) through a detailed section of the LLH were obtained in an attempt to find some differences in the composition of the magmas.

According to the borehole 23 (fig. 1), four rhythmic of the LLH with a total thickness of 21.5 m lie on the mesocratic gabbronorite containing rare 5-cm interlayers of leucocratic rocks. Approaching the base of the horizon from below, rock composition becomes leuco-mesocratic, and blue quartz appears. The bottom of the LLH (and the bottom of its first thickest cycle) is a layer of fine- to medium grained melanorite. Interlayering of gabbronorites and leucogabbronorites is observed in the middle of the cycle. Mottled rock of leucogabbronorite-anorthositic composition with relatively distinct spots caused by amphibolization and saussuritization occurs at the base of the leucocratic part of the unit. There are leucogabbronorites with relatively thin layered mesocratic and olivine-bearing varieties at the top of the cycle. In comparison to the first cycle of the LLH, the upper cycles are thinner and have more simple internal structures. Well-expressed thin layering is rare, and a mottled structure is weakly developed. Relatively thin (15-55 cm thick) coarse grained olivine melanorite layers at the base of these units are a characteristic feature. Sporadic grains of olivine also occur in leucogabbronorites at the top of the first and of the second cycles. The overlying unit is represented by homogeneous fine-medium grained gabbronorites with rare interlayers of coarse and medium grained varieties.

PGE mineralization in the LLH (Fig. 1) occurs near the lower margins of the upper cycles and is associated with interstitial irregular disseminated sulfides (up to 0.5 vol.% of pentlandite, chalcopyrite and pyrrhotite). Disseminated sulfides are most abundant in the upper part of the first cycle, whereas they are hardly visible in the upper cycles.

The most important aspects of analytical data are shown in Fig. 1. According to these data it appears that additional magma injections, with similar concentrations of compatible elements to the parental magma, differ from the latter by lower concentrations of Ti (and also Th, Pb, Hf, Zr,Ta, Nb etc.; not shown) and rare earth elements. Of note are also the relatively high anorthite component in plagioclase in the LLH and the positive Eu anomaly in the LLH and in the overlying unit.

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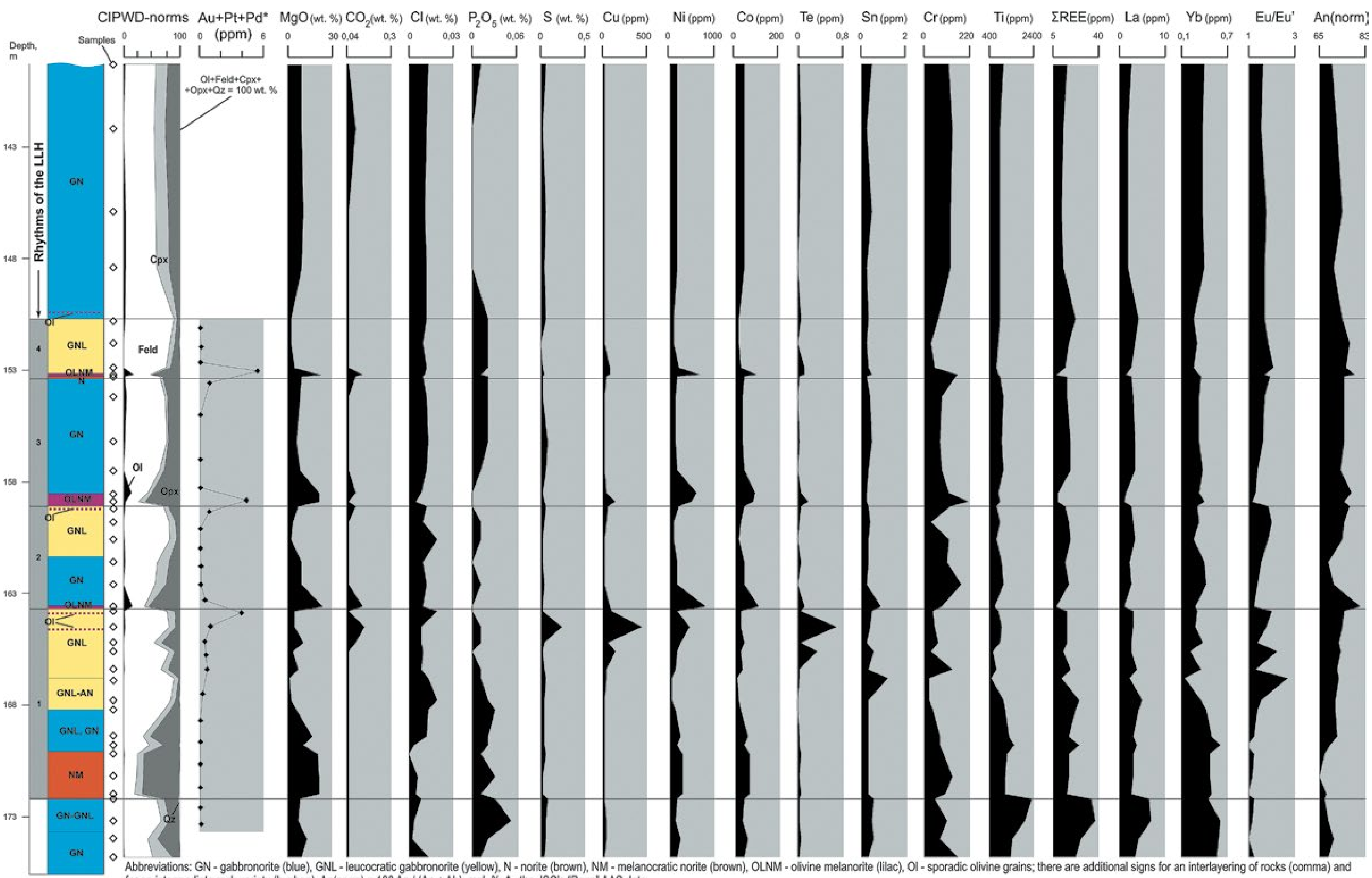

Abbreviations: GN - gabbronorite (blue), GNL - leucocratic gabbronorite (yellow), N - norite (brown), NM - melanocratic norite (brown), OLNM - olivine melanorite (lilac), Ol - sporadic olivine grains; there are additional signs for an interlayering of rocks (comma) and for an intermediate rock variety (hyphen). An(norm) = 100 An / (An + Ab), mol. %. * - the JSC's "Pana" AAS data.

*Fig. 1*. Distribution of PGE mineralization and compositional variations of rocks through the section of the LLH (borehole 23, Kievey Deposit)

# INVESTIGATION OF PLATINUM GROUP ELEMENTS OF THE SARANOVSKY CHROMITE DEPOSIT

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**ABSTRACT.** The Saranovskiy massif is a layered ultramafic intrusion similar to the Bushveld Complex. Based on outcrops and placers, two types of chromite deposits are encountered in the area. The distribution of platinum group elements in both types of chromite deposits was estimated using inductively coupled plasma mass-spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) analysis. It was determined that the platinum content in chromite of outcrops is higher than that in placer deposits. The content of platinum in source rocks ranges from 0.03 up to 0.18 ppm and that in the placer deposits from 0.005 to 0.008 ppm.

There are many known layered ultramafic intrusions in the world. Some of them contain high grade platinum mineralization. The Bushveld Complex and the Great Dyke in Africa, and the Stillwater Complex in southwestern Montana are the most famous layered igneous intrusions in the world. The Saranovsky massif has a similar origin, structure and mineralization (Ivanov, 1990).

The Saranovsky massif is located on the western slope of the Middle Urals, within the Perm Region (Russia). It is of Neoproterozoic age (Iblaminov, 2002) and consists of dunite and harzburgite layers. All the rocks of the massif experienced significant alteration. The Saranovsky massif has a complicated structural history resulting in steeply dipping layers.

The Saranovsky massif contains several chromitite layers. Three of the chromitite layers are of economical importance. These are the Western, Central and Eastern ore bodies. The ore bodies are embedded in serpentinite rock. The deposits of cobble-size chromites form the surrounding placer deposits.

Previously, nine samples of massive chromite ore were investigated by atomic absorption spectrometry (AAS). It was found that only two specimens contained platinum. The result of the analysis showed that samples from the Western ore body contained 0.03 ppm platinum, and those from the Central ore body indicated platinum values as high as 0.18 ppm. These samples were collected at the southern flank of massif.

Analyses of chromites pebbles from placers showed that all platinum group elements are uniformly distributed throughout the study area. The estimated average content of platinum group elements is 0.421 ppm. The predominant elements were Pd (average content 0.231 ppm) and Ru (0.120 ppm). Lower average concentrations were established for Ir (0.037 ppm), Rh (0.026 ppm), and Pt (0.007 ppm).

*Future work should focus on determining the distribution of platinum group elements in a complete cross-section of the Saranovsky massif.*

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# PGE MINERALIZATION HOSTED BY MAFIC-ULTRAMAFIC INTRUSIONS OF RUSSIA: GEOLOGY AND PETROGENESIS

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**ABSTRACT**. There are two major types of PGE deposits: Cu-Ni-PGE sulphide-rich deposits hosted by picrite intrusions, e.g., Norilsk and Jinchuan, and Pt-Pd-rich, sulphide-poor deposits hosted by layered ultramafic-mafic intrusions, e.g., Bushveld, Great Dyke, Skaergaard. Russia and South Africa produce over 90% of platinum group elements (PGE) in the world. In Russia, Pt-bearing ultramafic-mafic intrusions of Paleoproterozoic to Mesozoic ages have been known in the Kola Peninsula, Karelia, Siberia and the Russian Far East. In terms of geodynamics, most of the Pt-rich ultramafic-mafic intrusions of Russia formed in an intra-plate setting, as part of large igneous provinces (LIP). In addition, there are Pt placers formed after Uralian-Alaskan type zoned complexes, e.g., in the Uralian, Aldan, and Koryak regions.

There are two early Precambrian LIPs in Russia: Kola (2500 Ma) and Karelia (2450 Ma). The Kola LIP consists of the North Kola belt of ore-bearing intrusions hosted by the Pechenga-Imandra-Varzuga rift structure. The North Kola belt includes the Monchegorsk intrusion, Imandra lopolith and Fedorovo-Pansky complex. The Monchegorsk intrusion has a complicated multi-phase structure consisting of Cu-Ni-PGE sulphide-rich ores and sulphide-poor ores hosted by pyroxenites (Sopcha seam) or anorthosites (Vyruchuaivench massif). The Fedorovo-Pansky Complex also has a multi-phase structure. It hosts commercially valuable sulphide-poor PGE mineralization formed during crystallization of late-phase magma, which intruded an already cooled early-phase layered intrusions (Mitrofanov et al., 2013).

The Karelian LIP extends from Karelia to Finland. In Karelia, the 2450 Ma ultramafic-mafic magmatism formed the Kivvaka and Lukkulaisvaara massifs of the Oulanka Layered Complex and the Burakovsky intrusion. In Finland, there are the Penikat, Portimo and Koillismaa Layered Complexes. The Kivvaka Massif is characterized by a rhythmic structure and non-commercial sulfide-poor PGE ores in the upper part of the layered intrusion. The Lukkulaisvaara massif also has a rhythmic internal structure and several sulfide-poor platinum-bearing reefs.

The Paleoproterozoic Siberian LIP (1880 Ma) includes the Chiney complex of layered intrusions: Chiney and Luktur. The Chiney multi-phase intrusion hosts two types of ore mineralization: Fe-Ti-V and Cu-PGE. Petrochemically, the layered series of the Chiney intrusion is similar to the upper part of the Bushveld pluton. Impregnated Cu-Ni mineralization occurs within a gabbro-norite sill located at the base of the main intrusion. The copper ore mineralization, which formed in the contact zone of the intrusion, is characterized by high concentrations of Pd (Rudny locality). The origin of the Cu-Ni-PGE sulfide mineralization has been generally linked to prolonged evolution of the magmatic system: the ores may form at various stages, from magmatic to post-magmatic.

Ultramafic-mafic massifs connected with the Franklin LIP (725 Ma) in the southern Siberian Craton includes the Ioko-Dovyren dunite-troctolite-gabbronorite intrusion in northern Transbaikalia and the Kingash mafic-ultramafic intrusion in East Sayan. The Ioko-Dovyren intrusion hosts two sulfide-poor PGE mineralized horizons in the upper part of the layered massif. The Kingash intrusion contains massive Cu-Ni-PGE mineralization. This LIP also includes smaller platinum-bearing ultramafic bodies of the Alkhadyr block similar to those of the Ioko-Dovyren and Kingash intrusions (Polyakov et al., 2013). Unlike the Paleoproterozoic layered intrusions, those of Neoproterozoic age are characterized by a different path of crystallization, Ol → Pl → Cpx → Opx, caused by a different composition of the parental melts. The Paleoproterozoic intrusions formed by crystallization of Si-Mg-rich magmas (boninite-type melt) resulting in early crystallization of orthopyroxene and finally formation of harzburgite, orthopyroxenite and norite. The Neoproterozoic (Riphean) and Phanerozoic intrusions were derived from picritic and ankaramitic melts to form troctolite, Ol-gabbro and wehrlite.

The formation of PGE deposits requires high-degree melting of mantle sources, high concentrations of PGE in parental melts and formation of a system of intermediate chambers allowing formation of sulfur saturated melts and sulfide-silicate liquation. The highest concentrations of PGE are typical of many LIPs formed in response to mantle plumes, e.g., the Siberian, Tarim and Emeishan plume-related LIPs. The central parts of these LIPs host world famous, highly productive PGE deposits (Norilsk, Kalatonge, Jinbaoshan) (Dobretsov et al., 2010).

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# PGE-Cu-Ni DEPOSITS IN NORTHERN TRANSBAIKALIA (SIBERIA, RUSSIA)

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**ABSTRACT**. There are several PGE-Cu-Ni deposits in the southern part of the Siberian Platform. The Kodaro-Udokan area is the most economically important region in terms of PGE resources. Magmatic deposits related to ultrabasic-basic intrusions dominate in this region. Four deposits are related to the Chineysky massif and one is located in its vicinity. Several deposits are located within rocks of the Luktur and the Mylove massifs. All these deposits represent two different genetic types, magmatic and hydrothermal.

The Chineysky anorthosite–gabbronorite massif is the most contrast layered intrusion in Russia. It is accompanied by large V and PGE-Ni-Cu deposits. Ore bodies are hosted by both magmatic (endomorphic ores) and sedimentary rocks (exomorphic, or aureole ores). Their thicknesses range from 10 to 35-40 m. The best explored Rudnoye Deposit is confined to the contact gabbroids of the eastern offshoot of the Chiney Massif and the host rocks of the Udokan formation. The mineralized zone is stratiform and extends along the whole length of the surface outcrop of gabbroids (about 9 km) with a gentle northwestward dip at 6°-12°. Its thickness ranges from 3 to 65 m. The content of sulfide minerals is in places as high as 50-60% in gabbroids and monzodiorites, and the ore acquires sideronitic texture in such cases. Ores are mostly disseminated, less frequently forming stockwork and breccias. Veined and lenticular ore bodies are less frequent. They consist mainly of pyrrhotite and chalcopyrite, whereas pentlandite is a rare mineral in the ores. The latter assemblage is of limited occurrence and typically contains minerals of the cobaltite–gersdorfite isomorphic series, lellingite, and safflorite. Sulfoarsenides and arsenides are often accompanied by palladium minerals – maichenerite, merenskyite, etc. Palladium phases have been recognized, among others, in large amounts in nickelite.

The exomorphic ores contain the highest PGE concentrations, because they usually correlate with copper, and palladium here dominates dramatically over platinum (Pd/Pt ratio is ranging from 10 to 110; Gongalskiy, Krivolutskaya, 2004). However, different nonferrous and precious metal proportions are also reported (Gongalskiy et al., 2008; Gongalskiy, 2011). Exomorphic ores sometimes form isometric by shape bodies with bonanza grades of 15 ppm Pt, 124 ppm Pd, 14 ppm Au, and 345 ppm Ag. Silver grade does not correlate with copper grades (Tolstykh, 2008). Ore bodies are characterized by variable strike and dip as well as wide thickness and grade variations. These ores contain cubanite, millerite, and bornite in significant amounts, whereas pentlandite is scarce and contains small amounts of cobalt (about 2-3 wt.%).

The Kontaktovoye Deposit is the second largest in size after the Rudnoye Deposit. It hosts disseminated chalcopyrite-pyrite ores. They have a layered shape, but valuable components are more evenly distributed in the ore bodies, delineated on the basis of sampling data. Copper grade, for instance, varies from 0.27 to 2.85 wt.%; palladium grades, from 0.47 to 2.25 ppm; platinum grades, from 0.1 to 1 ppm, and gold grades are 0.1-0.2 ppm. These grades, however, was not confirmed during the follow up work, particularly in the interval between the Verkhnechineysky and Skvoznoye deposits.

PGE-Cu-Ni ore occurrences and deposits of the Luktur massifs have been discovered in its upper part, among coarse-crystalline gabbronorites and norites. Ores are disseminated with up to 30% sulfide minerals. They differ from the deposits of the Chiney massif by elevated Ni grades in ores reducing Cu/Ni ratios down to 0.5–0.8 typical of Norilsk-type deposits. Major ore minerals are chalcopyrite and pyrrhotite, and minor minerals are pentlandite (poor in cobalt with < 2 wt.% Co) and pyrite. As in the Chiney massif, horizons strongly enriched in titanomagnetite have been established. They often contain elevated nonferrous and noble metal grades (PGE concentrations are as high as 0.8 ppm).

Copper–nickel ore occurrences in the gabbroids of the Maylav massif (Gongalsky & Krivolutskaya, 2004) were discovered by the author in a left tributary of the Ingamakit River west of the Udokan deposit, where elevated metal concentrations of up to 2.7 % Cu, 0.1% Ni, 0.9 ppm Pt, 2 ppm Pd, and 4.2 ppm Ag were found in titanomagnetite-bearing gabbronorites. The mineralized zones resemble the deposits of the Chiney massif, Kontaktovoye in particular, in relative nonferrous and noble metal abundances and specific mineral composition.

The Pravoingamakitsky Deposit is of hydrothermal origin. It is located 2 km from the Chineysky massif. It contains sulfide-quartz veins with noble metals (39 ppm Ag, 0.2 ppm Pd, 0.5 ppm Au, and 0.1 ppm Pt). Ore bodies of this area are quartz veins and lenses (up to 1 m thick and ten to twenty meters long), with sulfide veinlets. The ores consist of pyrite and chalcopyrite varieties, with veined and brecciated textures. Less frequent are quartz veins with chalcopyrite–bornite mineralization and disseminated ores in sandstones. They are characterized by high and widely varying Cu/Ni ratio values (from 10 to 700). The Ni-rich veins host – millerite and pentlandite (Gongalskiy et al., 2007). These ore varieties are also enriched in noble metals: 39 ppm Ag, 0.2 ppm Pd, 0.5 ppm Au, and 0.1 ppm Pt. They also contain fine (up to 10 μm) Ag, Cu, and Pb telluride and selenide aggregates. Cu-rich ores are markedly enriched in silver (up to 370 ppm). Worthy of notice is that they always contain Pd ranging between 0.4 to 1 ppm.

The Udokan-Chiney area is unique for its potential to study magmatic, hydrothermal, and sedimentary deposits formed at different depths due to displaced crustal blocks at the margin of the Siberian craton. Fractionation of magmas and consistent separation of valuable components was the main source of metal deposits. Until now, they were considered to form part of (i) magmatic copper- PGE-Ag-Au deposits and (ii) hydrothermal noble metal formation – quartz veins. However, we believe that these deposits formed in a common magmatic-hydrothermal system. Deposits have deep roots in deep-seated layered mafic-ultramafic massifs. The depth and morphology of these deposits were constrained by 3D modeling of geological structures using modern processing of geophysical fields.

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# MAGMATIC STRATIGRAPHY CONTROL ON PGM MINERALIZATION OF THE EAST PANA LAYERED MASSIF

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**ABSTRACT**. The East Pansky layered massif (Kola peninsula, NW Russia) hosts 3 horizons of low sulfide PGM mineralization confined to the boundaries of cyclic units. One of the horizons, confined to the contact of the GNZ1 and GNZ2 zones is of economic importance. In the course of exploration, pothole-like transgressive structures have been studied and were often found to be favorable for PGM mineralization. Analysis of stratigraphic relationships has been used as an efficient exploration method.

The East Pansky massif (2487 Ma) is the easternmost one of 4 layered mafic massifs of the Fedorova – Pansky intrusive complex located in the central part of the Kola peninsula (NW Russia). The complex cuts Archean gneisses and alkaline granites and in turn is overlain by Palaeproterozoic mafic volcanic rocks of the Imandra – Varzuga zone. The magmatic stratigraphy of the East Pansky massif shows a cyclic structure. The massif is subdivided into 4 principal units. From the base to the top, these are: Marginal Zone (MZ), Gabbronorite Zone 1 (GNZ1), Gabbronorite Zone 2 (GNZ2) and Gabbro Zone (GZ). This subdivision is based on cumulus associations. Pyroxenites and olivine-bearing cumulates are typical for the basal parts of the cyclic units (zones). Each cyclic unit shows specific cumulus associations, rock textures and chemistry. Erosive boundaries between units are quite typical. Based on interpretation of cumulus associations and trace element geochemistry, the GNZ 2 and GZ cyclic units are considered to have formed as a result of magmatic chamber replenishment by new pulses of fractionated magma.

Three PGM-bearing levels were identified at the boundaries of units as PGM zones A, B and C (listed from the footwall to the top). PGM zones are confined to the boundaries of cyclic units: GNZ1 footwall – PGM Zone A; GNZ1 – GNZ2 boundary – PGM Zone B; GNZ2 – GZ boundary – PGM Zone C (Fig. 1). PGM zone B has been proven to contain significant PGM mineralization including East Chuarvi, the first economic reef-type PGM deposit in Russia. PGM mineralization of this level forms a reef package of high-grade low-sulfide mineralization without obvious lithological control on PGM distribution.

In the course of exploration the relationships between PGM mineralization and stratigraphy have been studied with special emphasis on pothole-like erosive structures. A schematic long section of the central part of the East Pansky massif (Fig. 2) shows that in different parts of the intrusion the GNZ1 – GNZ2 boundary penetrates to different levels of the underlying stratigraphy up to 150m below its normal position. It is important that areas where the contact reaches the particular level of poikiltic rocks of GNZ1 are much more favorable for PGM mineralization than other areas. This observation has been successfully used as an exploration tool which led to the discovery of a series of low sulfide PGM occurrences along the GNZ1-GNZ2 contact.

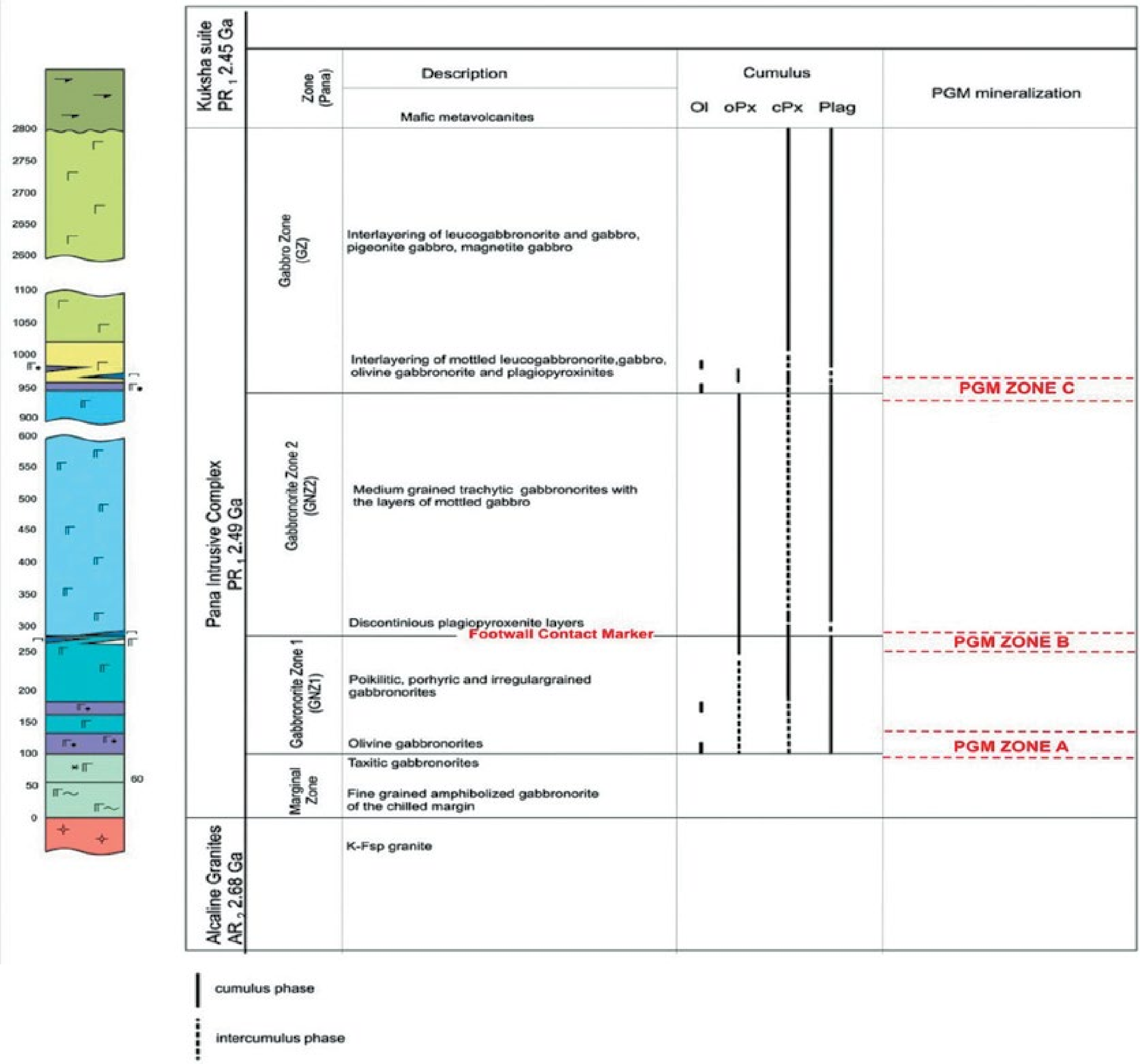

*Fig. 1*. Principal stratigraphy of East Pansky layered massif

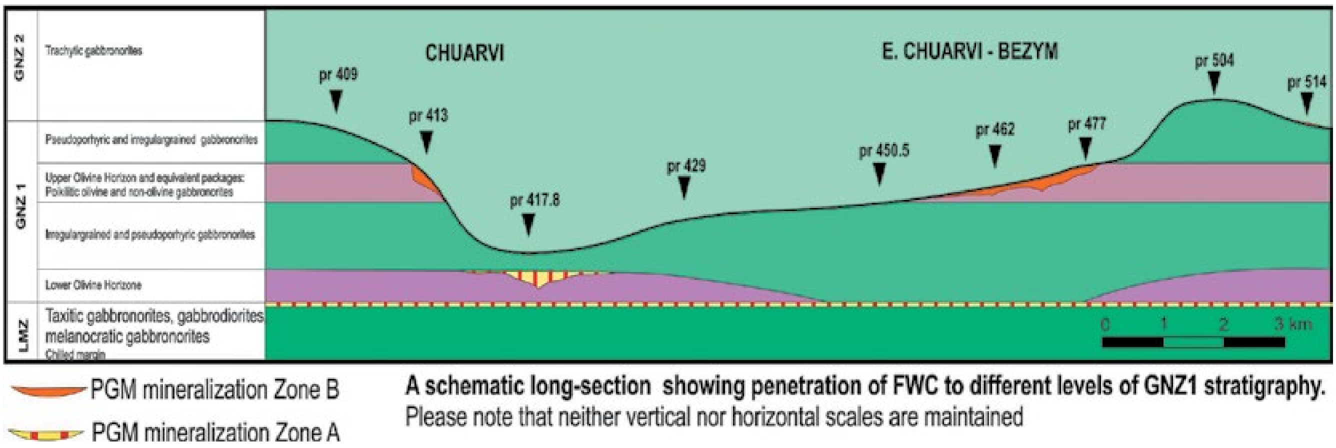

*Fig. 2.* Schematic long section. PGM mineralization controlled by position of erosive contact of GNZ1 and GNZ2 cyclic units

# THE IOKO-DOVYREN INTRUSION, NORTHERN TRANSBAIAKALIA, RUSSIA: SULPHIDe Ni-Cu-PGE AND LOW SULPHIDE PGE MINERALIZATIONS

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**ABSTRACT**. The Ioko-Dovyren intrusion includes both sulfide Ni-Cu-PGE and low sulphide mineralization which differ in their composition and genesis.

The Ioko-Dovyren layered dunite-troctolite-gabbro intrusion is located in Northern Transbaikalia (56°30‘N and 110°E). It is a 26 km long and up to 3.5 km wide sill-like body, which was intruded almost concordantly into Neoproterozoic carbonate-terrigenous rocks, along the axis of the Synnyr rift zone. The Ioko-Dovyren intrusion was emplaced in the Late Proterozoic (728±3.4 Ma; Ariskin et al. 2013). The massif consists, from the bottom upward, of: a lower marginal zone (up to 200 m thick), ultramafic zone (up to 1000 m), layered zone (up to 1000 m), and a gabbroic zone (up to 1100 m). The rocks of the massif are characterized by changes in cumulate mineral assemblages in the order: Ol+Chr → Ol+Pl+Chr → Ol+Pl+Cpx → Ol+Pl+Cpx+Opx. Gabbronorites occur as a sill in the uppermost part of the massif, as well as sills and dykes which cut plagioperidotites at the bottom of the massif and the adjacent country rocks.

Ni-Cu mineralization in the Ioko-Dovyren massif has been known since 1949, with the area subjected to geological prospecting from 1959 to 1963. This mineralization is observed in plagioperidotites of the Ioko-Dovyren massif and within sills of the same composition that cut the footwall of the intrusion. Both disseminated (locally net-textured) and massive sulphide Ni-Cu mineralization occurs. It is irregularly distributed and mostly occurs in places where plagioperidotites were cut by dikes and sills of gabbronorites and gabbro-pegmatites. Disseminated mineralization is more common than net-textured and massive ores. Outcrops of rocks including disseminated sulphides have been traced along the strike for 1400 to 1700 m in surface exposures. Their width typically varies from 8 to 25 m, locally reaching 80 m. The lenses of disseminated mineralization are oriented parallel to the sills and the bottom zone of plagioperidotites. Veins of massive sulphide mineralization most commonly occur inside the disseminated ore zones. The largest sulphide vein occurs in the northeastern part of the massif. It extends along the base of the massif for 650 m and is 0.7-1.0 m wide. Drilling data indicate that the veins dip almost vertically and extend to depths of more than 500 m.

Sulphide mineralized zones at Ioko-Dovyren are enriched in PGE (up to 0.5 ppm Pt, 2.2 ppm Pd, 0.24 ppm Rh), Au (up to 0.32 ppm), Ag (up to 16 ppm), Se (up to 23 ppm) and Te (up to 14 ppm). Sperrylite $PtAs_2$, geversite $PtSb_2$, sudburyite (Pb,Ni)Sb, mertieite-I $Pd_5(Sb,As)_2$, naldrettite $Pd_2Sb$, and also electrum (Ag,Au) were found at the vein ores. The size of the PGM grains ranges within 9-63 microns. Note that 0.08-0.19 of Pd % was found in maucherite $Ni_{11}As_8$.

The presence of the low-sulphide PGE mineralization in the Ioko-Dovyren intrusion was documented by Kislov et al. (1993). This mineralization is confined to horizons of rocks within the gabbroic part of the massif, and has been traced along its strike for ~ 20 km. The lowest and most PGE-rich horizon (I) is observed within a transitional zone between rhythmic layered troctolite – olivine gabbro and the olivine gabbro (500 to 600 m above the first appearance of cumulate plagioclase).

The PGE ore zone is composed of concordant veins and lenses of coarse-grained and taxitic troctolites, olivine gabbros, pegmatites and anorthosites. Both schlieren and lens-like bodies of anorthosites surrounded by gabbro-pegmatites are widely abundant in the area. The anorthosite bodies are commonly a few cm to 1 m thick and extend for 2 to 5 m along the strike of the massif (rarely >40 m), forming discontinuous ore zones with an en echelon-like distribution. The horizon I consists of three separate layers over a 200 m vertical interval. The PGE-bearing rocks contain olivine, plagioclase and chromespinel as a cumulate assemblage. The intercumulus domains contain clinopyroxene, plagioclase and rare orthopyroxene.

The bulk PGE content in the rocks may reach as much as 12.1 ppm as well as 0.71% Cu and 0.43% Ni. Leucogabbro and anorthosites contain up to 4.1 ppm Pt and 7.8 ppm Pd. The prevalence of Pt over Pd is characteristic, with the average Pt/Pd ranging within 1.03-2.93. Concentrations of the other platinum-group elements reach 0.018 Os, 0.130 Ir, 0.060 Ru and 0.080 ppm of Rh.

Twenty minerals of precious metals were revealed, with tellurides and bismutotellurides of Pt and Pd being predominant. Fe-Pt alloys are less abundant, whereas arsenides, stibnides and stannides are rarely observed. The main minerals are moncheite $(Pt,Pd)(Te,Bi)_2$, potarite PdHg, tetraferroplatinum PtFe and kotulskite PdTe; thus > 50% of the PGM contain platinum. Both gold and silver minerals are also widespread (up to 14%). The unknown phase $(Pd,Hg)_2(Cu,Fe)S(Te,Pb)_2$ was found in association with kotulskite. Pentlandite from the horizon contains up to 360 ppm Pd, thus including almost half of the total Pd budget of the rocks.

Pd is more abundant than Pt in the Ni-Cu mineralized plagioperidotites. The low sulphide PGE horizons are characterized by the predominance of Pt over Pd, and relatively high Au concentrations. This suggests that different mechanisms of Pt and Pd fractionation proceeded in the ultramafic and mafic parts of the intrusion. Pt enrichment in the mafic melt seems to have been related to change of cumulate layers and evolution of the intercumulus melt, so that its residual derivative was finally enriched in fluid components and sulphide melt. The reduced fluids enriched in chlorine played an important role in the transport of PGE. The horizons (reefs) with ore concentration of PGE corresponded to borders of the layered series where a change in cumulare assemblages occurs. These sites are areas of decreased cumulus porosity, serving as specific traps for residual melt and volatiles, squeezed out of the underlying consolidated horizons. In the process of its upward migration through the thick cumulate mush the fluid (carrying precious metals) arrived in the zones of decreased porosity. Finally, the low-porosity intercumulus melt crystallized by interacting with a limited volume of co-existing sulphide liquid and the Cl-enriched fluid (containing small amounts of Te, As, Hg, Sb). The occurrence of PGMs including Pb, Sn, and Ag indicates the possible contamination of the magma by crustal material. This is supported by results of studies of S isotope compositions (Glotov et al., 1998), as well as helium and argon isotopes (Konnikov et al., 2002). The reduced character of the magmatic fluids was probably responsible for the primary crystallization of alloys and native metals.

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# DISTRIBUTION OF PLATINUM GROUP ELEMENTS IN SULFIDE ORES FROM ULTRAMAFIC MASSIFS OF THE ALKHADYR TERRAIN (SOUTHERN SIBERIA, RUSSIA)

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**ABSTRACT**. The distributions of platinum group elements (PGE) in weakly disseminated, disseminated, net-textured, and massive sulfide ores have distinct features. Specifically, weakly disseminated ores have substantially lower IPGE contents, whereas massive ores exhibit Pt depletion relative to other PGEs.

Three large areas of ore-producing (PGE-Cu-Ni) ultrabasic–basic magmatism are recognized within the Alkhadyr terrain (Southern Siberia, Russia): Barbitai, Uda–Biryusa, and Biryusa–Tagul. The ore-bearing massifs consist of an association of dunite, peridotite, pyroxenite, and gabbroic rocks. In the Barbitai and Biryusa-Tagul areas, there are outcrops of numerous boudin-like bodies with different shapes. These outcrops were formed by ultrabasic rocks that vary in the composition from lherzolite to olivine pyroxenite. The massifs in the Uda–Biryusa area are larger than the intrusive bodies in the Barbitai area; these massifs are nonboudinaged and have preserved many characteristics of the internal structure and morphology. Moreover, the massifs in the Uda-Biryusa area are composed of a differentiated series of rocks ranging in the composition from dunite and peridotite to melanocratic olivine gabbro. Previous studies have demonstrated their parental magmas to be picritic for all intrusions (Polykov et al., 2013).

There are four primary types of sulfide mineralization in these massifs: weakly disseminated, disseminated, net-textured, and massive. All ore types are typical for hosting peridotites; massive ores can also occur in country rocks. Weakly disseminated ores exhibit small sulfide abundances (<5 modal %). Disseminated ores generally contain 5−15% modal sulfide, including pyrrhotite (3−8%), chalcopyrite (2−5%), and pentlandite (approximately 1%). Net-textured ores contain 15−40% modal sulfide: pyrrhotite (10−20%), pentlandite (4−15%), and chalcopyrite (1−5%). Massive sulfide ores primarily consist of pyrrhotite (50−60%), pentlandite (30−40%), and small amounts of chalcopyrite (5−10%).

The weakly disseminated ores are characterized by PGE patterns with positive slopes, i.e., low Os, Ru, Rh and Ir concentrations combined with a relative enrichment in Pt and Pd. These patterns are consistent with (Pt+Pd)/(Os+Ir+Ru+Rh) ratios ranging from 4 to 320. The disseminated, net-textured, and massive ores are characterized by a relatively flat PGE distribution pattern and (Pt+Pd)/(Os+Ir+Ru+Rh) ratios between 4 and 15. The PGE spectra for individual samples are primarily parallel, which indicates similar inter-element ratios. An interesting feature of the massive ores from both peridotite and country rock is that these ores exhibit variable scales of the Pt depletion relative to the other PGEs. Similar Pt depletions of massive ores have been reported in several mafic-ultramafic intrusion-hosted deposits (Yang et al., 2006; Maier et al., 2008; Chen et al., 2013; Munteanu et al., 2011) and in komatiite-hosted ore bodies (Barnes, 2004; Collins et al., 2013).

The PGE content of the sulfide ores is highly variable. However, the Pd/Ir ratio versus the Ni/Cu ratio indicates an underlying magmatic control so that the massive ores are characterized by higher Ni/Cu ratios. We propose that the PGE distribution patterns of massive ores from both peridotite and country rock are the result of an overprinted hydrothermal process.

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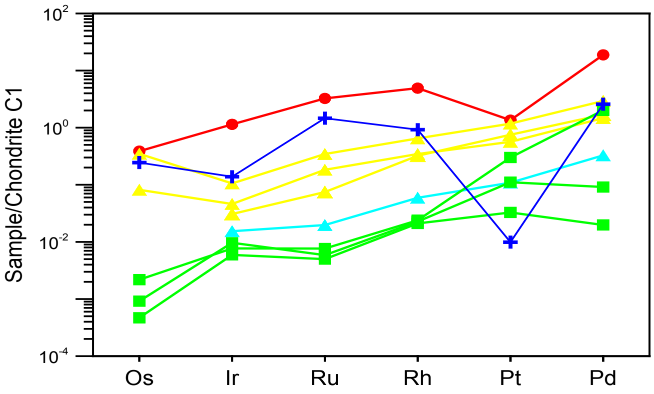

*Fig 1.* Chondrite-normalized PGE patterns for weakly disseminated (the green square), disseminated (the cyan triangle), net-textured (the yellow triangle), massive (the red circles) ores, and massive sulfides from country rocks (the blue cross)

# STUDY OF THE PGM MINERALIZATION IN ZONED MAFIC-ULTRAMAFIC MASSIFS IN RUSSIA BY AUTOMATED MINERALOGY

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**ABSTRACT**. We provide the results of studies of platinum mineralization by automated mineralogy in zoned mafic-ultramafic massifs of Russia, including Galmoenansky, Svetloborsky, Nizhny Tagil, Kondyor and Inagli (Kozlov & Chanturiya, 2014 , Kozlov et al., 2011; Tolstykh et al., 2011). These methods have been continuously improved for the last 30 years and allow us to determine mineral composition, granulometry of valuable minerals, and to analyze intergrowths, characterize small inclusions and element distributions in mineral phases.

To study the discrete platinum mineral grains with high average atomic number we applied an MLA algorithm – search for the grains by BSE, elemental analysis in the geometric center of the particle and the collection of the data in a mineralogical data base.

In total, 11 epoxy pressings were studied, with 29 separate allocated areas, which allowed to get comprehensive statistics on the qualitative and quantitative composition of platinum mineralization, granulometry, and relationships between different productive phases in platinum-bearing zoned mafic-ultramafic massifs of the Urals, the Aldans and Kamchatka. Amongst other phases, a eutectic decay phase in isoferroplatinum characterized by a grain size of less than 5 microns has been studied in detail.

*Acknowledgment: This study was supported by the Presidium of the Russian Academy of Sciences (program no. 27) and the Russian Foundation for basic research (project no.12-05-00260).*

Table 1

**PGM modal mineralogy of Kondyor samples, MLA algorithm**

| *Mineral* | *Wt%* | *Area%* | *Area (micron)* | *Particle Count* | *Grain Count* |
|---|---|---|---|---|---|
| Izoferroplatinum | 88.50 | 86.74 | 8981540.61 | 795 | 12624 |
| Tetraferroplatinum | 6.58 | 7.45 | 771019.32 | 708 | 6657 |
| Cooperite | 0.58 | 0.99 | 102741.74 | 79 | 116 |
| Tulameenite+Ni | 4.07 | 4.41 | 456884.07 | 615 | 4369 |
| Sperrylite | 0.27 | 0.41 | 42504.51 | 330 | 1179 |
| Total | 100.00 | 100.00 | 10354690.26 | 2527 | 24945 |

Table 2

**PGM granulometry of Kondyor samples, MLA algorithm**

| Sieve Size, μm | 710 | 600 | 300 | 250 | 125 | 75 | 45 | 13.5 |
|---|---|---|---|---|---|---|---|---|
| Retained wt.% | 0 | 2.68 | 17.18 | 11.36 | 44.19 | 18.64 | 5.27 | 0,68 |
| Cum. Retained wt.% | 0 | 2.68 | 19.86 | 31.22 | 75.41 | 94.05 | 99.32 | 100 |
| Cum. Passing wt.% | 100 | 97.32 | 80.14 | 68.78 | 24.59 | 5.95 | 0.68 | 0 |

Size definition was based on equivalent circle approximation

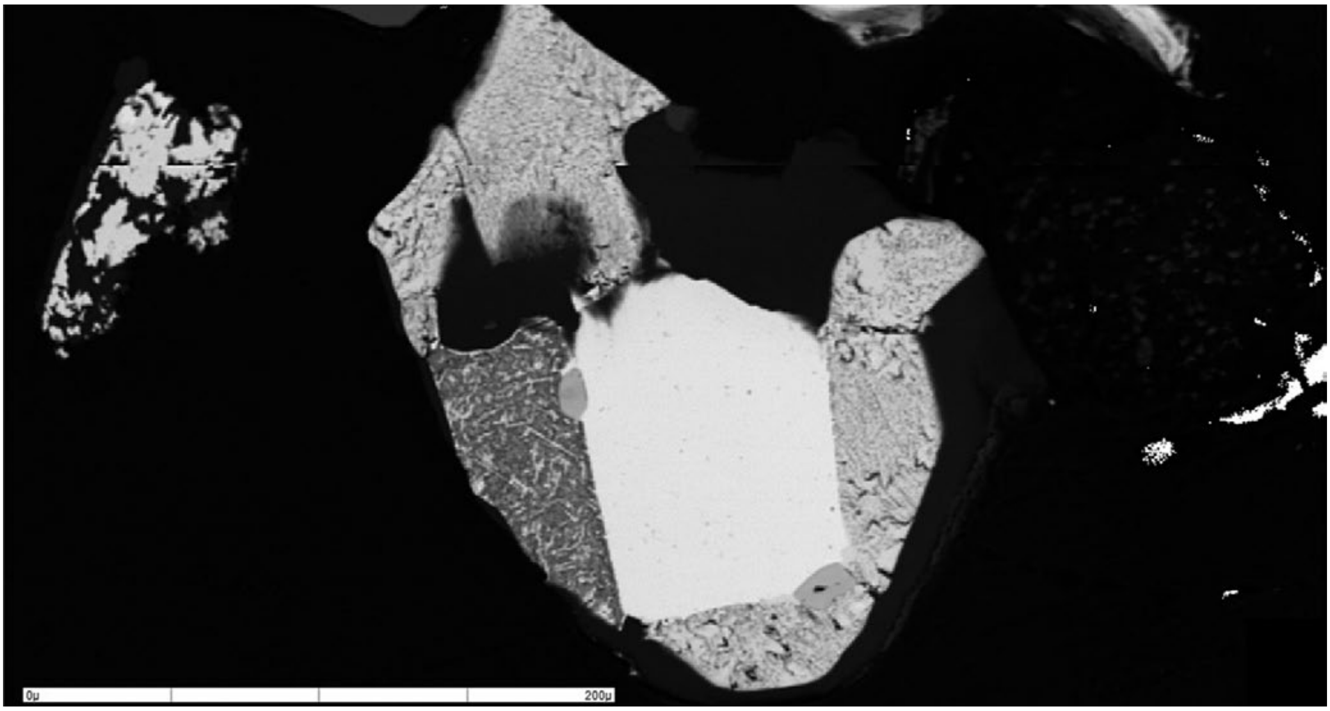

*Fig. 1.* BSE image of PGM-bearing sample from the Kondyor massif

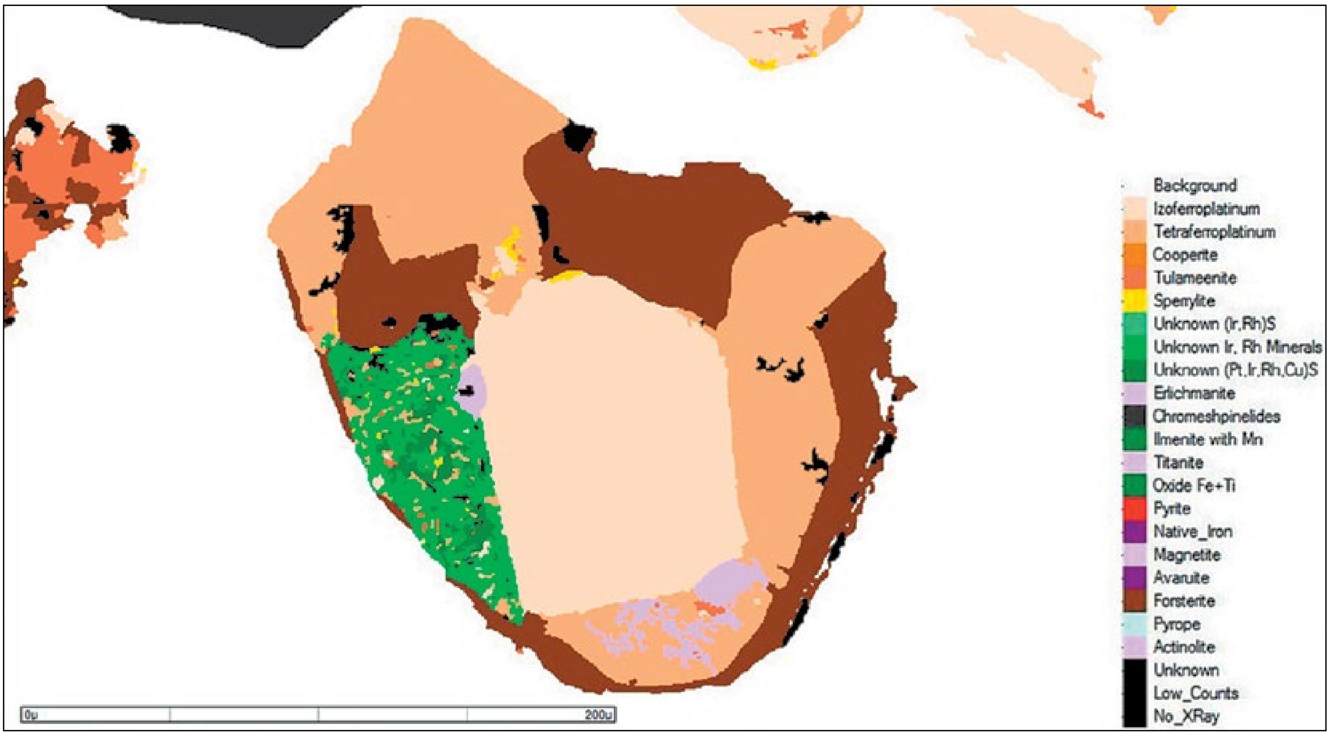

*Fig. 2.* Processed image of PGM-bearing sample from the Kondyor massif (MLA algorithm)

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# PLATINUM-GROUP ELEMENTS IN CHROMITITES OF THE KONDYOR MASSIF: GEOCHEMISTRY AND MINERALOGY

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**ABSTRACT**. New data on the composition of isoferroplatinum during „in situ" investigation of the platinum-group minerals (PGM) from chromitites of the Kondyor massif show its evolution from early magmatic to post-magmatic stages.

The Kondyor massif is one of the several concentric-zoned ultramafic massifs that have intruded the Precambrian rocks of the Aldan Shield, south-eastern Siberia (e.g. Gurovich et al., 1994). The Kondyor massif is composed of a dunite core surrounded by an irregular composite aureole of wehrlites and olivine-bearing clinopyroxenites in its inner part and of magnetite-amphibole (±plagioclase) clinopyroxenites in the outer rim. The dunites contain schlieren and massive lenticular bodies of chromitites.

There are many publications devoted to the platinum-group minerals of world-class platinum-group elements (PGE) placer deposits associated with the Kondyor massif (e.g., Nekrasov et al., 1994; Lazarenkov et al., 1992; Malitch & Thalhammer, 2002; Nekrasov et al., 2005). However, the data on the PGE mineral assemblage and PGM compositions present within chromitite samples from the Kondyor massif are not so numerous (Rudashevsky et al., 1992; Cabri & Laflamme, 1997; Malitch et al., 2003). We report new results on the nature of the PGE mineralization and PGE geochemistry of chromitite samples from the Kondyor massif.

The PGM were located in polished sections by reflected-light microscopy at 200–1000× magnification, and then were investigated by electron-microprobe. Analyses were performed at the Vinogradov Institute of Geochemistry SB RAS, using an JXA-8200 instrument equipped with both energy-dispersive (EDS) and 5 wavelength-dispersive spectrometers (WDS), operated at an accelerating voltage of 20 kV and a beam current of 20 nA, with a beam diameter of about 1 μm. The X-ray *K*α lines were used for S, Cr, Fe, Ni and Cu, *L*α lines for Ir, Ru, Rh, Pt, Pd, and As, and the *M*α line for Os. Pure metals were used as standards for PGE, $Cr_2O_3$ for Cr, and synthetic NiCoFe, $FeS_2$ and $CuFeS_2$ for Ni, Fe, Cu, and S, and FeAsS for As. The interferences between Ru–Rh, Ir–Cu, and Ru–Pd were corrected off-line. Total PGEs were determined by ICP-MS.

The majority of the platinum-group minerals of the Kondyor massif are concentrated in chromitites, and 90 percent of them is isoferroplatinum. A detailed study shows that the isoferroplatinum can be classified on the basis of composition, grain morphology and location. It has been divided into four different morphological groups:

1) euhedral crystal,
2) subhedral crystal,
3) anhedral grains,
4) anhedral „porous" grains.

The euhedral crystals are included in unaltered chromian spinel. These grains typically contain Cu and Ir up to 3 and 2 at.%, respectively. Compositions calculated on the basis of four atoms per formula unit cover the range from $(Pt_{2.90}Ir_{0.04})_{2.94}(Fe_{0.95}Cu_{0.11})_{1.06}$ to $(Pt_{2.88}Ir_{0.03}Rh_{0.02})_{2.93}(Fe_{0.95}Cu_{0.12})_{1.07}$. This type of isoferroplatinum often contains thin exolution lamellae of native osmium. The subhedral isoferroplatinum occurs in interstices of chromian spinel grains. These crystals have an average composition expressed by the formula $(Pt_{2.88}Ir_{0.04})_{2.92}(Fe_{0.99}Cu_{0.09})_{1.08}$. This is close to the composition of the first type, except for higher Fe and lower

Cu and Ir which is not exceeding 2.5 and 1.0 at.%, respectively. The anhedral isoferroplatinum also occurs in interstices of chromian spinel grains. Its average composition corresponds to the formula $(Pt_{2.93}Ir_{0.03}Pb_{0.01}Cu_{0.03})_{3.00}Fe_{1.00}$.

The anhedral „porous“ isoferroplatinum consists of a fine-grained mixture of Pt-Fe alloy and a siliceous phase. It occurs in interstices of chromian spinel and/or serpentine grains and along cracks cutting across chromian spinel. It is replaced along the contact with chromite by tulameenite, malanite and contains inclusion of ehrlichmanite and kashinite. Contrary to the varieties of isoferroplatinum described above, in this type there is a progressive increase in Ni (up to 1.7 at.%) at the expense of Cu.

The chromitites display two types of CI-chondrite normalized PGE patterns. Both types of PGE distribution pattern are characterized by an M-like shape. The first type has marked peaks of Pt and Ir and $Pt_N/Ir_N$ ranging from 30 to 90. It is found in massive lenticular bodies of chromitite. The second type, with $Pt_N/Ir_N$ ranging 2-12, is found in schlieren chromitites. This pattern closely matches that of earlier published data on Kondyor chromitites (Lazarenkov & Malich, 1992; Rudashevsky et al., 1992) and sample UK6 from chromitites of the Uktus massif (Garuti el al., 2003). The CI-chondrite normalized PGE patterns of dunites are characterized as a whole by very low total PGE concentrations and a weak enrichment in Rh+Pd+Pt (PPGE) relative to Os+Ir+Ru (IPGE), which causes a positive slope between IPGE and PPGE. Among the PGE, small positive anomalies of Ir and Pt are also present.

The results of this study show that the primary composition of isoferroplatinum corresponded to $(Pt,Ir,Os)_3(Fe,Cu)$. The euhedral and subhedral isoferroplatinum precipitated at the highest temperatures before and together with chromite, whereas the anhedral homogeneous isoferroplatinum crystallized after chromite at a late magmatic stage. The „porous“ isoferroplatinum may be interpreted to have crystallized at a relatively low temperature as a result of interaction between the anhedral isoferroplatinum with hydrothermal fluids that leads to re-mobilization of Cu and PGE, expressed in the formation of tulameenite and PGE sulfides. The relatively high concentrations of Pt and Ir in Kondyor dunites, in general, may reflect a feature of the parent melt and the PGE distribution pattern of the chromitites could be caused by PGE fractionation.

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# PGE-Cu-Ni SULPHIDE MINERALIZATION IN THE ULTRAMAFIC ROCKS OF THE ZHELOS AND TOKTY-OY MASSIFS (EAST SAYAN)

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**ABSTRACT**. PGE-Cu-Ni sulphide mineralization in the Zhelos and Tokty-Oy massifs (East Sayan) ultramafic rocks has been studied. The ores are hosted in peridotites. The sulphide minerals and aggregates are composed of pentlandite and pyrrhotite and contain platinum group minerals. It is suggested that the ores formed by sulfide liquid immiscibility. Analysis of the original magmatic melt and immiscible sulphide liquid was carried out on silicate and sulphide inclusions in chrome spinel.

During investigation of the ultramafic-mafic complexes in the basement of the southern portion of the Siberian craton, several platinum metal ore mineralizations and deposits related to plagioperidotite-gabbronorite and dunite-peridotite-pyroxenite rocks were found in recent years. In the Iya-Kuksher ore district the richest PGE-Cu-Ni sulphide mineralization is in the Zhelos and Tokty-Oi massifs (Polyakov et al., 2013). It is represented by a series of lens-shaped bodies of different thickness and formed by variably altered peridotite and dunite. These bodies were deposited in Neoproterozoic volcanic sedimentary sequences, and metamorphosed in the amphobolite and epidote-amphibolite facies.

The composition of the original parent melt to the intrusions is defined by silicate inclusions in chrome spinel. The composition corresponds to alkali picrite ($SiO_2$ – 46.57, $TiO_2$ – 0.68, $Al_2O_3$ – 7.23, FeO* – 10.06, MnO – 0.12, MgO – 26.64, CaO – 8.03, $Na_20$ – 0.61, $K_20$ – 0.06) and is compositionally similar to that obtained by other methods (Polyakov et al., 2013).

PGE-Cu-Ni mineralization in both massifs is confined to the peridotites bodies. Relative to the primary silicate rock-forming minerals it is syngenetic and closely related to the magmatic processes responsible for the formation of the massifs. At the same time, the following metamorphic processes reworked the ores. Sulphide minerals are often composed of pentlandite and pyrrhotite and most commonly of their intergrowths. Chalcopyrite is scarce. Grains with compositions corresponding to the troilite and hexagonal pyrrhotite mixture prevail. Troilite often forms in the hexagonal pyrrhotite thinly laminated, lens-shaped, flexed lamellae. As experimental works have shown (Taylor, 1970), the formation of such structures occurs due to subsolidus transformations of monosulphide solid solution (*Mss*) at a temperature below 150°C.

Usually, pentlandite forms small grains. Compositions of pentlandite and pyrrhotite group sulphides are clearly correlated (Fig. 1.) More ferrous pentlandite coexists with troilite and less ferrous pentlandite with monoclinic pyrrhotite. Such a correlation is typical for the many Cu-Ni deposits and suggests that pentlandite formed as a result of subsolidus breakdown of monosulphide solid solution (*Mss*). Correlation of the compositions of pentlandite and pyrrhotite group minerals reflects increase of sulphur activity during the evolution of the sulphide liquid, which is caused by the compositional change of the residual silicate melt coexisting with the sulfide liquid.

By means of the electron microscope we found and identified in the ores of the Zhelos and Tokty-Oy massifs the following platinum metal minerals: sperrylite $PtAs_2$, irarsite IrAsS, stibiopalladinit $Pd_5Sb_2$, frudite $PdBi_2$, mertieite II $Pd_8Sb_3$, and also unknown phases of $Pd_{2.971}Sb_{1.002}(Bi_{0.742}Te_{0.284})_{1.026}$, $Pd_{1.993}Bi_{3.007}$ и $Pd_{2.064}Bi_{0.977}Te_{1.959}$. Electrum, acanthite and native silver represent Au and Ag minerals.

The most widespread PGM, and the only mineral of Pt is sperrylite, which forms the largest grains with a size up to 0.3 mm. Compositionally, Pd minerals show more diversity and are represented in combination with Sb, As, Bi, Te and S, rarely reaching 0.001 mm in size. Association with sulphides is typical for the precious metal minerals pointing to their crystallization from the sulphide melt with the subsequent accumulation of As, Te, Sb and Bi in the residual melt.

We have studied the composition of the sulphide melt in the Tokty-Oy massif by analyzing the compositions of polyphase sulphide spherocolloids in chrome spinels, originating as a result of recrystallization of immiscible sulphide liquid droplets, which have been captured during the growth of the spinel. Analyses of two pyrrhotite-pentlandite shperocolloids from different ore samples considering the quantitative ratio and density of sulphides showed the following compositions: Fe – 57.7 and 58.1; Ni – 3.2 and 6.0; S – 39.0 and 36.0, respectively. On the experimentally studied (Kullerud et al., 1969) ternary system Fe-Ni-S (Fig. 2), both compositions (1 and 2) fall within the field of high temperature *Mss*, existing at 860 °C. Th PGE-Cu-Ni compositions of the ores from the two massifs (recalculated to 100 % sulphide) also fall within the mss field.

Thus, taking into account that spinel formed almost simultaneously with olivine as a liquidus phase, we can suppose that the separation of sulfide melt from silicate liquid occurred before the crystallization of the high-chromium spinel.

*Acknowledgments. The study was supported by the Integration Program of the Branch of Earth Sciences RAS 2.1.*

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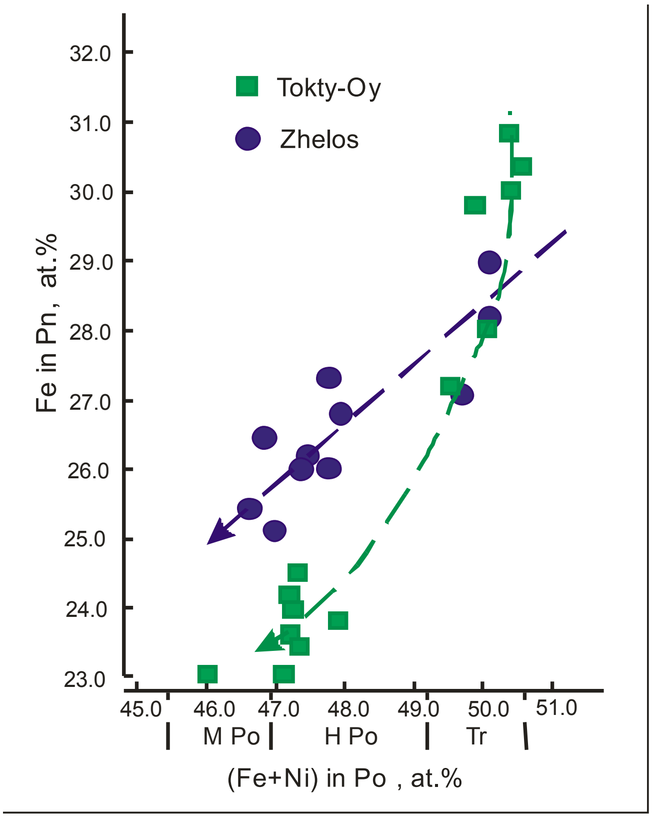

*Fig. 1.* Diagram of (Fe+Ni) ratio in pyrrhotite plotted vs Fe content in coexisting pentlandite

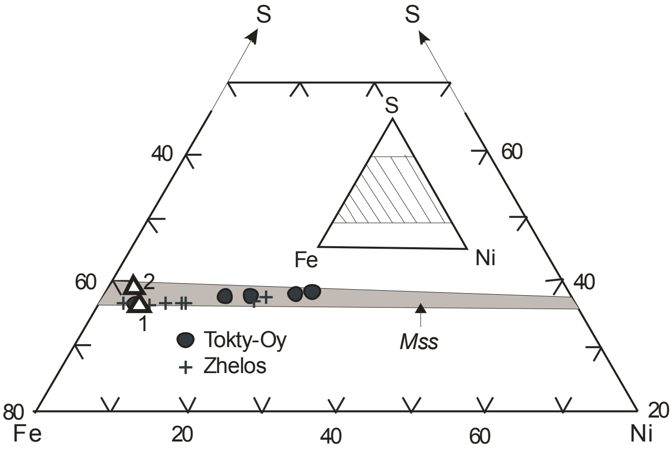

*Fig. 2.* Position of the sulphide melt compositions, estimated from sulphide inclusions in chrome spinels, and compositions of the ores (recalculated to 100 % sulphide) on the ternary Fe-S-Ni diagram

# THE COPPER-NOBLE METAL MINERALIZATION OF THE SHCHEKURINSKY ULTRAMAFIC MASSIF (NORTHERN URALS)

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**ABSTRACT**. In the present contribution, the copper-noble metal mineralization of the clinopyroxenites of the Shchekurinskiy massif, represented by sulfides of copper and silver, antimonides of palladium, tellurides and arsenides of platinum, as well as native gold, has been studied. Based on the petrographic and petrogeochemical data, the northern portion of the Shchekurinsky massif cannot be related to the other intrusions of the Uralian Platinum belt.

The Shchekurinsky massif is located on the eastern slope of the Subpolar Urals and represents a complex body consisting of large xenoliths of ultramafic rocks of the Kachkanarsky formation ($O_3k$), occurring in a matrix of basic rocks belonging to the Tagil-Kytlymsky formation ($S_1t$), which in their turn are intruded by diorites and plagiogranites of the Verkhnetagilsky formation ($S_2v$) that are related to platinum-bearing Alaskan-Uralian type massifs.

The ore mineralization is observed both in clinopyroxenites of the Kachkanarsky formation, and in basic rocks of the Tagil-Kytlymsky formation. Visually, the copper sulfide mineralization is diagnosed by green sulfate-carbonate products of oxidation.

Mineralized clinopyroxenites are dark green and characterized by medium-grained textures. The rocks show symplektitic and poikiloblastic textures resulting from the replacement of pyroxene by amphibole and development of poikiloblasts of amphibole with poikilitic inclusions of pyroxene. The pyroxene is substituted by amphibole until complete transformation into hornblendites. The size of the rock-forming minerals in the hornblendite is 2 x 3 cm. The olivine bearing clinopyroxenites are marked by much less pervasive alteration.

Petrochemically, the studied rocks resemble hornblende perodotite. The average contents of rock-forming components in mineralized clinopyroxenites are (vol. %): $SiO_2$ 43.67; $TiO_2$ 0.41; $Al_2O_3$ 9.76; $Fe_2O_3$ 0.53; FeO 6.23; MnO 0.20; MgO 17.35; CaO 12.76; $Na_2O$ 0.75; $K_2O$ 0.09.

The rocks contain two generations of magnetite. Chalcopyrite contains rims of secondary sulfides of chalcocite and covellite. Bornite is substituted by covellite in microcracks and found only once. The clinopyroxenites of the Kachkanarsky formation reveal many micromet-

Table 1

**Chemical composition (wt. %) and empirical formulas of noble metal minerals**

| *Mineral* | *Cu* | *As* | *Pd* | *Ag* | *Sb* | *Te* | *Pt* | *Au* | *Empirical formula* |
|---|---|---|---|---|---|---|---|---|---|
| Sperrylite | – | 42.6 | – | – | – | – | 57.4 | – | $Pt_{1.10}As_{1.90}$ |
| Sperrylite | – | 44.1 | – | – | – | – | 55.9 | – | $Pt_{0.98}As_{2.02}$ |
| Sperrylite | – | 44.8 | – | – | – | – | 55.2 | – | $Pt_{0.96}As_{2.04}$ |
| Gold | – | – | – | 23.6 | – | – | – | 76.4 | Au(Ag) |
| Copper-bearing gold | 13.1 | – | – | 5.0 | – | – | – | 81.9 | Au(CuAg) |
| Mertieite-II | – | 2.6 | 70.2 | – | 27.2 | – | – | – | $Pd_{7.91}(Sb_{2.68}As_{0.41})_{3.09}$ |
| Mertieite-II | – | 2.4 | 69.3 | – | 28.4 | – | – | – | $Pd_{7.82}(Sb_{2.80}As_{0.38})_{3.18}$ |
| Moncheite | – | – | 1.2 | – | – | 55.9 | 42.9 | – | $(Pt_{0.99}Pd_{0.05})_{1.04}Te_{1.96}$ |

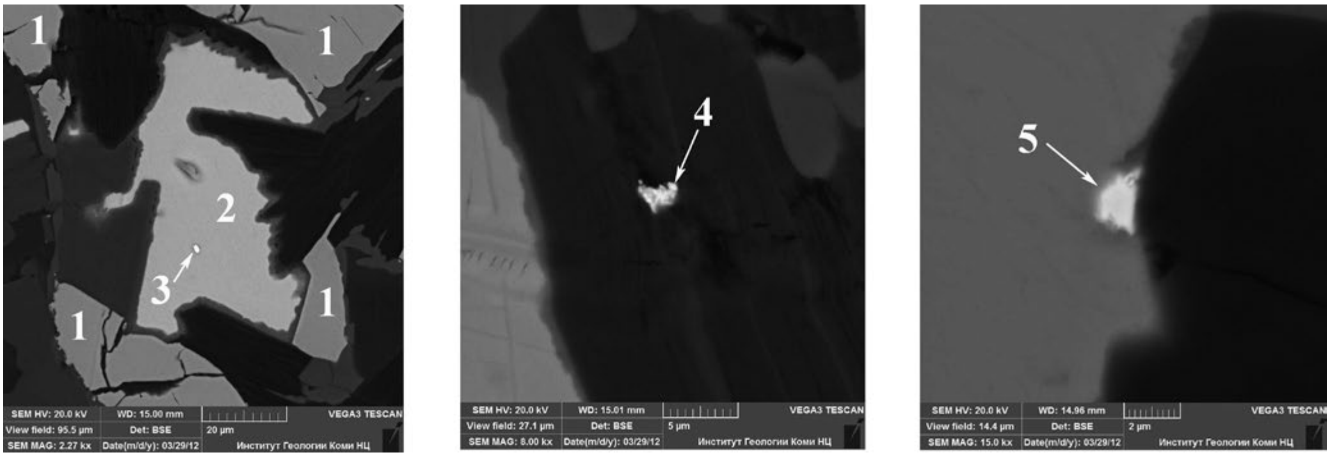

*Fig. 1.* Noble metal minerals in clinopyroxenites and hornblendites. 1 – magnetite, 2 – chalcopyrite, 3 – native gold, 4 – sperrylite, 5 – mertieite-II

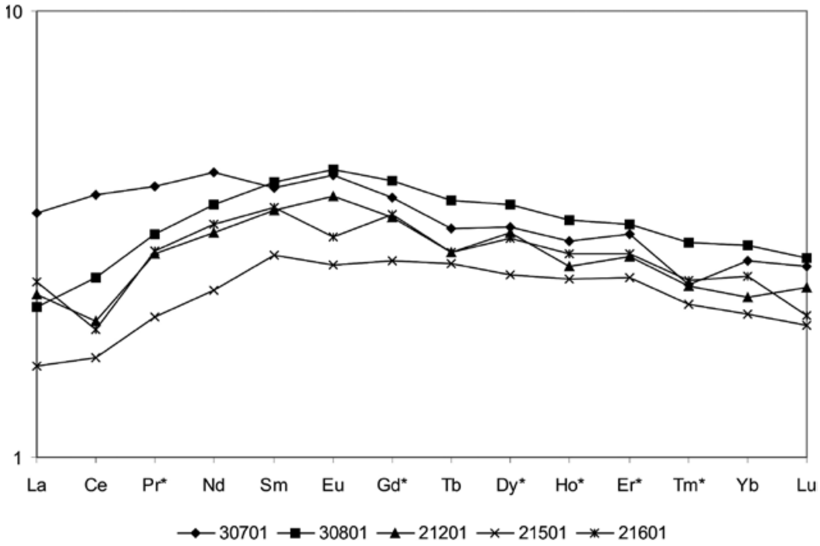

*Fig. 2.* Chondrite-normalized rare earth element patterns of clinopyroxenites and hornblendites

ric (1-10 microns) particles of arsenides, antimonides and silver tellurides, platinum and palladium, native gold, nickel, arsenic (Table 1). Generally, minerals of precious metals form close intergrowths with chalcopyrite, but also occur in the form intergrowth within rock-forming silicates (Fig. 1).

Arsenides and platinum tellurides, in particular sperrylite and moncheite, are most abundant. Palladium minerals are represented by mertieite-II. Native gold contains considerable impurities of silver and copper.

Similar copper-noble metal mineralization occurs in the potentially commercial „Ozernoe“ deposit in the Polar Urals (Kuznetsov et al., 2007). Ore-bearing ultramafic rocks of this ore occurrence are related to the plutonic complex of the Voykaro-Syninsky massif related to Paleozoic ophiolites (Pystin et al., 2011). Petrographic and geochemical properties of ultramafic rocks of the Shchekurinsky basite-ultrabasite massif (Fig. 2) closely resemble the ore-containing pyroxenites of the Kershorsky Voykaro-Syninsky plutonic complex. Therefore, the accuracy of the classification of the Shchekurinsky massif as a component of the concentric-zoned platiniferous intrusions is doubted.

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# THE PRECIOUS METALS MINERALIZATION OF Cu-Ni SULPHIDE DEPOSITS KUN-MANIYE AND MALYI KURUMKAN (SOUTHEAST OF ALDANO-STANOVOY SHIELD)

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**ABSTRACT**. The sum of the PGE in sulfide ores of the Kurumkan ore field rarely exceeds 1 g/t, commonly, Pt is more abundant than Pd, the average Pt/Pd ratio being 1.2, and Os+Ir are subordinate. The dominant minerals are merenskyites, Pd-melonites, and palladium tellurides of the kotulskite type. At the Iken prospect, PGE sulfoarsenides are also found, including irarsite, as well as zonal grains of sulfoarsenides Co–Ni–(Fe)–PGE. There are PGM sulphides occur rarely, for the first time there have been defined Ru and Os sulfides whose composition is very similar to that of the erlichmanite-laurite solid solution.

In the South-Eastern part of the Aldan-Stanovoy Shield, on the border of the Khabarovsk region and the Amur region, a new type of Cu-Ni sulfide ores has been discovered recently (Guryanov et al., 2009). The embedded sulfide ores replicate contours of the parent bodies. The Kurumkan ore field is most prospective for the platinum-copper-nickel mineralization in the basin of the Maya and Kun-Maniye rivers. It is 31 km long ranging in width from 1 to 3 km and hosts the Kun-Maniye and Malyi Kurumkan deposits, as well as about 10 highly prospective occurrences. We have studied PGEs in the core from several boreholes drilled in different parts of the Kun-Maniye and Malyi Kurumkan deposits. It was found that despite high contents of base metals (Ni, Cu, Co), precious metal concentrations are relatively low, with the total PGE rarely exceeding 1 g/t. The lowest PGE contents are recorded in Malyi Kurumkan (0.33 g/t) and the average content at the Iken prospect is 0.57 g/t. Commonly, Pt is more abundant than Pd, the average Pt/Pd ratio being 1.2. The opposite distribution is revealed at the Shlyapa prospect, where Pt/Pd=0.9 and an increase in the total PGE contents is observed down the section. There is a high positive correlation between Pt and Pd, which also correlate well with Ni and S), and, to a lesser extent, with Cu. A distinctive feature of these deposits is that Os+Ir are subordinate and Pd and Pt are dominant. The observed PGM distribution pattern in the ore bodies is characteristically associated with Fe, Ni, and Cu sulfides and ore bodies can be delineated within their contours. The dominant mineral phases are merenskyites containing Pt (5-15.99 wt.%), Pd (17.6-20.39 wt.%) and Bi (0-4.13 wt.%), Pd-melonites with highly variable contents of Ni (4.7-14.8 wt.%), Te (61.4-76.0 wt.%), and Pd (5.0-8.2 wt.%), as well as palladium tellurides of the kotulskite type. At the Iken prospect, PGE sulfoarsenides are also found, including irarsite, with 47.3-35.7 wt.% Ir, 24.1-25.9 wt.% As, 12.5-15.3% wt. S, and 11.2-14.5% wt. Pt. In addition, two zonal grains of sulfoarsenides Co–Ni–(Fe)–PGE are discovered. In the latter, the PGE-enriched zones are developed in the central, „nuclear“ parts of the grains and are represented by the series which is closest to the hollingworthite-irarsite, and peripheral parts form series of cobaltite-gersdorffite solid solutions. For the first time there have been defined Ru and Os sulfides whose composition is very similar to that of the erlichmanite-laurite solid solution, in one case, with admixture of Rh up to 8.4 wt.% and in the other, with admixture of Pt up to 3.65 wt.%.

Sperrylite (Pt 51.4-54.9 wt.%) is characterized by the presence of copper (0.98 wt.%). There occurs a rare mineral $(Re,Cu)S_2$ with Pt up to 2.27 wt.%. The fact that PGMs commonly occur with abundant Au-Ag minerals suggests their joint formation. Although major minerals of copper-nickel ores belong to the class of sulphides, the latter practically do not occur among PGMs, which may evidence a deficiency of sulphur and some offsetting into the low-temperature area of the temperature interval of PGE genesis in relation to the temperature interval of sulphide formation.

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# GEOLOGICAL STRUCTURE AND PGE MINERALIZATION OF THE SOUTH SOPCHINSKY MASSIF (MONCHEGORSK AREA, KOLA PENINSULA, RUSSIA)

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**ABSTRACT**. This abstract presents data on PGE mineralization in the southeastern part of the Monchegorsk layered complex (Monchepluton). We discuss two areas of similar geological structure: The South Sopchinsky massif (SSM) and the Moroshkovoe Lake target (ML). Platinum-group minerals were found in mafic veins within mafic-ultramafic rocks and in strongly metamorphosed and tectonized mafic rocks. According to our data, the SSM and the ML share many compositional and lithologic features with the two largest layered complexes in the region- the Main Ridge and the Monchepluton.

The so-called South Sopchinsky massif (SSM) is located at the southeastern margin of the Monchepluton. It extends for 10 km in NW -SE direction, and dips to the southwest at an angle of about 60 degrees. In the southwest the SSM is bordered by Early Proterozoic volcano-sedimentary rocks, whereas in the northeast it is in contact with Archean diorite-gneisses, and in the north with rocks of the Monchepluton (2.50 Ga). It was previously proposed that the SSM is a layered intrusion: the upper (southern) part of the massif is formed by gabbronorites, whereas the lower (northern) one consists of norites, pyroxenites and peridotites. Resent exploration (during the late 1990th) by JSC Central Kola Expedition identified PGE mineralization associated with disseminated sulfides in the north- eastern part of the SSM. In the SSM peridotites, Pt grade varies from 0.3 to 9 ppm, and Pd – from 0.71 to 9 ppm (Ivanchenko & Davydov, 2009).

According to our observations, metapyroxenites and metagabbronorites in the SSM have complex, undulating contacts. The contact zone between the metapyroxenites and metagabbronorites is marked by thin (1-2 cm) actinolite-chlorite rim. Xenoliths of metapyroxenites within metagabbronorites, interpreted as magmatic breccias, are surrounded by chlorite rims. Magmatic breccias are also observed in the Moroshkovoe Lake target (ML) area where large xenoliths of melanocratic norite-pyroxenites occur in coarse-grained gabbronorites.

Metapyroxenites in the SSM contain veins of orthopyroxenite (predominant), plagiopyroxenite, norite, and amphibole gabbro. Some of the veins have siliceous compositions that reflect the presence of quartz and myrmekite. The thickest veins consist of coarse-grained plagioclase-pyroxene rocks with various amounts of disseminated magnetite and sulfides (from several grains up to 3 % in volume). According to our data, sulfide and PGE mineralization is associated with veins of magnetite-plagioclase-pyroxene composition located in metapyroxenites (Rundkvist et al., 2011).

Field studies have shown that the SSM rocks extend for 1 km to the north, constituting the Moroshkovoe Lake target (ML). Metapyroxenites in the ML are intersected by mafic veins of variable thickness, composition and morphology. Vein lithologies are similar to those of the SSM, but in addition include gabbroic pegmatite bodies. All veins contain magnetite, sulfides and platinum group minerals (PGM). Sulfide mineralization in plagiopyroxenite veins consists mainly of bornite-chalcopyrite-millerite, closely associated with oxide magnetite-ilmenite. The PGM commonly occur at the contacts of Cu-Fe-Ni sulfides with hydrous silicates. A number of distinct PGM were identified by electron microprobe analysis: most common are kotulskite and vincentite, with sperrylite, clausthalite, sopcheite and hollingworthite being less abundant, and braggite and palladoarsenite being rare (Chernyavsky & Miroshnikova, 2013).

PGE mineralization within the ML occurs in the strongly metamorphosed and tectonized mafic rocks (PGE+Au grade is about 2.5 ppm). Geochemical data suggest that the ore-bearing rocks are intensively altered gabbronorites of the SSM. However, within the SSM itself, such rocks do not contain sulfide and PGE mineralization. Therefore, we believe that the sulfide and PGE mineralization in the tectonic zone of the ML is of an epigenetic nature and probably formed by mobilization of PGE from the mafic veins and their host rocks (metapyroxenites).

The distribution of major elements, rare earth and other rare metals (Rb, Th, U, Nb, Ta, Sr, Nd, Hf, Zr,Ti) in the SSM metapyroxenites and metagabbronorites is variable. This fact together with the nature of the contacts between the two types of rocks was the main argument why the rocks were assigned to different intrusions. Comparison of our results and literature data show that the major element contents in the coarse-grained metagabbronorites of the SSM overlap with the rocks of the upper zone of the Monchetundra intrusion (MI) of the Main Ridge layered complex, whereas the SSM metapyroxenites are similar to the rocks of the lower part of the Nude-Poaz massif of the Monchepluton. Therefore, we suggest that the SSM metapyroxenites belong to the Monchepluton, in particular, to the „Verhny Nude“ tectonic block. If our assumptions are correct, then the contact between the two largest layered complexes in the region – Main Ridge (MI) and Monchepluton („Verhny Nude“), is exposed in the SSM. Probably, these are the two major phases of a giant magmatic intrusion. The most important geological features of the composite SSM-ML complex (two magmatic bodies in contact with each other, magmatic breccias in the border zone, two types of PGE mineralisation with economic metal contents) resembles the Fedorova Tundra deposit – the largest PGE deposit in the Kola region.

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# ON THE HISTORY OF THE 20-th CENTURY DISCOVERY OF THE LARGEST PLATINUM NUGGETS IN THE WORLD

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**ABSTRACT.** This contribution is dedicated to the 20th Anniversary of the discovery of the largest PGM nuggets of the 20th century which were found in the unique Kondyor placer deposit, Far East, Russia. Specific features of the deposit and the morphology of platinum are reported. The large and unique platinum nuggets found 20-30 years ago are briefly described. The author compares the Kondyor nuggets with platinum mineralization discovered at the same time in the Koryak-Kamchatka province, and the unique platinum nuggets from Middle Ural placer deposits of the 19th century.

In 2013 is the 20th Anniversary of the 20th Century discovery of the largest platinum nuggets in the world. They were found in the Khabarovsk Region of Russia, in the Kondyor massif.

The Kondyor alkaline-ultramafic massif is almost perfectly circular in plan, resembling an ancient asteroid astroblem. The massif (Efimov, 1978; 1998; Lazarenkov et al., 1992) is situated in the northern Khabarovsk Territory of Russia, about 250 km west from the coast of the Okhotsk Sea along the middle stream of the Maya River. The boundary ring of the Kondyor range, about 7 km in diameter, towers for about 1000-1400 m above sea level. The circular Kondyor River basin was formed in the centre of a dome-shaped intrusion as a result of intensive non-uniform erosion.

A remarkable feature of the upper part of the Kondyor placer deposit is the significant amount of platinum nuggets, including those with a regular crystal shape (which are extremely rare at other localities globally). The first large platinum nuggets over 1 kg were found in the Nizhny Begun stream during 1985. Three nuggets were found, with weights of 1645, 1565, and 1575 g. The largest of these nuggets was found at the confluence of the Begun and Malyi streams. Later, even larger platinum nuggets were found here in 1993 -1994. The total content of platinum nuggets in some cases was as high as 28-30 (!) wt.% (Sushkin, 1995; 1996; 2006).

In August 1993, two platinum nuggets, weighting 1810 and 1855 g, were found in the placer of the Kondyor River at the above-described locality near the confluence with the Dvuglavyi stream. These nuggets measure 85 x 65x 20-50 mm and 103 x 60 x 40 mm in size. The first nugget is oval in shape, whereas the second nugget has an angular outline. On 10 September 1993, a platinum nugget weighing 3521.7 g was found at the same locality. This is one of the largest platinum nuggets to be found in the history of twentieth century platinum mining (Fig. 1). The size of this unique nugget is 111 x 78 x 55 mm. Like the largest Gold nugget of Russia (the “Big Triangular”, 36.2 kg, found in the South Urals in 1842) this unique Platinum Nugget from Kondyor also has an irregular triangular shape with rounded edges and specific groove- like cavities (Sushkin, 1995; 1996). The last large find in the locality was on August 1994, in the form of an unusual dumbbell – like platinum nugget weighing 2227 g. During three decades of Kondyor placer deposit mining more than twenty large nuggets weighing above 1 kg, were found in addition to thousands of small and medium nuggets. All the above – mentioned unique Kondyor platinum nuggets are similar in composition, have uniform medium – grained textures and contain inclusions of black chrome- spinel crystals (5-25 %), 1-5 mm in size. Euhedral platinum crystals are mainly cubic in habit. They contain various twins and intergrowths of two – three individuals, up to 15 – 20 mm in dimension. Gold films, 0.05 – 1.0 mm thick surround many platinum crystals and small grains. Native silver occasionally

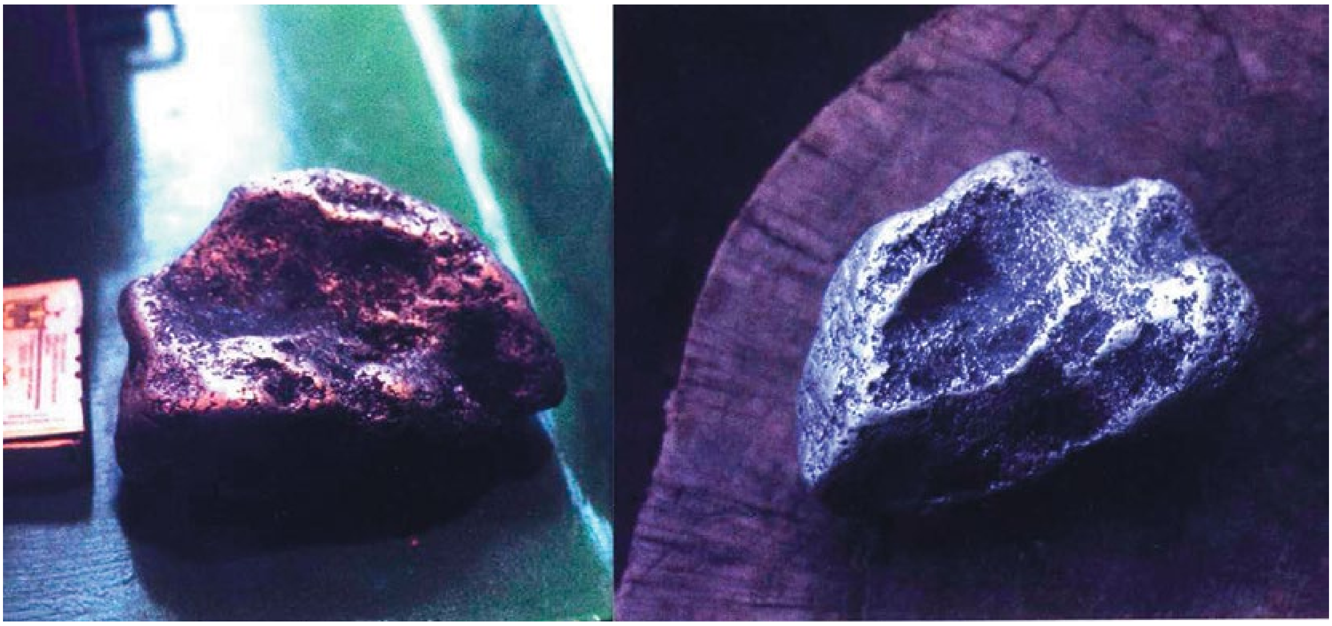

*Fig. 1.* Unique platinum nugget, weighing 3521.7 g, was found September 10, 1993 in the upper part of the Kondyor River

occur in the form of nuggets that have weight from 3-5 to 200 g. More than 50 PGM, Au- and Ag-bearing minerals including new and very rare species were identified in this unique deposit over last 30 years (Mochalov, 1994; Lennikov et al., 2004; Platinum of Amur, 1997; Sushkin, 1995; 1996; 2006). The finding of the largest platinum nuggets at Kondyor has nearly coincided in time with the great discovery of economic platinum placers of the Koryak highlands in Kamchatka, but these placers contain nuggets weighing below 0.5 kg. The Kondyor nuggets are comparable only with the platinum nuggets found in the unique placers of the Middle Urals in the XIX century (Vysotsky, 1913), where more than 100 samples weighed over one kg, and the largest was 9635 g. The platinum nuggets from Urals and Kondyor will form the most important component of the State Noble Metal Collections of the Russian Gohran and Diamond Fund of the Moscow Kremlin.

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# MINOR ULTRAMAFIC-MAFIC INTRUSIONS OF WESTERN TUVA: POTENTIAL FOR DISCOVERY OF PGE-Ni-Cu ORES

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**ABSTRACT**. More than 200 minor ultramafic-mafic intrusions are known to occur in western Tuva and adjacent territories of northwestern Mongolia. We have established that their formation took place in two stages – the Early Devonian and Early Carboniferous. In one of the Early Carboniferous intrusions situated in Mongolia a small manifestation of Cu-Ni ores with PGE mineralization was found. Thus there is potential to find similar deposits in other intrusions of this age.

A large number of ultramafic-mafic intrusive bodies are located in the Tsagaan Shuvuut and Western Tannu-Ola ridges in western Tuva. These are traditionally regarded by many researchers to belong to the Devonian-Carboniferous Torgalyk complex. However, on the maps of the third generation developed by the Russian Geological Survey (scale 1:1 000 000), most of the intrusions are grouped into the Permo-Triassic Chazadyr complex. The present authors consider that they are associated with the magmatic pulse synchronous with the Siberian Traps. Intrusions of similar type are also known in North-Western Mongolia, where they were interpreted to form the first stage of the Uuregnuur Devonian-Carboniferous complex. Studies carried out in the last decade found that some of these bodies, which occur to the south of the large sublatitudinal fault (Fault of 1905 year) are of Cambrian age (Izokh et al., 2010) and are the source of isoferroplatinum placers (Oyunchimeg et al., 2009). These bodies were regarded as the Uuregnuur volcano-plutonic association, which consists of ultramafic intrusive rocks and extrusive picrites (including hyaloclastites). These rocks combine typical island arc and plume geochemical features and a high K content. Our studies revealed that there are substantial differences from ultramafic-mafic intrusions, which are located north of the fault, in the Tsagaan Shuvuut area in Mongolia and Tuva. In this area many sills and stock-like bodies intrude Devonian and Silurian volcanic and sedimentary strata, wherein the majority of mapped bodies have clear spatial arrangement to the periphery of the large Tuva depression, the formation of which began in the Early Devonian time and continued in the Carboniferous. It is important that these bodies do not have intrusive contacts with Carboniferous sedimentary rocks and its geochemical features indicate that the initial melts have compositions intermediate between N-and E-MORB which are typical for rift zones (Izokh et al., 2011). On this basis their relation to the Permo-Triassic intraplate magmatism looks rather controversial.

Back in the 1960s, Krivenko (1965) showed that among the small ultramafic-mafic bodies in Western Tuva it is possible to allocate two complexes – Early Devonian Bayankol (subvolcanic intrusions from dolerite to granite porphyry) and Late Devonian – Early Carboniferous Torgalyk which includes peridotites, gabbrous, syenites, alkaline and biotite granites. It is important to note that A.P. Krivenko suggested ultramafic rocks are characteristic only of the second (Torgalyk) stage. The data obtained in recent years for intrusions in the Mongolian part of the Tsagaan Shuvuut area allowed us to partially confirm his results. Isotope studies revealed that there are at least two pulses of ultramafic-mafic magmatism in this area – Early Devonian (407-392 Ma) and Early Carboniferous (348-334 Ma). Furthermore, ultramafics are present in intrusions of both stages.

In one of the Early Carboniferous intrusions (348±3.2 Ma, Ar-Ar biotite) a narrow elongated zone (about 0.2 x 30 m) enriched in sulfides has been found. For this reason, this intrusion was named Rudny (Ore-bearing). This is a very small body which outcrops over about 200 x 70 meters. It has been sub-divided into 2 units, an older leucocratic and a younger melanocratic unit. The zone enriched in sulfide is confined to the most magnesian part of the second unit (up to 27 wt.% MgO). Most of the sulfides form globules that are rounded, slightly flattened or elongated in shape. In addition, small grains of sulfide minerals are disseminated between the silicates. Sulfide globules in the upper part of the sulfide enriched zone are relatively large and often flattened (to 1x3 cm), whereas at the lower part they are smaller and spherical. Similar globular sulfide clusters (sulfide droplets or blebs), which are the result of separation of ultramafic-mafic melt to silicate and sulfide liquids are known in many of the largest Ni-Cu deposits, like Norilsk, Sudbury, etc.

Studies carried out by electron microscopy (with EDS) allowed to detect and study the composition of PGE minerals, most of which are localized in pentlandite, with fewer being located in chalcopyrite and rare in pyrrhotite. Common to both types of globules are moncheite group minerals $(Pd,Pt,Ni)(Te,Bi)_2$ and sperrylite $PtAs_2$. Moncheite group minerals are the most widespread phase, accounting for up to 70% of all grains that were analyzed. In large globules we also found hessite $Ag_2Te$, and more rarely sopcheite $Ag_4Pd_3Te_4$, paolovite $Pd_2Sn$, taimyrite $(Pd,Ag)_3Te$, telargpalite $(Pd,Cu,Pt)_3Sn$, and Pt stannotelluride closely associated with hessite.

Analysis of the PGE contents, and other rare and trace elements was carried out using ICP-MS, ICP-OES and ICP-MS with NiS fire essay collection in Intertek Lab (Genalysis), Australia. Samples from different parts of the sulfide-bearing zone were analyzed. However, the results were broadly similar: total PGE – 720-750 ppb (540-570 and 120-130 ppb Pd and Pt, respectively), Au – 200-300 ppb, Ag – 850-930 ppb, Cu – 0.34 wt.%, Ni – 0.50-0.55 wt.%. PGE tenor (metal content in 100% sulfide) reaches 20 ppm, which is comparable to the deposits of Norilsk area.

These data suggest the possibility to discover PGE-Cu-Ni ores associated with minor ultramafic-mafic intrusions of Torgalyk (Chazadyr) complex in Western Tuva and Northwestern Mongolia related to Early Carboniferous magmatic activity. To highlight the petrological, geochemical and mineralogical criteria for referring these intrusions to Early Devonian or Early Carboniferous stage and assess their ore potential additional studies are required.

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# MANTLE SOURCE OF 2.4-2.5 GA PLUME MAGMATISM IN THE FENNOSCANDIAN SHIELD: EVIDENCE FROM OS ISOTOPE COMPOSITION OF CHROMITE

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**ABSTRACT**. Wide-spread mafic-ultramafic magmatism occurring in the Fennoscandian Shield at 2.44-2.50 Ga is believed to be related mantle plume activity. Significant PGE-Cr mineralization has been discovered in layered intrusions, such as Kemi, Portimo, Penikat, and Koitelainen in Finland and Monchegorsk in Russia. It is proposed that part of the magma was derived from asthenospheric mantle as evidenced by positive eNd values of related mafic dykes. However, most of the intrusions show negative eNd values of about -1 to -2. A potential explanation is crustal contamination of asthenospheric mantle-derived magma (Huhma et al., 1990; Hanski et al., 2001), but another possibility is that the magma came from metasomatised subcontinental lithospheric mantle (SCLM) (Huhma et al., 1990; Amelin et al., 1996).

The composition of asthenospheric mantle and SCLM is different in terms of Re-Os isotopes. The former has close to chondritic Os isotope composition, while the latter normally shows sub-chondritic Re/Os ratios after earlier melt extraction, and thus sub-chondritic γOs through time (Shirey & Walker, 1998). In this study, we analyzed chromite samples from both the Monchegorsk and Kemi intrusions to constrain the mantle source of the related mafic magmatism.

The Sopcha Lake chromitite deposit in the Monchegorsk intrusion contains olivine with a higher Fo content (up to 87 mole %) than olivine in the lower zone of the Kemi (82-83) and Koitelainen (82) intrusions, indicating that the Monchegorsk intrusion originated from a more primitive magma. Based on chilled marginal rocks the parental magma of the Akanvaara intrusion had an MgO content of about 6-8 wt.%, i.e. being basaltic in character (Hanski et al., 2001), and comparable to that of Koitelainen. This is consistent with the higher Os content and Cr/Fe ratios in chromite from Monchegorsk compared to the other intrusions (Fig. 1).

All analyzed chromite samples have low Re contents, indicating that Re is incompatible in chromite. On the $^{187}Re/^{188}Os$ vs. common Os diagram, all samples define a negative trend, demonstrating that chromite derived from the most primitive magma has the highest Os content but the lowest $^{187}Re/^{188}Os$ ratio.

The Monchegorsk samples show near chondritic initial γOs ranging from 0.8±0.6 to 1.2±1.4. The constant γOs values and the high Os contents suggest that the magma was derived from an asthenospheric mantle source and the Os isotope composition of the most primitive magma was not changed by crustal contamination. On the other hand, some samples from Kemi, Koitelainen and Akanvaara have slightly elevated γOs values up to +6. On the γOs vs common Os diagram (Fig. 1), the general negative correlation indicates that crustal contamination played an important role. It is proposed that the magma was derived from an asthenospheric mantle, and the negative $\varepsilon_{Nd}$ values in these layered intrusions resulted from crustal contamination. Due to the high Os content of the magma and low Os content of the crustal contaminant, the Os isotope composition was not changed before the magma's emplacement. However, after some fractional crystallization, the Os content of the evolved magma decreased, and contamination with crust led to elevated γOs values as indicated by the Koitelainen and Akanvaara intrusions.

Samples from both Kemi and Koitelainen show a slightly negative initial γOs value, which is interpreted to be the result of over age-correction because these samples have relatively low Os contents and high Re/Os ratios (Fig. 2). Smolkin & Tessalina (2007) reported negative γOs values of chromite samples from Monchegorsk. The samples have comparable Os contents to our samples, but show much higher Re/Os ratios and deviate from the trend of chromite from other intrusions (Fig. 2), consistent with later addition of Re by alteration and over age-correction of radiogenic Os.

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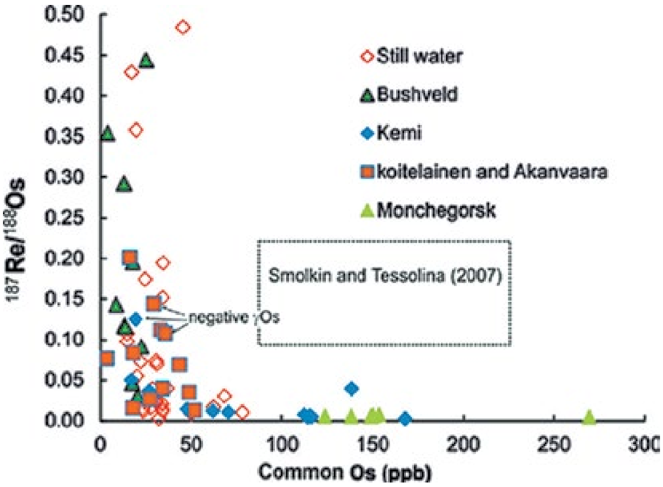

*Fig. 1.* γOs vs. common Os of chromite separates from chromitite samples of Mongchegorsk, Kemi, Akanvaara and Koitelainen. Data of Akanvaara and Koitelainen are from Hanski et al. (2001)

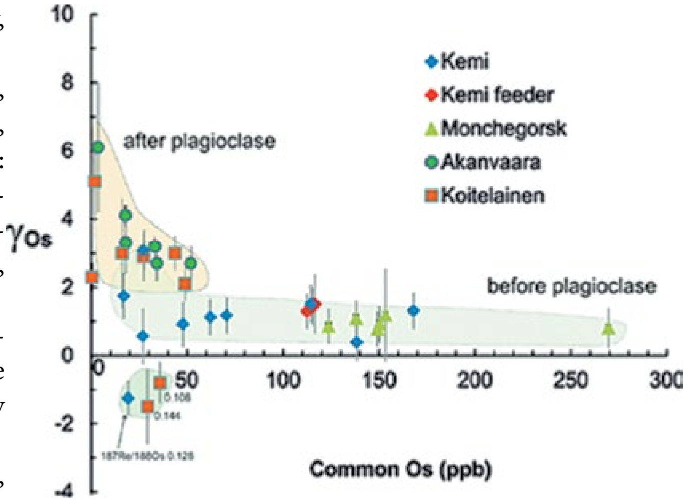

*Fig. 2.* $^{187}$Re/$^{188}$Os vs common Os diagram for chromite separates from chromitite samples of Mongchegorsk and Kemi, and compared with Akanvaara, Koitelainen, Stillwater and Bushveld. Data of Akanvaara and Koitelainen are from Hanski et al. (2001), and Stillwater from Lambert et al. (1994), Bushveld from Schoenberg et al. (1999)

# THE EFFECTS OF THE INTRUSION OF A NEW BATCH OF MELT IN THE REDISTRIBUTION OF CHEMICAL COMPONENTS

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**ABSTRACT**. Research on the layered platinum-bearing Lukkulaisvaara intrusion (Olanga group of intrusions, Northern Karelia) demonstrated the important role of magma replenishment in the formation of the platinum group element (PGE) mineralization (Klyunin et al., 1994; Semenov et al., 2008; Latypov et al., 2008). Clearly, these magma injections have also affected the structure of the layered series of the intrusion, which is seen from the reversals to higher-temperature cumulus associations containing olivine in the upper basite part of the section (Semenov et al., 2008). In this work, we present the physical description of such magma injection, which leads, in particular, to the redeposition of PGE.

The Data on the Formation Conditions of the Lukkulaisvaara Intrusion. The pressure of a magma during intrusion ($P_0$) was estimated for three layered intrusions, namely Kivakka (1), Lukkulaisvaara (2) and Tsipringa (3). The value of the $P_0$ was obtained from the space analysis of gravity for rocks which contain the intrusive body. The observed gravity anomaly near the boundary of the intrusion were induced by the stress which was produced due to the intrusive action. The $P_0$ may be presented as: $P_0=P_1+s$ (stress), where the $P_1$ is the lithostatic pressure for the contained rocks. For the intrusions above the values of the $P_0$ are:

$P_0(1)=9.8\pm1.2$ kbar, $P_0(2)=8.3\pm1.0$ kbar,
$P_0(3)=7.3\pm1.9$ kbar.

After formation of the magma chamber, the $P_0$ goes to the $P_1$, due to relaxation.

It was previously shown that the average weighted composition of Lukkulaisvaara intrusion corresponds to undifferentiated magma:

$SiO_2$–51.02 mass/%, $TiO_2$-0.28, $Al_2O_3$-15.35, FeO-7.82, MnO-0.16, MgO-12.69, CaO-9.61, $Na_2O$-2.00, $K_2O$-0.33, $P_2O_5$-0.03, Cr-514 ppm (Semenov et al., 2008).

This allowed the present researchers to determine the P-T conditions of magma generation by studying the subliquidus phase proportions at different pressure. We conducted these calculations using the COMAGMAT program (Ariskin & Barmina, 2000). The pressure value obtained for the depth area of magma generation is 11.0 kbar, which fairly well corresponds to the data of (Berkovskii, 1999): $P_0= 8.3\ \pm1.0$ kbar, while the discrepancy of ~2.7 kbar can probably be explained by the limited applicability of the used calculation method.

The lenticular bodies of fine-grained gabbronorite are resulted from the secondary injections a fresh magma. At least some portions of the new magmas were trapped in the solidified part of the intrusion. The isotope-geochemical evidence and the data on magma composition of the secondary intrusions, which are close to the chemical composition of the magma of the "primary" intrusion (Semenov et al., 2008), suggest that these injections came from the close sources and, hence, have the close intrusion conditions.

The formation of Grt-Hbl-Pl±Qtz superimposed mineral associations is peculiar to the exocontact gabbroids edging the bodies of fine-grained gabbro-norites and allows to estimate the crystallization conditions of the secondary minerals by the TWEEQU (Aranovich & Berman, 1996) method. P – conditions derived from garnet assosiations may be a result of additional injection of fresh magma into the crystallized (solidified) part of the chamber. The results gave $P_0\leq13.0$ kbar. Thus high pressures ($P_0\approx13.0$ kbar) obtained for the garnet-bearing associations indicate the influence of the fresh magma influx ($P_0$) on the containing environment and correspond to the magma injection conditions.

The Effects of the Intrusion of a New Batch of Melt in the Redistribution of Chemical Components. For the intrusive (2): $P_1 < 4{,}5$ kbar. An opening of a canal between a source of magma under pressure (Pq) and formed chamber induces the movement of a new portion of a magma from the source to the chamber (due to the condition: $(Pq - P_1) > 0$). The pressure of a new portion may be expressed as: $Pq' = Pq(1-(r_m/r_c))$, where $(r_m/r_c) < 1$ ($r_m$, $r_c$) – the average densities of the magma colomn, and rocks, which contain the colomn. It is evident that: $P_1 < Pq'$. Thus the new portion compresses the chamber filled with the initial portion, as well as an initial portion compressed the contained rocks. The influence of the new portion on the initial one is analogous to the influence of a press and depends on the velocity ($v_0$) of a new portion´s movement. In general case $v_0 \neq 0$ and the influence presents like water hammer. However, if the time of the influence more, than the time for passing of deformation waves through the body (chamber), the effect is analogous to one for a static press. We used this approximation. We obtained; that: The initial portion near the contact with the new portion is compressed by the stress X; The new portion near the contact is under the tension X, that can be a reason to a satiation of the zone near the contact with a fluid (with useful components); $X = Pq' - P_1$. It was obtained, that the X induces not only a stress-induced diffusion (weak for non-metals like the rocks and the magma); but a thermal diffusion too, induced by a local gradient of the temperature (which, in turn, is produced by the water hammer). The thermal diffusion must change the distribution of components near the contact. After the „water hammer" the system exists under a cooling and decompression that may produce a new change of the distribution of components.

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# SESSION 3

## PGE–Cu–Ni sufide–bearing ultramafic–mafic intrusions of the Noril'sk Province: insights into ore genesis and exploration

**Conveners: Kreshimir Malitch & Chusi Li**

Despite the long-term study of the 'Noril'sk-type' intrusions (e.g., Noril`sk-1, Talnakh and Kharaelakh), they remain a subject of ongoing debate related to their origin. A broad range of different or contradictory ideas for the formation of ore-bearing ultramafic-mafic intrusions in the Noril'sk region has been proposed. These include (a) differentiation of a single magma, (b) emplacement of multiple magmas with distinct compositions, (c) volcanic feeder systems, (d) a crust-mantle interaction model, (e) assimilation and (f) metasomatic models. A common assumption in these models is that the intrusions are coeval with the 250 Ma Siberian flood basalts, which erupted over a period of ~1 Ma or less, despite the fact that the age range of the intrusions is considerably larger. We invite contributions that use mineralogy, petrology, geochemistry, geochronology and structural controls to improve our understanding on the origin of ultramaficmafic intrusions with different degrees of PGE-Cu-Ni sulphide mineralisation (i.e., economic, subeconomic and non-economic) in the Polar Siberia. New isotope-geochemical data that can be used for the exploration of PGE-Cu-Ni sulfide deposits are particularly welcome.

# SULFIDE SLURRIES, TWO-WAY CIRCULATION IN MAGMA CONDUITS AND THE FORMATION OF Ni SULFIDE DEPOSITS

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**ABSTRACT**. Downward flow of dense slurries of sulfides and/or oxide ore minerals, together with mineral grains and rock fragments, plays an important but little recognized role in the formation of Ni-Cu sulfide and Fe-Ti-V oxide deposits.

The formation of magmatic Ni-Cu sulfide deposits is directly linked to the interaction between mafic-ultramafic magma and rocks of the continental crust. This interaction decreases the solubility of sulfide in the magma and/or adds sulfur to generate an immiscible sulfide liquid. Strongly chalcophile Ni, Cu and PGE concentrate in the sulfide and if this phase accumulates in sufficient quantity and with sufficient tenor, an ore deposit is formed. Most models identify gravitative settling of dense sulfide liquid as the cause of sulfide accumulation but inspection of the textures and structures of some ore bodies indicates that the process is not always that simple. Accumulation on the basal contacts of intrusions is by no means universal, especially in mafic-hosted systems. Many ores consist of crystal mushes or breccias that have been injected in pulses into the host intrusions; and massive sulfides commonly penetrate rocks beneath or adjacent to the intrusions. These features can be explained if sulfide-rich masses of magma migrated down from higher in the magmatic plumbing system. As the magma ascends it loses heat, and interacts with country rocks. This causes crystallization and incorporation of country rock fragments, which may be accompanied by the appearance of sulfide droplets. As a consequence, a dense slurry of sulfide liquid, silicate crystals (typically olivine or pyroxene) and country rock fragments develops along the intrusion margins. Many ore-bearing intrusions are hosted in conduits with sloping margins. As magma flows up along these margins, the denser sulfide/inclusion/crystal-rich mush accumulates near the lower border while a sulfide/inclusion/olivine-poor silicate liquid ascends along the upper part. This process differentiates the magma, producing evolved decanted liquids that flow upwards and erupt. The magma interacts with the sulfide in the lower part of the conduit, enriching the sulfide in chalcophile metals. The mush layer periodically becomes unstable and slumps down the conduit, to be injected as pulses into deeper parts of the intrusions. Where the slurry contains abundant assimilated volatiles, final crystallisation gives rise to vari-textured "taxitic" breccias and associations between sulfides and hydrous magmatic phases, common in many deposits. Jogs, throats and other bottlenecks in conduits cause "logjams" of xenolithic fragments and crystals, which also serve as filter beds to trap sulfide droplets.

# THE CHONOLITH Ni-Cu MODEL: EXPANDING THE FOOTPRINT OF Ni-Cu DEPOSITS

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**ABSTRACT**. We outline a new model for the physical controls on emplacement of Ni-Cu deposits. The focus of this model is on expanding the exploration footprint of Ni-Cu deposits.

Magmatic Ni-Cu deposits are hosted in mafic-ultramafic intrusions of varying geometries that are emplaced within very large magmatic provinces, most of which are voluminous enough to be called Large Igneous Provinces (LIPs). These host intrusions represent the surficial expression of very large linked crustal size intrusive complexes. The deposit and even the host intrusion are however small and represent challenging exploration targets in their own right. Most of the host intrusions are less than 300 m in width!

In recent years it has become clear that the deposit scale footprint for mafic intrusion-hosted Ni-Cu deposits of massive sulfide deposits hosted at the base of intrusions or funnel shaped intrusions does not apply to the entire class of the deposit and in particular not to the larger deposits. There are a diversity of deposit styles and intrusion geometries (and emplacement). We propose a new classification for Ni-Cu deposits based on intrusion geometry i.e. the definable distal footprint of Ni-Cu deposits. We find this a useful practical guide in exploration as opposed to mineralization style or geotectonic setting, both of which are poorly or unknown during area selection in exploration.

The largest Ni-Cu deposits are associated with an unusual and somewhat unique intrusion termed a chonolith. A chonolith is an irregular to pipe like intrusion that is spatially associated with either sills or dykes. The structural setting suggests they were emplaced into neutral or radial stress regime, which along with the petrological characteristics suggest they represent overpressured intrusions. The primary structural control on the intrusion emplacement is either existing fold geometry or intersection lineations along sills or dykes. Chonoliths are rare and represent a spatial and temporal discrete intrusive event in the emplacement of magmatic provinces.

The intrusion geometry defines the outer footprint of the Ni-Cu sulfide deposit. The deposit itself is hosted within and often fills or is centrally located within the intrusion i.e. not restricted to the basal contact (Figure 1). The host intrusion is zoned in terms of macro scale lithologies, and rarely exhibits any evidence of layering. A key feature is that the massive sulfides are often discordant with respect to disseminated sulfides and are hosted in a distinctive variably textured facies of gabbroic to peridotitic origin. These varied textured zones grade into igneous breccias. The geometry of these zones can be discordant with respect to the zoning within the host intrusion. These varied zones are inferred to represent zones of multiple magma input of varying melt, crystals, xenoliths, autoliths and importantly volatile content (water, carbon dioxide, and halogens). These zones include pulses, sills, dykes, brecciated sills, pegmatoidal zones, and autolithic rich domains. As the descriptive name implies these are highly variable and visually distinctive rocks. Varied textured rocks are not unique to Ni-Cu deposits. For example they form at the top of the cumulate zone in ophiolites where pooled fractionated melt concentrates, and in the immediate roots of porphyry Cu causative intrusions.

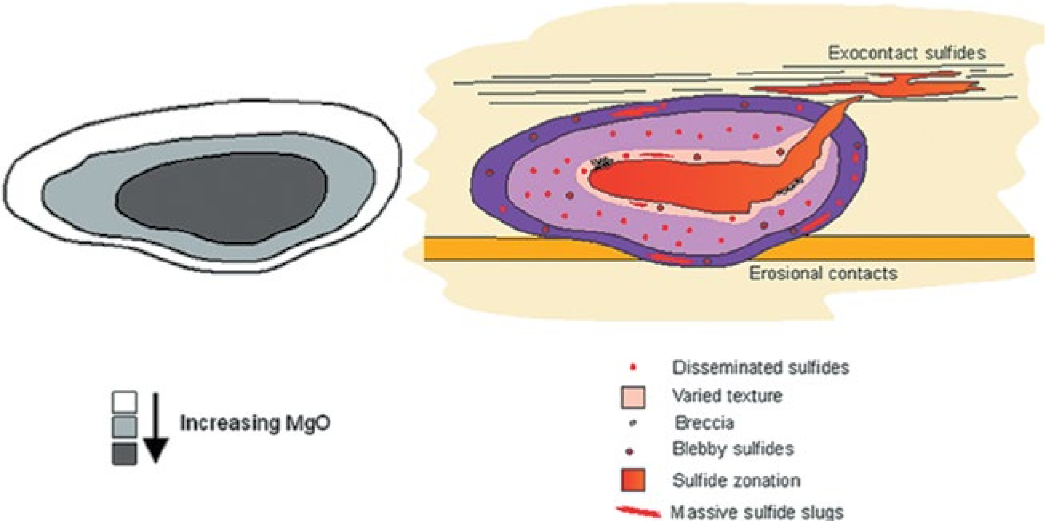

*Fig. 1.* Schematic model of a chonolith-hosted Ni-Cu deposits in cross section. Massive sulfide are hosted at either the bottom or top contact but most commonly are centrally located. Sulfides commonly fill the intrusion. The host intrusion is zoned (schematized above as variations in purple colouration). Mineralization is largely contained to within the intrusion but exo-contact sulfides are noted in several deposits especially where hosted in carbonates or evaporitic country rocks

At present, like most mineral systems, the Ni-Cu mineral system is challenged at the transition from larger scale geodynamic scale targeting to the use of detection methodologies. Area selection, especially under cover is comprised at this so called camp scale. This transition occurs at the scale where datasets are usually pre-competitive. The area selection decision is thus a huge opportunity cost, especially so in Ni-Cu systems because of the small footprint cf other large base metals systems like IOCG and Sedimentary Copper deposits. The footprint is small and rare but there are significant advantages over other deposit styles, if the footprint can be imaged in pre-competitive datasets, because the geometry is intimately linked to deposit size and also the probability of an economic threshold. This later point has driven us to embark on innovative approaches to expand this footprint and image chonoliths at various stages in the exploration process. This has required new approaches to dealing with magnetic remanence, and the development of new automated mapping techniques.

The theory of constraints suggests focusing innovation at the weakest point in our understanding of the mineral system, i.e. camp scale, will lead to the best chance of improving the overall probability of new discoveries.

# THE GIANT NORIL'SK-TALNAKH Cu-Ni-PGE DEPOSITS

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**ABSTRACT**. A multistage petrological-geodynamic model for the formation of the Noril'sk-Talnakh magmatic Cu-Ni-PGE ore deposits based on the concept of a mantle superplume beneath the Siberia Craton is proposed. These ore deposits belong to a triple rifting system that developed in one branch of the superplume. Critical ore-forming materials and processes include core- and mantle-derived fluids, deep-seated liquid immiscibility, crustal contamination, magma differentiation at depth, plus the formation of favorable crustal structure.

The base and precious metal ore deposits of the famous Noril'sk mine district are located in the NW part of the Siberia Craton. These deposits formed in the late-Paleozoic to early-Mesozoic (240-250 Ma). They are hosted in mafic-ultramafic intrusions. Among them the Noril'sk-Talnakh Cu-Ni-PGE (platinum-group elements) deposits are the largest. In term of the total Ni and PGE tonnages, the Noril'sk-Talnakh deposits almost match the Sudbury Ni camp and the Merensky PGE-bearing reef of the Bushveld Complex in South Africa.

The distribution of the Noril'sk and Talnakh deposits are controlled by the Noril'sk-Khaerlakh regional fault system. The ore-forming magmatic event produced picritic basalts and many ore-barren mafic-ultramafic intrusions as well as sulfide ore-bearing mafic-ultramafic intrusions. Both disseminated and massive sulfide ores are present. The ore deposits are genetically related to each other by deep-seated magmatic processes. The entire ore-forming magmatic system lasted for ~300 Ma.

The Noril'sk and Talnakh ore fields are characterized by occurrence of three different types of layered mafic-ultramafic intrusions formed during a short period of time injections. These intrusions differ in the degrees of differentiation that took place in the staging chambers, in the degrees of mineralization and in the types of country rocks such as sulfate-bearing carbonates versus volcanic rocks. The most important differences are perhaps different MgO contents of host rocks and the locations of sulfide ore zones in the intrusions.

The ore-bearing intrusions in the Noril'sk-Talnakh district are characterized by medium MgO content (12-13 wt.% MgO). They contain usually high amounts of platinum metals (Pd>Pt), Ni, Cr and K. The concentrations of volatile components in these intrusions such as H, $OH^-$, F, Cl and S are also very high. The ore-bearing intrusions and coeval picritic basalts show a komatiitic differentiation trend. Their distributions are controlled by rift-related structures.

I propose a multistage petrological-geodynamic model for the formation of the Noril'sk-Talnakh magmatic Cu-Ni-PGE ore deposits based on the concept of a mantle superplume beneath the Siberia Craton. The Noril'sk-Talnakh ore deposits belong to a triple rifting system that developed in one branch of the superplume. Critical ore-forming materials and processes include core- and mantle-derived fluids, deep-seated liquid immiscibility, crustal contamination, magma differentiation at depth, plus the formation of favorable crustal structure. The formation of thick (up to 30-50 m) massive sulfide layers in the Talnakh ore system is yet to be studied.

The Imangdinsko-Mikchandiskaya ore-forming system in the western side of the Tunguska syncline is less known due to scare studies. In this region the magma-ore-controlling structure is the Imangda-Letninsky regional fault. The Imangda intrusion is the most interesting one in this region. This intrusion contains both high-sulfide Cu-Ni-PGE ores and low-sulfide PGE mineralization. Numerous exploration prospects are present in this region. Further exploration in this region is warranted because it is not too far from the Noril'sk smelting facility.

# REFINEMENT OF THE MODEL FOR SULFUR CONTENT AT SULFIDE SATURATION (SCSS) IN BASALTS AS FUNCTION OF OXYGEN FUGACITY ($fO_2$)

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**ABSTRACT**. One of the critical aspects of understanding the formation of massive sulfide deposits is assessing the conditions that would trigger sulfide saturation in a magma. Typically, the main variables considered are pressure, temperature and the FeO content of the melt. These are valid assumptions for most magmatic systems, in which sulfur is likely present as sulfide species ($S^{2-}$). However, under certain conditions, sulfate species ($S^{6+}$) may also be present in the magma and when sulfate species are present the amount of S that can be dissolved in the melt increases, delaying or preventing the appearance of sulfides. Thus, it is important to be able to assess the effect that changes in oxygen fugacity ($fO_2$) have on the sulfur content at sulfide saturation (SCSS). Here, a revised model to assess the effect of ($fO_2$) on SCSS is presented. Previous models mostly addressed partial melting of the mantle and the generation of PGE rich basalts. In contrast, the revised model presented here takes into consideration experimental data on the SCSS in basaltic melts at crustal pressures and temperatures as well as a more accurate calibration for the change in S speciation as function of $fO_2$. Therefore, this model is more appropriate to understand how crustal contamination or any process affecting the $fO_2$ of the magma may affect the stability of sulfides during magmatic emplacement, a key aspect in the generation of massive sulfide deposits.

Models to assess the importance of $fO_2$ on SCSS were previously discussed in Jugo (2005) and Jugo (2010). Jugo (2005) showed that there was a significant contrast in the amount of S that could be dissolved in basaltic magmas under very reduced and very oxidized (sulfate-saturated) conditions but lacked information in the region in which the transition occurred; however, the effect of assimilation of highly reducing crustal components, such as carbon or highly oxidizing agents such as anhydrite was clearly outlined. Jugo (2009) showed how interaction of an anhydrite-saturated melt with graphite would create a steep reduction front and result in the formation of a sulfide cloud as the reduction front converts the dissolved sulfate into iron sufides. Jugo (2010) presented a more complete model, which accounted for the exponential increase in SCSS with increase in $fO_2$. However, that model was based on data at high pressure (10 kbar) and high temperature (1300 °C) which are more relevant for the conditions of partial melting in the mantle and the enrichment in PGE of primitive melts during partial melting of metasomatized (hence relatively oxidized) mantle peridotites.

The refined model presented here (Fig. 1) is based on two aspects. First, the geometry of the curve that described the exponential increase in SCSS was better constrained by Jugo et al. (2010) using synchrotron analyses (X-ray absorption near-edge structure or XANES) of the sulfur speciation in basalts using hydrous basaltic glasses equilibrated at 2 kbar and temperature ranging from 1050 °C to 1250 °C prior to quenching. Those results showed that the exponential increase in SCSS is slightly steeper and shifted to lower $fO_2$. The second improvement is the use of experimental data on the sulfur content at sulfide saturation for highly reduced basalts (S present only as sulfide species) and highly oxidized basalts (S present only as sulfate species) derived from a different set of basaltic melts equilibrated at 2 kbar and temperature ranging from 1050 °C to 1250 °C (Beermann et al., 2011). Thus, the revised model is more appropriate for magmatic systems at crustal conditions.

The main implication for ore deposits is that for magmas equilibrated at $fO_2$ between FMQ+0.5 and FMQ+1.5 small variations in $fO_2$ will have a significant effect in the stability of sulfides. Such relatively oxidized conditions were previously assumed to exist mostly in subduction-related magmas; however, XANES analysis of plume-related basalts, such as Kilauea and Loihi (Jugo et al., 2010) show that those basalts had significant amounts of sulfate species and higher S contents.

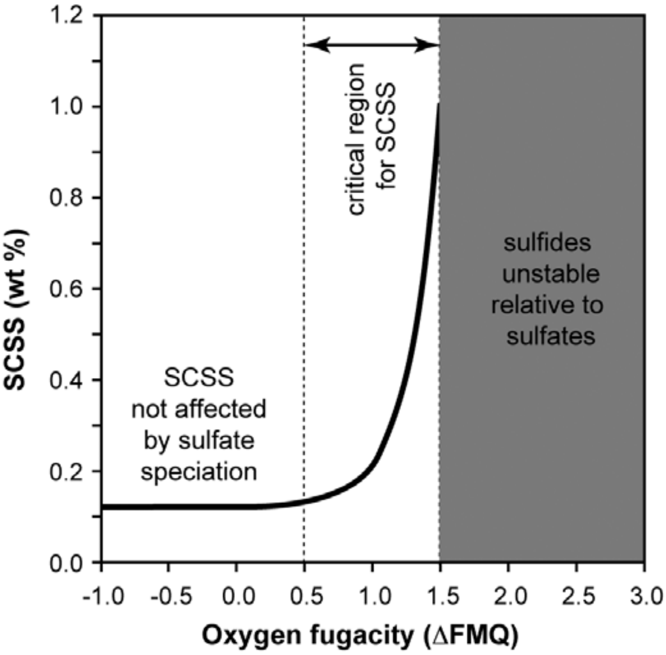

*Fig. 1*. Revised model for the change in sulfur content at sulfide saturation (SCSS) with changes in oxygen fugacity ($fO_2$). The model is simplified from Jugo et al. (2010) to consider only the curve for sulfide content at sulfide saturation. The region at which sulfides are not expected to be stable is shaded in grey. The region for which the influence of sulfate species is expected to be insignificant is toward the left side of the diagram. The central portion (bounded by the dashed lines) is the region for which small changes in $fO_2$ can have a large effect in the SCSS either triggering sudden sulfide saturation (i.e. if the magma is suddenly reduced). Conversely, oxidation would destabilize sulfides preventing sulfide saturation or dissolving (entirely or partially) any sulfides already present. The curve for the revised model is constrained by data form basaltic melts at 2 kbar (Bermann et al., 2011)

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# Pt-Cu-Ni NORIL'SK DEPOSITS: GEOLOGY AND ORIGIN

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**ABSTRACT.** The main problems for the genesis of the Noril'sk deposits are evaluated: 1) evolution of magmatism in the Noril'sk area, 2) the positions of ore-bearing intrusions in the Siberia trap, 3) geochemical classification of the intrusions, 4) magma compositions of ore-bearing intrusions, and 5) degree of assimilation in magma chambers. Based on the geology and geochemistry of igneous rocks, a long-term formation of the deposits in a rift zone is suggested.

The uniqueness of the Noril'sk deposits as compared to other magmatic Pt-Cu-Ni deposits in the world (the setting of the Noril'sk region in the world‘s largest Siberian flood-basalt province in a continental setting, the early-Triassic ages, and the combination of high-sulfide and low-sulfide types of PGE mineralization within the same intrusion) continues to attract people's interest in both purely theoretical and applied fields. The principal relations and trends revealed by the Noril'sk deposits facilitate exploration for similar types of deposits not only in the Noril'sk region and the Siberian craton but also in the other trap provinces.

Several genetic aspects of the Noril'sk deposits are still debated. These include the mechanism of metal enrichment and the origin of large amount of high-PGE tenor sulfide ores from small amount of magma as indicated by the host intrusions. Some geologists (Godlevsky 1959; Likhachev 2006) believed that the unusual characteristics of the deposits can be explained by high-Mg magmas. In contrast, other researchers (Rad‘ko, 1991; Naldrett, 1992) believed that the deposits were produced by typical tholeiitic magmas in a sub-volcanic environment. The main difference between these two schools of thoughts is the closed versus open magmatic systems during the generation of the ores. Almost all of the genetic models emphasize the importance of crustal assimilation by the magma. The anhydrite-bearing country rocks are considered by some researchers as the source of external sulfur (Ripley et al., 2003 among others).

My recent results (Krivolutskaya, 2011) are summarized below. The extensive studies of the volcanic rocks in Niril'sk area have made it possible to distinguish two major tectonic-magmatic regimes (rifting-related and trap-related magmatism for the tuff-lava sequence which can be further divided into four cycles (Formations): the Ivakinsky-Syverminsky, Gudchikhinsky, Nadezhninsky-Tuklonsky, and Morongovsky-Samoedsky. The basalts of the stratigraphically lowermost formations (Ivakinsky – Nadezhdinsky) were present only within the Noril‘sk-Igarka ancient rift zone and give insight into the rift development in the region. The chemical compositions of these rocks are different from those of other formations such as the Tuklonsky – Samoedsky ones. (widespread far away from the Norilsk-in the Putorana Plateau and Tunguska Syncline). My new contributions to the study of volcanism include the discovery of two simultaneously active magmatic centers in the Noril‘sk region (in the western and eastern parts of the territory). The western center recorded the evolution of the rift system whereas the eastern one marked the onset of trap magmatism. These conclusions are based on geochemical data for the volcanic rocks of the Nadezhdinsky and Tuklonsky formations that occur in the western and eastern parts of the territory, respectively and which are present alternatively in a vertical section in the central part of the territory because of simultaneous eruption of tuffs with compositions corresponding to those of the Nadezhdinsky and lavas of the Tuklonsky formations.

Intrusive rocks in the Noril‘sk region are classified (based on the abundance of trace elements and isotopic data) into three types in accord with the Gudchikhinsky (Dymtaleysky type of intrusions), Nadezhdinsky (Lower Talnakh Type), and Morongovsky (Noril’sk type) Formations. Based on geological relations between the basalts and intrusions, it is recognized that the Noril‘sk Intrusive Complex was formed after the Low Nadezhdinsky lavas. Comparison of major and trace element compositions between the ore-bearing intrusions and the associated lavas formed in this stage reveals some significant differences between them such as whole-rock MgO concentrations (10-12 wt.% in the intrusions and 6-7 wt.% in the volcanic rocks), whole-rock $TiO_2$ concentrations and whole-rock La/Yb ratios as well as isotopic compositions (e.g., $\delta^{34}S$ from+1 to -5 and 18‰ in the basalts and intrusions, respectively). The absence of geological evidence for a genetic relationship between the intrusions and lavas, plus their differences in geochemistry has led me to conclude that the ore-bearing intrusions and volcanic rocks are not comagmatic. As suggested by many researchers (Godlevsky, 1959; Likhachev, 2006 among others) the Norilsk intrusions were formed by a distinct magmatic pulse of activity after the Nadezhdinsky eruption. This study is the first to estimate the composition of the parental magma for ore-bearing and barren intrusions based on study of melt inclusions trapped by olivine and pyroxene. The results show that the ore-bearing intrusions were produced by high magnesian basaltic magma (up to 8 wt.% MgO), which crystallized *Ol* and *Pl* phenocrysts at depth. The parental magma also shows geochemical signatures of crust (negative Ta-Nb and positive Pb anomalies). It contains 0.5-0.7 wt.% $H_2O$, trace $CO_2$ and up to 0.2 wt.% Cl.

It was suggested that heavy sulfur isotopic composition of the sulfide ores (up to 18‰, Grinenko, 1985), which is atypical of magmatic deposits, has been contributed to the assimilation of sulfate-bearing country rocks by the magma. Our new data of sulfur isotopes for the anhydrite are inconsistent with the hypothesis that anhydrite from the country rocks was an external sulfur source for the Noril‘sk ores. Sulfur isotopic compositions of basalts and some intrusions in the Taimyr Peninsula may be used to address this issue. The highest $\delta^{34}S$ values among all formations were found in the primitive rocks from Gudchikhinsky picrites ($\delta^{34}S$=8.6 ‰; Ripley et al., 2003) and Dyumtaleysky ($\delta^{34}S$=12.2‰) gabbro. These data support the hypothesis of Likhachev (2006) that the heavy S isotopic composition of the Noril’sk ores is a mantle characteristics, which could have resulted from recycling of biogenic sulfides by subduction.

The following conclusions are outlined below.

1. The volcanic rocks of the Norilsk region formed by two episodes (rifting and trap) which can be further divided into four cycles.

2. The ore-bearing intrusions are not comagmatic with the tuff-lava sequence; they formed by separate magmatic activity during the development of the trap.

3. The intrusions formed by high-Mg tholeiitic magma.

4. The fluids-associated with trap magmatism were dominated by $H_2O$-$CO_2$, the parental magmas of both ore-bearing and ore-barren intrusions contained similarly low $H_2O$, $CO_2$ and F.

5. Assimilation processes did not play a major role in the formation of the ore deposits.

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# Nd-Sr-Hf-Cu-S ISOTOPE SYSTEMATICS OF ORE-BEARING ULTRAMAFIC-MAFIC INTRUSIONS FROM POLAR SIBERIA (RUSSIA): GENETIC CONSTRAINTS AND IMPLICATIONS FOR EXPLORATION

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**ABSTRACT**. The study evaluates the usefulness of Nd-Sr-Hf-Cu-S isotope information, providing insights into origin of mafic-ultramafic intrusions and associated Ni-Cu-PGE sulfide ores of the Polar Siberia. New indicators for the economic potential of Ni-Cu-PGE sulfide deposits are suggested.

It is commonly assumed that ultramafic-mafic intrusions and associated PGE-Cu-Ni sulfide deposits of Northern Siberia represent a small component of a major episode of mafic activity at ~250 Ma, which included formation of the most extensive flood-basalt province on Earth (Campbell et al., 1992). Recent studies, however, advocated protracted evolution of the ore-forming magmas parent to the Noril'sk-type intrusions (e.g., Malitch et al., 2010; 2012). Mafic-ultramafic intrusions and Ni-Cu-PGE (platinum-group elements) sulfide deposits in the Noril'sk-Talnakh region (Russia) are considered to be closely linked, indicating that primitive mantle-derived materials are intrinsic to their petrogenesis (Tuganova, 2000; Arndt et al., 2005; Malitch et al., 2013 among others).

This study assesses Hf-Nd-Sr-Cu-S isotope data for the same suite of lithologies and associated PGE-Cu-Ni sulfide ores from 12 ultramafic-mafic intrusions of the Noril'sk province and two ultramafic-mafic intrusions (i.e., Binyuda and Dyumptalei) of the Taimyr province. Intrusions of the Noril'sk Province were subdivided into three main types in terms of sulfide mineralization style and economic significance.

Type 1 comprises the economic ore-bearing intrusion that hosts commercial reserves, including the Noril'sk-1, Talnakh and Kharaelakh intrusions, which contain well-defined horizons of plagioclase-bearing dunite and wehrlite with elevated contents of Cr and taxitic-textured rock assemblage and host disseminated, veined and massive ores. In the upper part of these intrusions a PGE-rich low-sulfide horizon is hosted by leucogabbro with lenses of ultramafic rocks. Rocks of these intrusions have "radiogenic" initial Sr ratios ($^{87}Sr/^{86}Sr_i$ = 0.7055–0.7075) against rather constant εNd values of ~ +1. Zircons from economic intrusions with U-Pb ages between ca. 230-340 Ma yielded $\varepsilon Hf_{(t)}$ values in the range from 2.3 to 16.3 (n=24) at Kharaelakh, from 0.1 to 16.2 (n=76) at Talnakh and from -4.7 to +15.5 (n=54) at Noril'sk-1, consistent with a model that involves interaction of distinct magma sources (Malitch et al., 2010; 2013; this study).

Type 2 comprises sub-economic intrusions that host non-commercial reserves, including the Chernogorsk, Zub-Marksheider, Vologochan, Yuzhnoe Pyasino and Imangda intrusions. Rocks of the sub-economic intrusions have lithology, mineralogy, geochemistry and Nd-Sr-Hf isotope systematics broadly similar to that of the economic intrusions. The sub-economic intrusions, however, have disseminated or more rarely vein-disseminated sulfide ores and may contain small- to medium-sized Ni-Cu sulfide deposits, and medium- to large-sized PGE deposits.

Type 3 comprises weakly mineralized mafic-ultramafic intrusions, the so-called Lower Talnakh type, as represented by the Nizhny Talnakh, Nizhny Noril'sk and Zelyonaya Griva intrusions. They contain low-grade disseminated Cu–Ni ores with ~0.2 wt.% of Cu and Ni, and low Cr and PGE (~0.005 ppm, rarely up to 0.02 ppm). Rocks from the Nizhny Talnakh, Nizhny Noril'sk and Zelyonaya Griva intrusions have more radiogenic initial Sr values ($^{87}Sr/^{86}Sr_i$=0.7076–0.7086), average εNd values of ca. -5 and εHf values of ~0.

Samples from the different intrusions in the Noril'sk Province have overall $\delta^{65}$Cu values ranging from -2.3‰ to 1.0‰ and $\delta^{34}$S values from -0.7‰ to 13.8‰ (Fig. 1). Samples from the three economic deposits have distinct mean $\delta^{65}$Cu values of -1.56±0.27‰ for Kharaelakh, -0.55±0.41‰ for Talnakh and 0.23±0.28‰ for Noril'sk-1, consistent with those for carbonaceous chondrite and iron meteorites. The variation of $\delta^{65}$Cu values is interpreted to represent a primary feature of the ores, although assimilation of external source at Kharaelakh cannot be ruled out. Sulfide ores from the three economic intrusions have distinct but restricted ranges of $\delta^{34}$S values with a mean of 12.7±0.5‰ for Kharaelakh, 10.9±0.6‰ for Talnakh and 9.2±1.8‰ for Noril'sk-1. The ores of the subeconomic Chernogorsk intrusion have homogenous $\delta^{34}$S values of 10.9±0.4‰, in contrast to the highly variable S isotopic compositions for those in the Vologochan, Yuzhnoe Pyasino and Zub-Marksheider intrusions (from 5.1‰ to 8.5‰, from 8.1‰ to 10.5‰, from -0.7‰ to 3.9‰, respectively) and sulfide accumulations from the non-economic intrusions (1.8–9.7‰). Given the Zub-Marksheider and Kharaelakh intrusions are located at the same stratigraphic level, their contrasting S isotopic compositions indicate that the immediate country rocks have little impact on the S isotopic composition of sulfide ores of the intrusions, whereas the interaction of magma with host rocks that took place deeper before final emplacement might be the major control (Malitch et al., 2014).

The observed wide range of εHf and $^{87}$Sr/$^{86}$Sr$_i$ values combined with a restricted range of εNd values, and the negative correlation of S and Cu isotope compositions along with a restricted range of $\delta^{34}$S and $\delta^{65}$Cu values for an individual intrusion are considered to be useful indicators of the potential for hosting Ni-Cu-PGE sulfide deposits.

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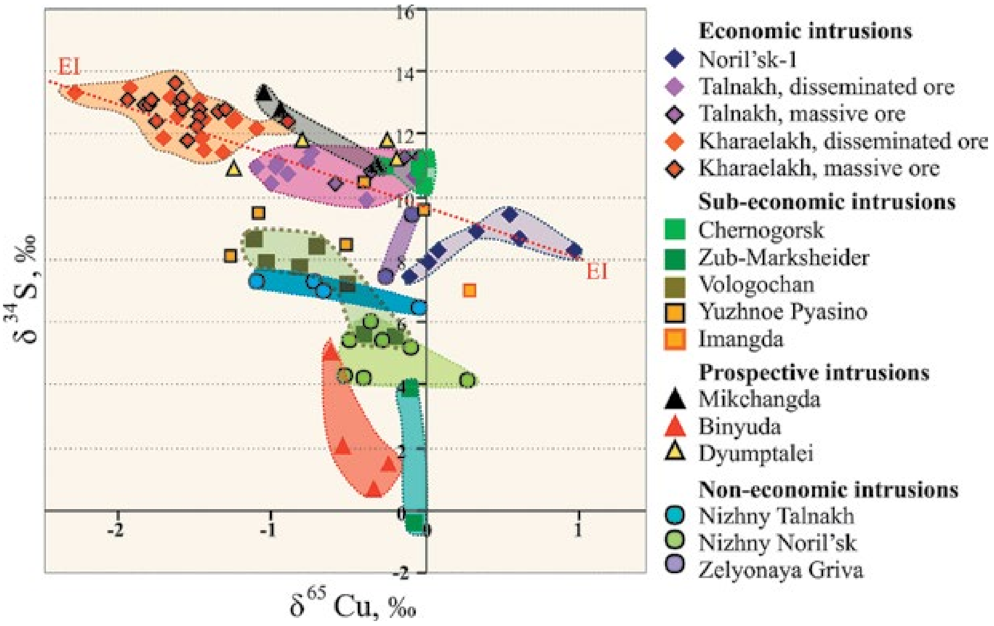

*Fig. 1.* $^{34}$S-$^{65}$Cu systematics of Cu-Ni sulfide ores from economic, subeconomic, prospective and non-economic intrusions of the Noril'sk and Taimyr provinces

# THREE TYPES OF APATITE FROM THE NORIL'SK SULFIDE ORES

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**ABSTRACT**. Apatite is a common mineral in the Noril'sk sulfide ores. It occurs as short to long prismatic crystals associated with the sulfide assemblages of Mss and Iss. Apatite-(CaCl) of the first generation (I) is most widespread. It is abundant in the pneumatholitic alteration aureoles above the sulfide droplets surrounded by Ti-biotite, kaersutite, Cl-bearing hastingsite and edenite. Apatite of the second generation (II) is commonly present as overgrowth on apatite I. The composition of apatite II varies from apatite-(CaClF) to apatite-(CaF). The apatite with high fluorine content commonly occurs solitarily as short prismatic crystal. In the epigenetic metamorphic-hydrothermal mineralization zones apatite I and II are partially or completely replaced by apatite-(CaOH) (III).

Apatite is considered to be an important collector of F and Cl in igneous rocks. Both F and Cl are important in the formation of PGM. Both apatite-(CaCl) and apatite-(CaFCl) are observed in the PGM-rich horizons in large layered mafic-ultramafic intrusions in the world such as the Bushveld and Stillwater complexes (Boudreau & McCallum, 1992; Mathez et al., 1985; Meurer & Boudreau, 1996).

Apatite-(CaF) in the Noril'sk sulfide ores was first described by Genkin & Vasil'eva (1961). We have found that apatite is common in the olivine-rich intrusive rocks and troctolites that contain magmatic sulfide droplets with diameter up to 50 mm in the Skalisty and Mayak (Talnakh intrusion) and Oktaybr'sky (Kharaelakh intrusion) mines. The sulfide droplets are composed of sulfide minerals formed by the breakdown of Mss and Iss. Pneumatholitic alteration aureoles up to 12 mm in thickness are present above the sulfide droplets. The alteration aureoles are composed of Ti-bearing biotite, apatite-(CaCl), apatite-(CaClF), anhydrite, Cl-bearing hastingsite, kaersutite, edenite and Cl-bearing alkaline sulfides such as djerfisherite and bartonite (Godlevsky 1959; Spiridonov 2010).

Micro-grains of PGM are also present in the alteration aureoles (Spiridonov, 2010). Apatite-(CaCl) and apatite-(CaClF) are associated with interstitial sulfides (Fig. 1) and sulfide droplets. The apatite grains occur as large pristmatic crystals with lengths up to 4 mm (Fig. 2). The apatite of the first generation (Fig. 3) contains high Cl and up to 2 wt.% total REE. Apatite II, which occurs most commonly as overgrowth on apatite I, has variable compositions from apatite-(CaFCl) to apatite-(CaF) (Fig. 3). The F-rich apatite occurs as short prismatic crystal solitarily. Apatite II contains up to 0.5 wt.% total REE.

The compositions of apatite I and II from the Noril'sk sulfide ores indicate that in the initial fluids derived from highly fractionated sulfide melts were enriched in chlorine. With time the fluids became enriched in fluorine instead.

In the epigenetic metamorphic-hydrothermal mineralization zones apatites I and II have been partially or completely replaced by apatite-(CaOH) (Fig. 4). The hydroxylapatite is present together with prehnite, pumpellyite, chlorite and others low-temperature silicate minerals. Fluorine was completely lost immediately during the replacement. In contrast, chlorine was leached out gradually.

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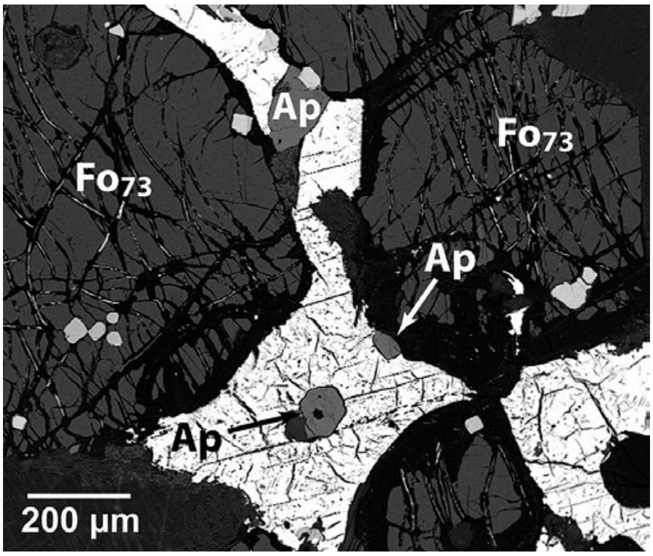

*Fig. 1.* Crystals of apatite-(CaCl) in the interstitial sulfides. BSE image

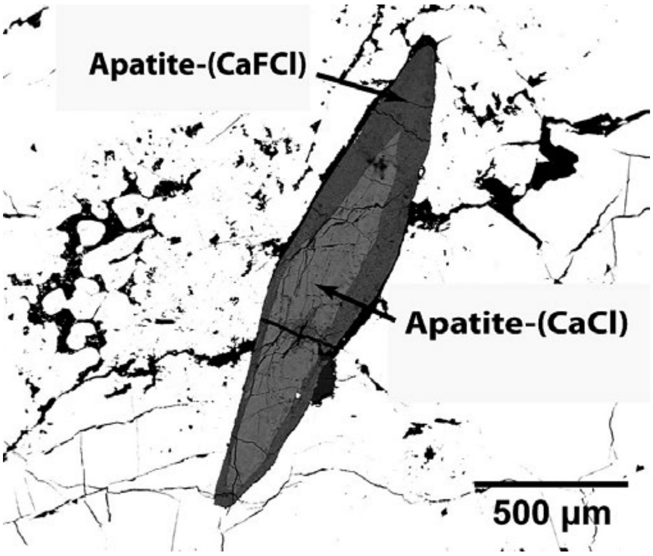

*Fig. 2.* Zoned crystal of apatite-(CaCl) (core) – apatite-(CaFCl) (rim) in the sulfide droplet. BSE image

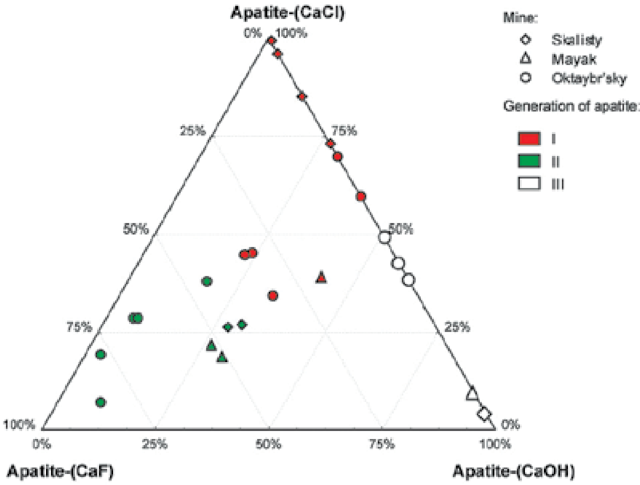

*Fig. 3.* Composition of apatite from sulfide ores of the Kharaelakh and Talnakh intrusions.

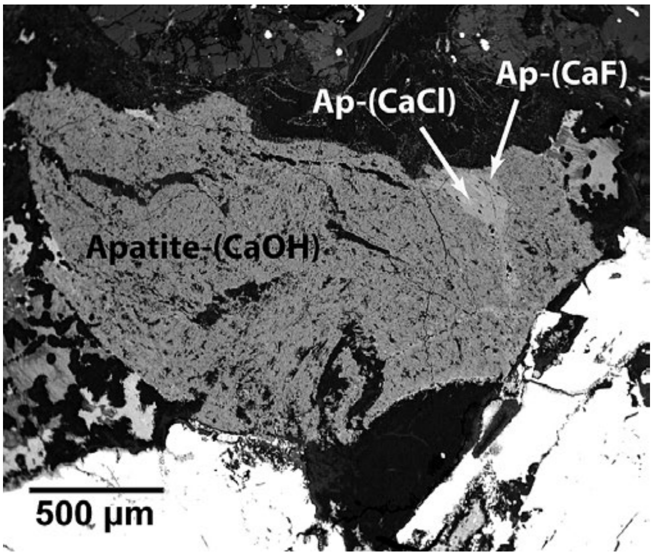

*Fig. 4.* Crystal of apatite-(CaOH) with relict of apatite-(CaCl) (white) and apatite-(CaF) (light grey), located above the sulfide droplet. BSE image

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# GEOLOGICAL AND ISOTOPE-GEOCHEMICAL CHARACTERISTICS OF PREDICTION AND SEARCH METHOD FOR THE PGE-BEARING MAFIC-ULTRAMAFIC LAYERED INTRUSIONS OF THE EAST-SCANDINAVIAN LIP

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**ABSTRACT**. For the East-Scandinavian Large Igneous Province (LIP), the indicators for important mineralization (low-sulfide Pt-Pd) in the Early Proterozoic mafic-ultramafic layered intrusions of the plume origin have been evaluated (Bayanova et al., 2009; Mitrofanov et al., 2013). These criteria are useful for predicting the occurrence of low-sulfide Pt-Pd mineralization in the mafic-ultramafic layered intrusions and the potential at the beginning of geological survey. The selected criteria reflect a combination of geological, geodynamic and geochemical factors that control the sizes and metal tenors of the low-sulfide (Pt-Pd) economic deposits. These methods are useful for regional exploration target selection and for regional resource evaluation of PGE and base metals.

The proposed criteria (Table 1) are for the prediction and exploration of low-sulfide Pt-Pd ore deposits in the mafic-ultramafic layered intrusions in the East-Scandinavian LIP. They can be used to identify areas that have potential for low-sulfide Pt-Pd mineralization in the layered maifc-ultramafic intrusions in the Archaean crystalline shields during the early stages of regional geological studies. The method is developed based on the geological characteristics of the mafic-ultramafic intrusions with variable degrees of PGE and base metal mineralization (Mitrofanov et al., 2013).

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Table 1

**Prediction and exploration indicators for low-sulfide Pt-Pd (with Ni, Cu, Au, Co and Rh) mineralization in mafic-ultramafic intrusions**

| *№* | *Search indicator* | *Parameters* |
|---|---|---|
| 1 | Geophysics | Presence of granulite-mafic (anorthosite) layer with crust-mantle characteristics (Vp = 7.7-7.1 km/s) due to plume-derived magma underplating (composition of the layer is defined on the basis of deep crustal xenoliths in the volcanic pipes) detected by the deep geophysical methods in the base of the crust. |
| 2 | Structure | Regional: distribution of a discordant rift-related volcano-sedimentary strata, dikes, and polyphase layered mafic intrusions over a vast area of Archaean basement. Local: ore bodies occur in the lower intrusive contacts, extended reefs, pegmatoid zones of mafic rocks, veins and offset. |
| 3 | Geodynamic setting | Large-scale, protracted, and multiple episodes of deep mantle plume or asthenosphere upwelling, the vast non-subduction-type basaltic magma in an intraplate continental setting (LIP's).<br>Change of Archean orogenic regime to intracontinental rifting (with origination of variously oriented ensialic belts). Ore-controlling mafic-ultramafic intrusions formed at an initial (pre-rift) stage of continental rifting. |
| 4 | Composition | Siliceous high-Mg (boninite-like) and anorthositic magmas. Cyclic (regular polystage style) structure of the layered intrusions and abrupt change of cumulus lithology and lithogeochemistry. There are two to five and more megacycles in the majority of the Palaeoproterozoic layered intrusions. The megacycles represent regularly layered series from ultramafic varieties to gabbro. The ore is confined to the most contrasting series of alternating thin rock layers with different compositions from leuco- and mesocratic gabbro to norite, anorthosite, plagiopyroxenite, and with different textures from leucocratic (leucogabbro, anorthosite, "spotted" gabbro), inequigranular to coarse-grained and pegmatoidic. All known stratiform reef-type deposits are confined to the borders of the megacycles, which mainly reflects the interaction between high-Cr magma with low-Cr one. Intense interaction with deeply derived reducing fluids resulted in the enrichment of volatiles such as C, F, Cl and $H_2O$ in the rock. Mineralogical factors: PGMs in disseminated sulfide mineralization, anomalously high concentrations of PGEs in the bulk sulfides, inferred platinum distribution coefficient between silicate and sulfide melts of >100000. |
| 5 | Isotope geochemistry | Deep mantle magma source enriched in ore components (fertile source) and lithophile elements. It is reflected in the isotope indicators such as εNd(T) from -1 to -3, $I_{Sr}(^{87}Sr/^{86}Sr)$ from 0.702 to 0.704, $^{3}He/^{4}He = (10^{-5}-10^{-6})$. Magma and ore sources differ from those of Mid-Ocean Ridge basalts, subduction-related magma but are similar to EM-I. |
| 6 | Geochronology | Intraplate mafic LIP with low-sulfide Pt-Pd mineralization (the East Scandinavian Province in the Fennoscandian (or Baltic) shield, the East Sayany Province in the Siberian Platform, the Huronian Province in the Canadian shield) formed at the very beginning of supercontinent break-up, mostly between Archean and Proterozoic, or at 2.6-2.4 Ga. For the East-Scandinavian province, it was the Sumi – Early Sariola epoch, or 2.53-2.40 Ga. Ore-bearing mafic complexes formed during a long period of time and by different episodes (2490±10 Ma; 2470±10 Ma; 2450±10 Ma; 2400±10 Ma), and by mixing between the boninitic an anorthositic magmas. |
| 7 | Metamorphism | Known economic ore deposits occur in the regionally unmetamorphosed rocks. Only Pt-Pd ore prospects are found in the regionally metamorphosed layered mafic complexes. There is evidence that amphibolite-facies metamorphism lead to metal decrease in the deposits. |

# THE ROLE OF HYDROCARBONS IN THE FORMATION OF THE PGE DEPOSITS IN THE SIBERIAN TRAPS

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**ABSTRACT**. A genetic model for the formation of the PGE deposits in the Siberian traps is presented. According to this model, PGEs are extracted from basaltic melt by hydrocarbon fluids, transferred by the fluids and accumulated at the geochemical barriers.

Three major types of Pt deposits are associated with mafic intrusions in the Siberian traps: PGE-Cu-Ni-sulfide, Pt-low-sulfide and native iron (-platinum) deposits. The PGE-Cu-Ni-sulfide deposits are represented by the Norilsk-type deposits. Disseminated sulfides in gabbro dolerites and massive ores in this type of deposits are confined to the base of the layered intrusions. The major ore minerals are pyrrhotite, chalcopyrite, pentlandite, cubanite and magnetite. PGEs in ores are mainly present as solid solutions in the sulfides, and to a lesser degree as platinum-group minerals (PGM) of varying compositions. Graphite and carboniferous phases are abundant in the mineralized rocks and massive ores. Rare tungsten carbide and palladium germanate are also present.

The Pt-low sulfide deposits are hosted in taxitic gabbrodolerites in the upper endocontact zones of the Norilsk-type intrusions. Pt-chromite (Cr-Sp up to 20-80%) and Pt-chromite free (Mg-Fe-Sp up to 7%) varieties of the Pt-low-sulfide ores are found in these zones (Ryabov et al., 2014).

The total amounts of sulfides in this type of ores are less than 3-7%. The content of $Cr_2O_3$ in the rocks is as high as 10 kg/t. The chromespinelides are mainly magnoalumochromites ($Cr_2O_3$ 26-43 wt.%). This type of ores is commonly accompanied by the Pt-skarn low sulfide ores in the Talnakh ore cluster. The skarns are characterized by a unique Cr-mineral assemblage: chromite ($Cr_2O_3$ 69.6-72 wt.%)+chrome-diopside ($Cr_2O_3$ 3.9 wt.%, $Al_2O_3$ 2.0 wt.%)+chromefassaite ($Cr_2O_3$ 5.2 wt.%, $Al_2O_3$ 7.5 wt.%)+uvarovite ($Cr_2O_3$ 19.4 wt.%). In this type of ores PGMs account for most of the PGEs, whereas the rest are accounted for PGE solid solutions in sulfides (Sluzhenkin et al., 1994). The ores contain graphite which occurs as globules containing micro- and nanotubes, graphenes and other structurized carbon forms in leucogabbro, and as inclusions in uvarovite crystals in the skarns (Ryabov et al., 2012).

Native iron (-platinum) deposits in the Dzhaltul-Yuzhnyi, Ozernaya Mount and Khungtukun intrusions have been studied in details (Oleinikov et al., 1985; Ryabov & Lapkovsky, 2010). The ores occur as native iron noddles hosted in olivine-bearing gabbrodolerites. The major ore minerals include native iron with varying Ni and Co contents (ferrite, kamacite, less frequently taenite, awaruite, wairauite), cohenite, native copper and graphite. Troilite, hercynite and muassanite are minor. The ores also contain rare cubical graphite, micro- and nano-structurized carbon forms, carboniferous phases and anthraxolite. The PGEs in the form of solid solutions are hosted in Ni-Fe alloys, arsenides, antimonides and stannides. PGMs are rare.

A common feature for all of the PGE deposits in the Siberian traps is the common occurrence of graphite, micro- and nanostructured carbon (microtubes, graphenes), carboniferous phases, bitumens and Fe, Si, W-carbides in the ores. The $\delta^{13}C_{(PDB)}$ of organic carbon in the gabbrodolerites and ores ranges from -10‰ to -35‰ (maximum value is -24‰) (Fig. 1). The following correlations are observed in the ores:

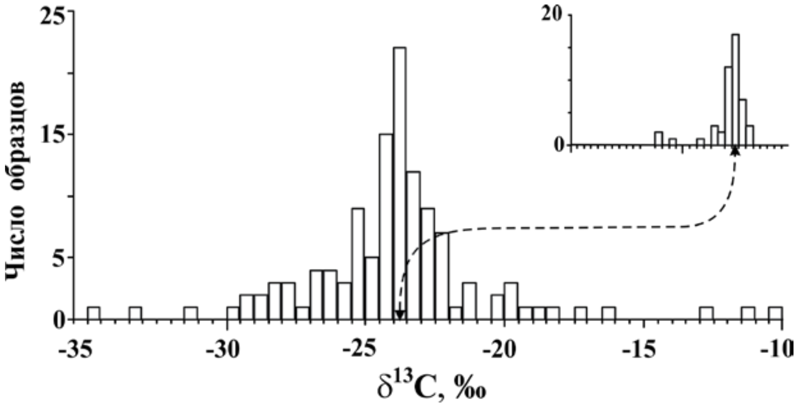

*Fig. 1.* Histograms of $\delta^{13}C$ distribution in rocks and ores of the PGE deposits of the the Siberian Platform (n=116). The inset shows the carbon isotope composition in coal and graphite beds of the $C_3$-$P_2$ age (n= 43)

(1) PGE – $\delta^{13}C_{(PDB)}$ (Ryabov et al., 2010);
(2) base- precious metals.

However, base- and precious metal contents in the ores are not controlled by the amounts of sulfides and native iron.

We suggest that the main source of the carbon in the ores was coal hydrocarbons derived from the sedimentary country rocks of the ore-bearing intrusions. This interpretation is supported by the presence of Ge in the ores (Ge is a typomorphic element for coals) as well as the correlation between (Cu+Ni+Co) and Ge, and between (Pt+Pd+Rh) and Ge (Ryabov & Lapkovsky, 2010). Moreover, a $Pd_2Ge$-phase was found in the PGE-Cu-Ni-sulfide ores (Kozyrev et al., 2002), and $Ni_2Ge$ and $(Ni,Pd)_2Ge$ phases were found in the native iron (-platinum) ores (Ryabov & Agafonov, 2013).

These results allow us to propose a genetic model which can be used for prospecting and exploration of the PGE deposits in the Siberian traps. The main conclusions are summarized below. The source of ore-forming metals was tholeiitic magma. Hydrocarbons from coals and bituminous carbonate country rocks were also involved. The hydrocarbon fluids extracted metals from the basaltic magma and transported them as metal-organic compounds. The change in physico-chemical parameters of the fluid-magmatic system led to dissociation of these compounds, the formation of PGMs, C- and Ge-bearing phases, and the accumulation of base and precious metals as solid solutions in sulfides and native iron which served as PGE collectors.

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# PGE DISTRIBUTION AND MODES OF OCCURRENCE IN VEINLET-DISSEMINATED AND BRECCIA-LIKE ORES IN CONTACT-METAMORPHIC AND METASOMATIC ROCKS IN THE NORIL'SK REGION

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**ABSTRACT**. Concentrations and modes of occurrence of noble metals depend on mineral composition of veinlet-disseminated and breccia-like ores. In pyrrhotite ores with low noble metal contents Pt and Au form discrete minerals, whereas Pd, IPGE and Ag mainly occur in structures of sulfides and to a lesser extent as discrete minerals. Minerals of noble metals predominate in chalcopyrite ore.

Veinlet-disseminated ores in contact-metamorphic and metasomatic rocks after terrigenous rocks of the Tungusska Supergroup and Devonian carbonate-sulfate-terrigenous rocks occur mainly at the lower and to a lesser extent at the upper exocontacts of the intrusions that host the Talnakh and Oktyabr'sk deposits. The host rocks for this type of ores in the lower exocontact of the Norilsk-1 intrusion are metasomatites after the Tungusska sedimentary tocks and late-Permian basalts.

The sulfide assemblages of these ores are pyrrhotite, chalcopyrite-pyrrhotite, pyrrhotite-chalcopyrite, pentlandite-chalcopyrite, millerite±pyrite-chalcopyrite and millerite-bornite-chalcopyrite. Cubanite-chalcopyrite assemblage is spatially closely related to massive Cu-rich mineralization and shows the zonal distribution from pyrrhotite-rich to chalcopyrite-rich varieties with millerite, bornite and pyrite. The zonation occurs in the contacts of the intrusions and massive sulfide body with country rocks. Primary sulfides are commonly replaced by secondary sulfides and silicates.

The noble metal contents in the ores are highly variable, showing good correlation with total sulfide content and Cu abundance for the samples with Ni/Cu <0.2. The total abundances of platinum group elements (PGE) vary between 3-10 ppm for the pyrrhotite ores and between 7 and 14.5 ppm for the chalcopyrite ores, and reach 19 ppm in the cubanite-chalcopyrite ores. The ratios of PGE (ppm)/S(wt. %) are from 0.1 to 1.1 for the pyrrhotite ores and from 1.7 to 4.8 for the chalcopyrite ores that have (Pt+Pd)/(Rh+Ir+Ru+Os) ratios ranging between 20 and 60.

Platinum forms discrete minerals, mainly as Pt-Fe alloys. Palladium occurs as solid solution in pentlandite. Rh, Ir, Ru and Os occur as solid solution in pyrrhotite and pentlandite. The discrete minerals are most abundant in the chalcopyrite ores. The major Pt mineral in the pyrrhotite-chalcopyrite ores is sperrylite. The Pd minerals are dominated by Pd and Pd-Ni arsenides, stannoarsenides and stibioarsenides such as menshikovite, phases with chemical compositions of $Pd_5As_2$, $Pd_2(SnAs)$, $(Pd,Ni)_2(As,Sb)$ and kotulskite. Pt-Pd-Ni sulfides (cooperite, braggite, vysotskite) and Pt-Fe alloys become predominant in the pentlandite-chalcopyrite, millerite±pyrite-chalcopyrite, millerite-bornite-chalcopyrite ores. Palladium, Pd-Ag and Pt tellurides and bismutides (kotulskite, sobolevskite, telargpalite, sopcheite, moncheite and minerals with the compositions of $(Pd,Ag)_5BiS_2$, $Ag_2PdS$) and Pd stibnides (mertiite-II, stibiopalladinite and laflammeite) are rare.

Breccia-like ores occur in the western flank of the Kharaelakh intrusion (the Oktyabr'sk deposit) where the intrusion splits into a series of apophyses surrounded by contact-metamorphised and metasomatised Devonian sulfate-carbonate sedimentary rocks. The apophyses formed by multiple injections of magmas containing different amounts of phenocrysts. The sulfide assemblages of the breccia-like ores are dominated by chalcopyrite, pyrrhotite-chalcopyrite and chalcopyrite. Secondary alteration in the breccia-like ores is less significant than that in the veinlet-disseminated type of ores.

The total PGE grades of the pyrrhitite ores varies from 3 to 4.5 ppm. The lowest PGE grade of the chalcopyrite ores is as high as 20 ppm. The total grades of the average ores are from 36 to 40 ppm. The highest grade ores contain 50-90 ppm total PGE. The bonanza millerite-chalcopyrite ores contain up to 350 ppm total PGE. These values are similar to those reported for the massive talnakhite and mooihoekite ores. However, the total PGE tenor (recalculated to 100% sulphide) of the millerite-chalcopyrite ore are higher. The PGE(ppm)/S (wt. %) ratios for this type of ores vary between 2 and 62.

The in-situ micro-PIXE measurements of PGE concentrations in sulfides show that pyrrhotite is the major carrier for Rh (0.07 ppm). The average Pd and Rh contents in pentlandite are 160- 170 ppm and 0.05-0.07 ppm, respectively.

The predominant proportion of Pt in the breccia-like pyrrhotite-rich ores occurs as discrete minerals (cooperite, sperrylite and Pt-Fe alloys). Pd in this type of ores occurs in the pentlandite structure and as discrete minerals (atokite, bismuthtellurides and stibiostannides). The Pt minerals in the chalcopyrite-rich ores include cooperite, braggite, Pt-Fe alloys, insizwaite, geversite, sperrylite, moncheite, stumpflite. Less than 30% of total Pd is hosted in pentlandite. The rest of Pd is accounted for by other minerals such as bismuthides and tellurides (sobolevskite, kotulskite, merenskyite), antimonides (stibiopalladinite and sudburyite), and rare sulfides (vysotskite).

It is suggested that the veinlet-disseminated and breccia-like ores formed by infiltration of fluid-rich sulfide melt in crystalline contact-metamorphic and metasomatic rocks. On cooling the hydrothermal fluids separated from these melts produced the chalcopyrite-rich mineralization with pyrite, millerite and bornite. Most of the discrete PGE minerals formed at the hydrothermal stage. The changes in the modes of occurrence of PGE minerals were controlled by the physical-chemical conditions of the fluids which in turn control the stability of hydrosulfide and by chloride complexes that bounded with the noble metals in the fluids.

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# NORIL'SK ORE FIELD: EUTECTIC PBSS–ISS SULFIDE VEINS WITH UNUASAL PGE ABUANDANCES AND PGM ASSEMBLAGES

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**ABSTRACT**. The unusually high contents of Pd (up to 5296 ppm), Pt (up to 6119 ppm), Ag (up to 4125 ppm), and Au (up to 88 ppm) in late sulfide veins that are composed of eutectic PbSss–Iss intergrowths (products of crystallization of low-temperature Fe-Cu-Pb-S melts) have been examined. The pneumatolytic noble-metal minerals formed at <490°C under highly reducedconditions with extremely low $fS_2$. The Pb isotope compositions of the intrusive rocks, ores, PbSss, and Pd intermetallides from the Noril'sk and Talnakh ore clusters vary significantly; Pb of the Talnakh cluster is more radiogenic than that of the Noril'sk cluster. These data indicate that there are genetic relations between sulfide ores, associated intrusions and the magma chambers beneath them in the Noril'sk and Talnakh clusters, i.e., higher degrees of crustal contamination for the parental magmas of the Talnakh cluster relative to the Noril'sk cluster. This may explain the different amounts of metal accumulation in these two ore clusters.

The Noril'sk ore field is located at the NW corner of the old East-Siberian platform, in the zone of edge dislocations. Intrusions and dykes of $P_2$-$T_1$ ages in the trap are accompanied by flood basalts of up to 4 km in thickness. The zircon U-Pb age of magmatism in the trap (flood basalts, leucogabbro, and magmatic sulfide Ni-Cu ores) is 251 ± 1-3 Ma. Magmatic Ag-Au-Pt-Pd-Co-Ni-Cu sulfide deposits are associated with the Noril'sk, Talnakh and Kharaelakh mafic intrusions. Some ore-bearing intrusions cross-cut the folded flood basalts. The trough-shaped intrusions with frame-shaped branches occur with dipping angles of 4-10° within the Noril'sk and Kharaelakh brachysynclines. They are 0.5-2 km wide, 0.1-0.3 km thick and > 20 km long. As indicated by Pb isotopic data, all of the intrusions in the trap have the same mantle source. The intrusive rocks are all enriched in K, REE and other geochemical characteristics that are consistent with crustal contamination (Naldrett & Ligthfoot, 1992; Naldrett, 2005).

The Pb sotope compositions of the ore-bearing intrusions and magmatic sulfide ores differ significantly between the Noril'sk and Talnakh ore clusters: the latter is characterized by much more radiogenic Pb. The Pb isotope compositions of the Talnakh magmatic PbSss and pneumatolytic galena and altaite vary slightly. The Pb isotope compositions of the PGM-bearing assemblages from the Talnakh ore cluster are almost the same. The Pb isotope compositions of the PGM-bearing assemblages from the Noril'sk and Talnakh ore clusters differs significantly: $^{207}Pb/^{206}Pb$–$^{206}Pb/^{204}Pb$ for PbSss (Kharaelakh), 0.85466(3)–18.172(2) for PbS (Talnakh-Kharaelakh), 0.85468(2)–18.170(2) for PbTe (Kharaelakh), 0.85467(2)–18.171(2) for plumbopalladinite and polarite (Talnakh), 0.85494(1)–18.171(1) for zvyagintsevite and Pb-atokite (Noril'sk-I), 0.86254(1)–17.984(1) (Spiridonov et al., 2010). These data indicate the genetic relations between sulfide ores and associated intrusions, different mantles sources for the Noril'sk and Talnakh ore clusters, and higher degree of crustal contamination for the Talnakh ore cluster than the Noril'sk cluster, which may explain the different sizes of ore deposits in these two clusters (Spiridonov, 2010).

A substantial portion of the sulfide melts was produced by sulfurization of the intrusive rocks and hornfels involving sulfur dioxide originated by means of reduction of the PZ anhydrite by carbonaceous gases which in turn were produced during contact metamorphism of the carboniferous country rocks beneath the flood basalts (Spiridonov, 2010). That explains the anhydrite-like isotopic compositions of the sulfide ores.

During cooling of the ore-bearing intrusions, most of the sulfide melts were squeezed into the frontal parts of the intrusions. Particularly this affects the fusible Ni-Fe-Cu-S melts. Some massive sulfide ore bodies occur in the lower parts of the ore-bearing intrusions or beneath them**.** The largest Pd deposit in the World is represented by the Kharaelakh massive sulfide ore body

(~3000 x 1000 x 5-75 m) beneath the Kharaelakh intrusion. The crystallization sequence of the sulfide melts are: Mss1 (Tcryst. ~ 1100°C), Mss2, Iss1, Iss2, Iss3, Iss4 and Iss5 (Tcryst. ~ 750°C) with high Cu and low Fe. This is the reason for the development of zonal structure in the sulfide ore bodies from small sulfide drops to giant sulfide bodies. The less-dense crystallization products such as the relatively more easily fusible Fe-Cu melts are concentrated in the roofs of the sulfide bodies. According to M.N. Godlevsky, the Noril'sk ores are the solid solutions "kingdom". The Pd/Pt values are ~3 for the typical sulfide ores.

A unique feature of the Noril'sk ore field is the presence of late-crystallized, easily fusible ($T_{cryst}$. ~ 600-550°C) euvtectic PbSss–Iss ores which are extremely rich in Pd (23-5296, mean 1204 ppm), Pt (5.5-6119, 537.5 ppm), Ag (233-4125, 1217 ppm), Au (0.11-88, 16.7 ppm). This type of ores on average (n=20) contain (in ppm) Rh 3.75, Te 2640, Bi 1271, As 866, Sn 453, Se 412, Sb 101 and Tl 81 (Spiridonov, 2010). The average Pd/Pt ratio is ~2 for the eutectic ores. Based on Pt and Pd grades and tenors, these ores are the richest in the world for magmatic sulfide ores. On cooling PbSss was transformed to galena (matrix) with altaite PbTe lamellas. The galena-chalcopyrite, -mooihoekite, -talnakhite eutectic intergrowths form nests and veins within the massive sulfide ore bodies that are associated with intrusive rocks or hornfels. The thicknesses of these veins are 0.01-0.2, rare up to 1m. Their lengths are up to 15 m. The striking of the veins is predominantly NW–SE. The nests and veins tend to concentrate in the roof of the Main Kharaelakh sulfide body, especially in its central part. This type of mineralization is also present in the other parts of the massive sulfide ore body and in other massive sulfide ore bodies of the Noril'sk and Talnakh ore clusters. The PGM-bearing assemblages form metasomatic ingrowths in the veins and nests of graphic ores and in their exocontacts, usually at a distance of n –n10 cm. Based on the observations by E.A. Kulagov in the 1970s, the sizes of sperrylite aggregates are up to 130 cm (Kharaelakh). Based on the observations by S.N. Belyakov in the 1990s, the maximum size of sperrylite intergrowths in these veins is 25×25×30 cm. The crystal sizes of the intergrowths increase from 2 cm across in the lower part to 2-7 cm and up to 11 cm in the upper part (Kharaelakh). Based on the observations by E.V. Sereda and I.N. Tushentsova, the sizes of paolovite and moncheite crystals are up to 2-5 cm, and the sizes of PGM aggregates are up to 6 cm. The normal, reversal, oscillatory, and complex zoning of gold particles (fineness 880-5, dominant 330-50) is mainly due to variations in Te activity in the fluids.

*Acknowledgments. This work was supported by a grant 13-05-00839 from the RFBR.*

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# FORMATION MECHANISM OF THE NORIL'SK TYPE ORE-BEARING INTRUSIONS

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**ABSTRACT**. Intrusive magmatic ore systems of the Noril'sk ore field are associated with the $P_2$–$T_1$ trap formation in the East Siberian Platform. I evaluate a possible version of formation mechanism for the Noril'sk type ore-bearing intrusions involving the injection of basaltic, picritic magma and immiscible sulfide liquid in a ratio of ~ 100:10:1 and their emplacement in the intrusive main bodies and their peripheries.

The Noril'sk ore field is located at the NW corner of the old East-Siberian platform, in the zone of edge dislocations. The trap formation of the East Siberian Platform is famous due to its magmatic ore systems in the Noril'sk district, which contains ~75% of Pd world resources and 15% of Pt world resources plus a significant portion of Ag and Au resources in Russia. The isotopic age of the trap formation (flood basalts, basic intrusion rocks, and magmatic sulfide Ni-Cu ores) is 251±1-3 Ma (Dalrymple et al., 1991; Campbell et al., 1992; Naldrett, 2005). The deposits are associated with the Noril'sk I, Noril'sk II, Talnakh (Upper Talnakh), and Taimyr (Kharaelakh) intrusions which are composed of olivine gabbro-dolerites, gabbronorite-dolerites, gabbro-anorthosites, picritic gabbro-dolerites, troctolites, and gabbro-dolerites (Godlevsky, 1959; 1968; Stepanov, 1981; Stepanov & Turovtsev, 1988). The ore-bearing intrusions occur as long ribbon- and saddle-like bodies cutting the country rocks at small angles (4-10º). The magmas of Noril'sk intrusions were injected into the Noril'sk brachysyncline from SW (almost from the platform boundary) to NE. The magmas of the Talnakh and Taimyr intrusions were injected into the Kharaelakh brachysyncline from NE (almost from the platform boundary) to SW. Slightly older, gentle-dipping bodies of chromite-bearing leucocratic gabbros and gabbro-dolerites were emplaced along the Noril'sk-Kharaelakh fault zone, filling the lateral parts of gentle-dipping magma-feeding zones (e.g., Stepanov & Turovtsev, 1988). This may explain why the younger ore-bearing intrusions have a narrow ribbon shape and contain leucocratic gabbro xenoliths.

M.N. Godlevsky proposed a complicated genetic model for the Noril'sk type ore-bearing intrusions, which contains many mysteries. Below are some possible solutions for these mysteries.

1. The Noril'sk type ore-bearing intrusions formed under compression. Under this condition foliation and lenticular openings formed in the stratified intrusive bodies according to Euler principle. These openings served as pumps. As a result, syntectonic injection of magma occurred in response to absorption and pressurization. The injection process took place as laminar flow without turbulence except for the marginal zones. The openings of magma passages were facilitated by the migration of superheated gases. The gases caused rapid solidification of the peripheries of the intrusions.

2. The parental magmas of ore-bearing intrusions are not homogeneous. They are composed of three immiscible liquids – (flood) basaltic, picritic and sulfide in a ratio of ~100 : 10 : 1. These three liquids formed coaxial cylindrical bodies in the chamber where the heaviest sulfide liquid occurred in the center, wrapped around by picritic and basaltic magmas outward. The configuration changed during sub-horizontal injection: the basaltic magma was injected into the upper and lower parts of the endocontacts and inside the intrusion, the picritic magma filled around of a central sulfide

stream. Heavy sulfide liquid percolated through the picritic and basaltic bodies during injection due to filter-pressing.

3. One of the striking features of the Noril'sk type intrusions is the presence of two picritic horizons. The lower one is typical for all of the stratified mafic intrusions. The upper one is present above the main gabbro-dolerite zones. The upper picritic horizon only occurs in the sills of leucocratic gabbros which form the roofs of the ore-bearing intrusions. It is deduced that separate picritic magmas were emplaced in numerous sections in the Noril'sk ore-bearing intrusions in the Noril'sk brachysyncline such as the E-17 borehole (Ergalakh), PE-92 borehole (Chibichey) and others. The picritic horizon has sharp upper and lower contacts and constitutes up to 60 % of the sections. The picritic horizon accounts for up to 7 % (in thickness) for some intrusive frontal parts in the Kharaelakh brachysyncline, i.e., the Talnakh and Taimyr ore-bearing intrusions. The picritic horizon is rare in the deeper, northern parts of the intrusions.

4. Dramatic increase in sulfide abundances is not present along the entire length of intrusion, but occurs sporadically matching the oscillation pattern of thickness variation of the picritic horizon. Sulfide droplets are common in the areas where the thicknesses of picrite and massive sulfide bodies increase. In other words, there is direct correlation between sulfide abundance and the thickness of the picritic horizon. Fluid activity and sulfide liquid segregation are independent from each other. There are abundant newly-formed metasomatic minerals such as biotite, apatite and other minerals above of the sulfide bodies. On cooling a significant portion of the sulfide liquid was pressed out of the ore-bearing intrusions. As a result, some of these sulfide veins occur up to 800 metres away from the ore-bearing intrusions, such as those in the north slope of the Rudnaya Mountain located to the north of the Noril'sk-I intrusion.

5. Gravitational settling of the picritic magma caused the opposite migration of the lower taxitic gabbro-dolerites. The lower taxitic gabbro-dolerites and the upper taxitic gabbro-dolerites have similar chemical compositions but different sulfide and chromite abundances, especially for the picritic gabbro-dolerites.

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# SESSION 4

## Models and exploration methods for magmatic Ni–Cu–PGE sulfide and PGE–oxide deposits from around the World

**Conveners: Sarah-Jane Barnes, Marina Yudovskaya & Judith Kinnaird**

The session is intended to cover how magmatic platinum-group element (PGE) deposits form and how to use this information to explore for them. The concentrations of PGE in ore are generally only at the g/tonne level and thus the fact that the rocks are enriched in PGE is not evident in hand specimen. Furthermore most PGE are not readily soluble and thus there is no halo around ore bodies. Therefore exploration for PGE deposits depends heavily on a combination of lithogeochemical sampling and searching for minerals such as Ni-Cu sulfides and oxides (in particular chromite) that are present in many PGE deposits. Consequently how Ni-Cu sulfide and oxide deposits form and why some contain platinum-group elements and some do not is also of interest in studying PGE deposits. Papers describing models for the formation of and exploration techniques for the deposits are welcome.

# THE FIRST REPORT OF PLATINUM-GROUP MINERALS IN THE MOUNT KAKOULIMA IGNEOUS COMPLEX, GUINEA

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**ABSTRACT**. The Kakoulima Igneous Complex (KIC) in Guinea is a mafic-ultramafic complex located at the northeastern end of the Conakry Peninsula, itself interpreted as a dunite dyke. The emplacement of this major intrusion is related to the opening of the Central Atlantic Ocean. The KIC, which intruded Archean basement and Ordovician sandstones, is composed of three units: a dunite unit, passing progressively into a pyroxene-peridotite unit, itself passing into a gabbro unit. The complex is characterized by almost no mineral layering. Disseminated base-metal sulphides occur in all units, but tend to be more abundant at their edges. PGM occur in the disseminated sulphides in pyroxene peridotite and gabbro. With the exception of one laurite included in a chromite crystal, they are attached to, or included in, base-metal sulphides. Their morphology is variable, from very thin laths to subhedral shapes, or more commonly irregular. Some PGM show evidence of secondary alteration.

## GEOLOGY

The Kakoulima Igneous Complex (KIC) is a mafic-ultramafic complex located at the northeastern end of the Conakry Peninsula in Guinea (Barrère, 1959). It is interpreted as 35 by 2 to 5 km dyke composed of dunite with minor wehrlite. The total length of the mafic-ultramafic exposures is about 56 km (Fig. 1). The emplacement of the gabbro unit is dated at 201.4±1.5 Ma. Over the past 20 years, Mount Kakoulima has been explored for Ni-Cu-PGE mineralization. Drilling in a gossan zone revealed a “sub-massive sulphides layer“, 100 x 100 m, 0.8 m thick, and an average content of 3.6% Ni, 1.1% Cu and 2 to 4 ppm PGE (Semafo, 1999). Further exploration work failed to find any significant mineralized zones in the KIC, the geology of which was poorly constrained.

Considering the potential interest of the KIC, we decided to reinvestigate this complex, better to understand its geology and mineralization. Several cross sections led to a better definition of the relationships between the various units, and provided samples for petrological and mineralogical studies. Fig. 2 summarizes the modal composition of the facies encountered in the complex; all characterized by different proportions of olivine, clinopyroxene, orthopyroxene, and plagioclase plus chromite and base-metal sulphides. Adcumulate and orthocumulate are the most common textures. Some wehrlite and gabbro show poikilitic textures. In spite of the lack of evidence of gravity-induced crystal settling, the mineral composition indicates a more pronounced differentiation trend in the gabbro unit (Fig. 2).

## MINERALIZATION

PGM where identified in all investigated BMS-bearing facies with a Tescan FE-SEM and were analysed with a CAMECA-SXFive microprobe. Except for one laurite included in a chromite crystal, all the PGM in the KIC occur attached to, or included, in base-metal sulphides. Their morphology is variable, including very thin laths, subhedral shapes, or more common irregular morphologies. Some PGM show evidence of intergrowth and alteration. Most of the grains are less than 1 µm in size, with a few in the 2–4 µm range; the largest grain (which is a complex PGM association) measures 20 by 5 µm (Fig. 3). The base-metal sulphide assemblage consists (in order of decreasing abundance) of chalcopyrite, pyrrhotite, pentlandite, and rare pyrite and millerite. PGM were found in the first three.

EPMA analyses of the PGM, rather complex due to the small size of the grains and the rare occurrence of multiphase particles, determined paolovite (ideal $Pd_2Sn$), michenerite (PdBiTe), kotulskite (PdTe), moncheite ($PtTe_2$), plumbopalladinite ($Pd_3Pb_2$), and unnamed (Pd,Pb)Te and laurite. (Pt,Pd)-(Bi,Te) minerals are the most abundant, with commom Pt-Pd and Bi-Te solid solution.

## DISCUSSION

In spite of its proximity to the Freetown Complex in Sierra Leone, the KIC presents major differences with this complex of a similar age, and geodynamic environment (early stage of Central Atlantic rifting, resulting in the Central Atlantic

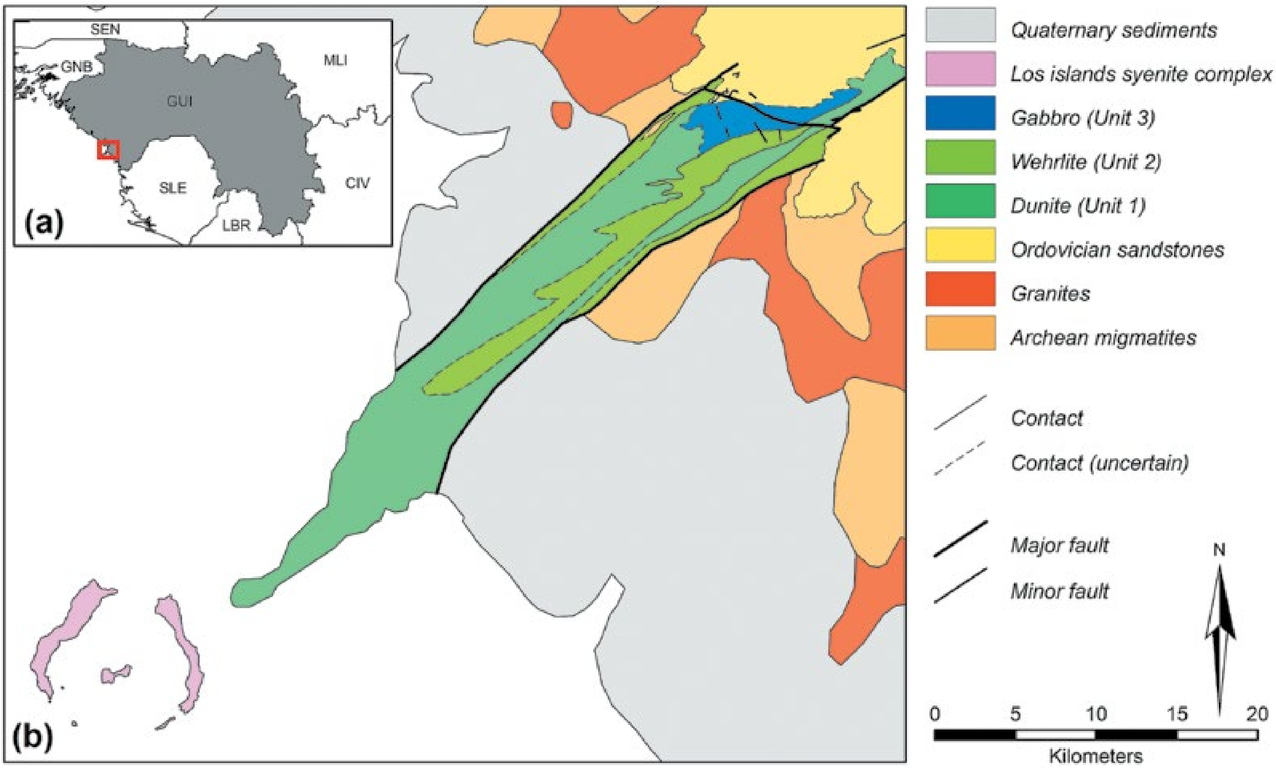

*Fig. 1.* Simplified geological map of the KIC and the Conakry Peninsula

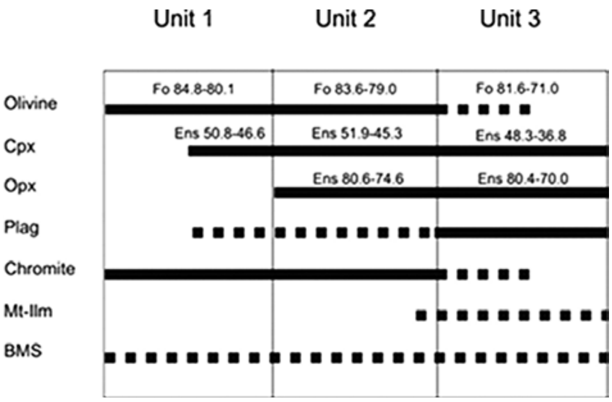

*Fig. 2.* Crystallization sequence of the KIC (not to scale)

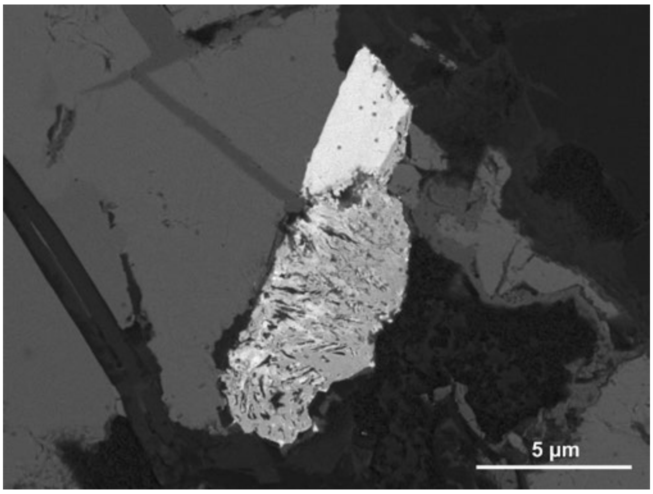

*Fig. 3.* BSE image of a complex association of (Pd,Pt)-(Te,Bi) compositions adjacent to BMS

Magmatic Province). Contrary to the Freetown Complex, where PGM occurrences occur in four stratiform layers, PGM in the KIC do not seem to be related to a specific horizon; this may be due to the lack of mineral stratification in the KIC. Our preliminary work demonstrates the systematic association of PGM with BMS, independently of any new injection of magma pulses in the chamber.

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# PLATINUM-GROUP AND CHALCOPHILE ELEMENTS GEOCHEMISTRY IN SULFIDES OF THE JINCHUAN Ni-Cu SULFIDE DEPOSIT, NW CHINA

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**ABSTRACT**. The distributions of the platinum-group and chalcophile elements of the Jinchuan Ni-Cu deposit have been determined by LA-ICP-MS. The pentlandite hosts large proportions of Co, Ni and Pd, and the pentlandite and pyrrhotite accommodate significant proportions of Re, Os, Ru, Rh, and Ag, whereas, no sulfides concentrates Ir and Pt. These results partly support the model of the fractionation of sulfide liquid. Furthermore, the Ir-bearing PGM crystallized from MSS and depleted the pentlandite and pyrrhotite in Ir, while sperrylite crystallized from intermediate solid solution (ISS) as discrete minerals on cooling. Diffusion of Pd from ISS into pentlandite resulted in enrichments of Pd in the pentlandite, and thus led to decoupling between Pd and Pt in the Jinchuan net-textured and massive ores.

The platinum-group elements (PGE) are hosted not only by platinum group minerals (PGM), but also by base metal sulfide minerals (BMS). Understanding the PGE and chalcophile elements locations and the processes that control their distributions elements are important for constraining petrogenesis of sulfide ores and improving recovery of PGE (e.g., Cabri et al., 2002, 2010). The giant Jinchuan Ni-Cu deposit (Song et al., 2006, 2009; 2012; Chen et al., 2013) is the third largest magmatic Ni deposit following the Noril'sk and Sudbury (Naldrett, 2004). Until recently, the precise location of the PGE and chalcophile elements in the BMS and the magmatic processes that have controlled their distributions in the Jinchuan Ni-Cu deposit are still poorly constrained. In this study, we have measured the concentrations of the PGE, Ag, Co, Re, and As in the Jinchuan BMS minerals using LA-ICP-MS at CODES, University of Tasmania.

Mass balance calculations indicate that pentlandite contains a large proportion of Pd in these ores (~69%, mean value of all samples, Fig, 1a). Pyrrhotite contains ~4.6% Pd. Osmium, Ru and Re are accommodated mainly by pyrrhotite and, to lesser extent, pentlandite (Fig, 1a), even though the latter have higher contents of these elements than the former. A moderate proportion of Rh is present in pentlandite. Pyrrhotite hosts less Rh than pentlandite in all ores. In most samples with one exception, cobalt is hosted mostly by pentlandite, and pyrrhotite. It is surprising that only 1-7% Ir is hosted by BMS for all samples (Fig, 1a), since Ir is expected to have similar geochemical behavior to Os and Ru. Similarly, only a very small portion of Pt (<5%, with one expectation of 32%) present can be accounted for by BMS and it is not preferentially distributed into any mineral (Fig, 1a). In addition, silver is mainly hosted by chalcopyrite, followed by pyrrhotite and pentlandite. The observed large proportions of Co, Re, Os, Ru, and Pd contained in pentlandite and pyrrhotite in Jinchuan are similar to what is observed in the Medvezhiy Creek, Noril'sk (Barnes et al., 2006), whereas the percentages of Ir and Rh are much lower (Fig. 1b). Compared to the Creighton sulfide deposit, Sudbury, BMS minerals in Jinchuan host similar proportions of Os, Ir, Ru, and Pd, but higher proportions of Re, Rh, and Ag (Fig. 1c, Dare et al., 2010).

Based on the experimental partition coefficients, one would expect that pentlandite and pyrrhotite, which represent the breakdown products of MSS, are enriched in IPGE. Indeed, our LA-ICP-MS results reveal that the distribution of the PGE and other chalcophile elements in Jinchuan BMS is mainly controlled by their partitioning behavior during fractionation of sulfide liquid and breakdown of MSS. Cobalt, Re, Os, Ru are concentrated in pyrrhotite and pentlandite

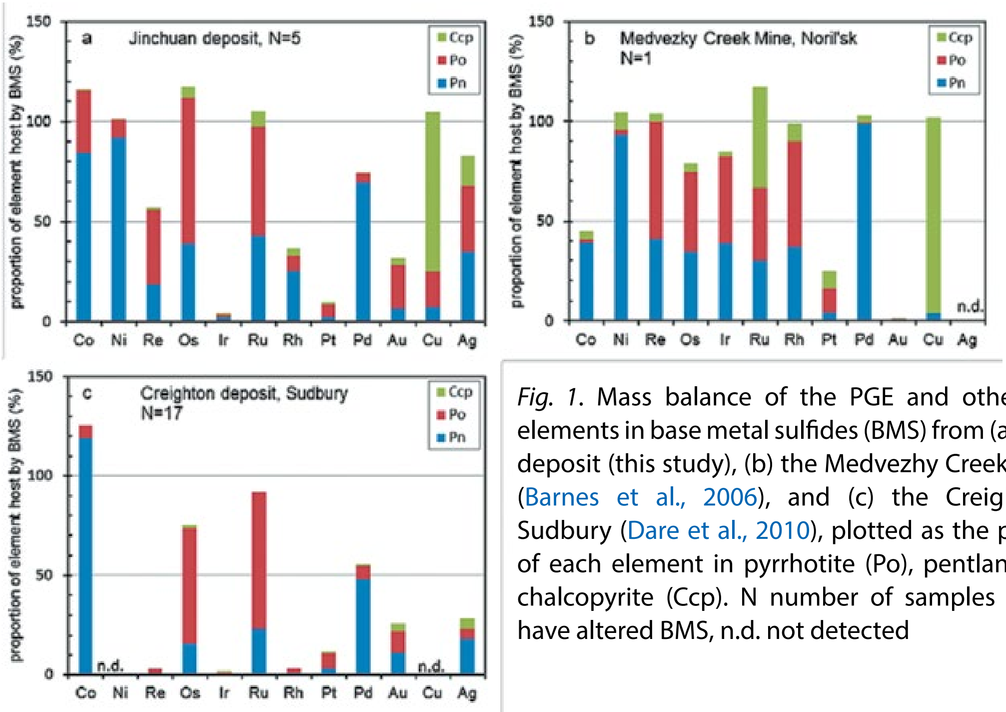

*Fig. 1.* Mass balance of the PGE and other chalcophile elements in base metal sulfides (BMS) from (a) the Jinchuan deposit (this study), (b) the Medvezhy Creek Mine, Noril'sk (Barnes et al., 2006), and (c) the Creighton deposit, Sudbury (Dare et al., 2010), plotted as the proportion (%) of each element in pyrrhotite (Po), pentlandite (Pn), and chalcopyrite (Ccp). N number of samples analyzed that have altered BMS, n.d. not detected

of the net-textured and massive ores. Pentlandite in the net-textured and massive ores has higher concentrations of these elements than pyrrhotite, indicating that these metals preferentially partition into pentlandite during MSS breakdown. We suggest that Rh concentrates preferentially into the Ni-rich MSS which forms pentlandite on cooling. The strong correlation between Co and, to a lesser extent, IPGE with Ni indicates that Co is mainly substituting for Ni in pentlandite. On the other hand, the tendency for Re and IPGE to concentrate in both pyrrhotite and pentlandite suggests that these elements substitute for Fe during MSS breakdown (Barnes et al., 2008). The extremely low proportions of Ir and Pt in Jinchuan BMS indicate that they occur predominantly as PGM (and/or metal-alloys). We propose the Ir-bearing sulfarsenide crystallized from MSS after it crystallization, while sperrylite crystallized from ISS as discrete mineral(s) on cooling. These resulted in Ir and Pt depletions in the BMS. Moreover, the enrichments of Pd in the pentlandite are attributed to diffusion of Pd from Cu-rich melt. This diffusion and the migration of Pt-bearing minerals result in decoupling between Pd and Pt and Pt-depletion in the net-textured and massive ores at Jinchuan.

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# SULFIDE-RICH PODS FROM THE LAC-DES-ILES Pd-ORE DEPOSITS, WESTERN ONTARIO, CANADA: PART 1. A GENETIC MODEL

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**ABSTRACT**. Massive sulfide pods from the Lac-des-Iles Pd-ore deposits (Western Ontario, Canada) show a variation in sulfide mineralogy and texture from essentially magmatic (pyrrhotite+pentlandite±chalcopyrite) to highly altered (pyrite±pentlandite±pyrrhotite±chalcopyrite). We suggest that the magmatic assemblage formed from crystallization of magmatic sulfide liquid. The pyrite (Py)-rich assemblage formed by Fe-loss to the surrounding silicates.

The Mine Block intrusion that host the Lac-des-Iles Pd deposits also hosts occasional sulfide-rich pods which have not been considered by previous studies. These pods are unusual in that they do not display typical magmatic features as they are not found at the base of the intrusion, they show a variation in sulfide mineralogy and texture ranging from magmatic to altered assemblages (Py-rich assemblages), and they are enriched in Pd (up to 67 g/t) with unusually high Pd/Ir and Pd/Pt ratios. There has been a long-standing controversy about the role played by fluids in the ore-forming processes at Lac-des-Iles (Talkington & Watkinson, 1984; Lavigne & Michaud, 2001; Hinchey & Hattori, 2005; Barnes & Gomwe, 2011; Hanley & Gladney, 2011; Djon & Barnes, 2012; Boudreau et al., 2014). The presence of unusual sulfide-rich pods adds another source of information to the ongoing debate. The present study examines the geology, petrography and whole rock geochemistry of Lac-des-Iles sulfide-rich pods in order to consider their origin and to assess the processes involved in their genesis and subsequent modifications.

The abundance of sulfides forming the pods is unlikely to be the result of cotectic precipitation from the mafic magma and therefore requires mobility and accumulation of the sulfides. Although the sulfide-rich pods occur across the stratigraphy of the intrusion, they do not form veins and are not associated with alteration halos which might indicate hydrothermal origin. Whereas some of the pods are massive, most of them are matrix and net-textured sulfides which negates the possibility of sub-solidus mobility of the sulfides. In addition, no evidence of deformation and/or recrystallization has been observed in the sulfides. Consequently the pods were more likely formed by accumulation of magmatic sulfide liquid into dilational jogs while the intrusion was emplaced and deformed (Fig. 1a.b). Nonetheless many of the pods have an excess of Py relative to the crystallization product of a magmatic sulfide liquid. Concentrations of immobile elements (IPGE+Rh) are correlated with one another regardless the amount of Py and the most soluble elements (Pd+Pt+Au) are not enriched in the most Py-rich pods. Furthermore Py-rich assemblages display similar metal patterns on a primitive mantle normalized basis to monosulfide solid solution (MSS) assemblages (i.e. decoupling between Ni and Cu, flat IPGE patterns, and Pt depletion). Therefore we suggest that the pods formed by fractional crystallization of magmatic sulfide liquid (Fig. 1c.d) and that Py-rich assemblages represent altered MSS assemblages. We also suggest that Pd enrichment was achieved prior to alteration resulting in the high Pd/Pt and Pd/Ir ratios regardless of the degree of alteration.

Instead of a strictly hydrothermal origin for the Lac-des-Iles sulfide-rich pods we favour a model whereby sulfides crystallized from a fractionating magmatic sulfide liquid prior to any modification by alteration. While alteration proceeded, trace elements were not remobilized. However the presence of excess Py requires either that S has been added or Fe has been lost from MSS. The combination

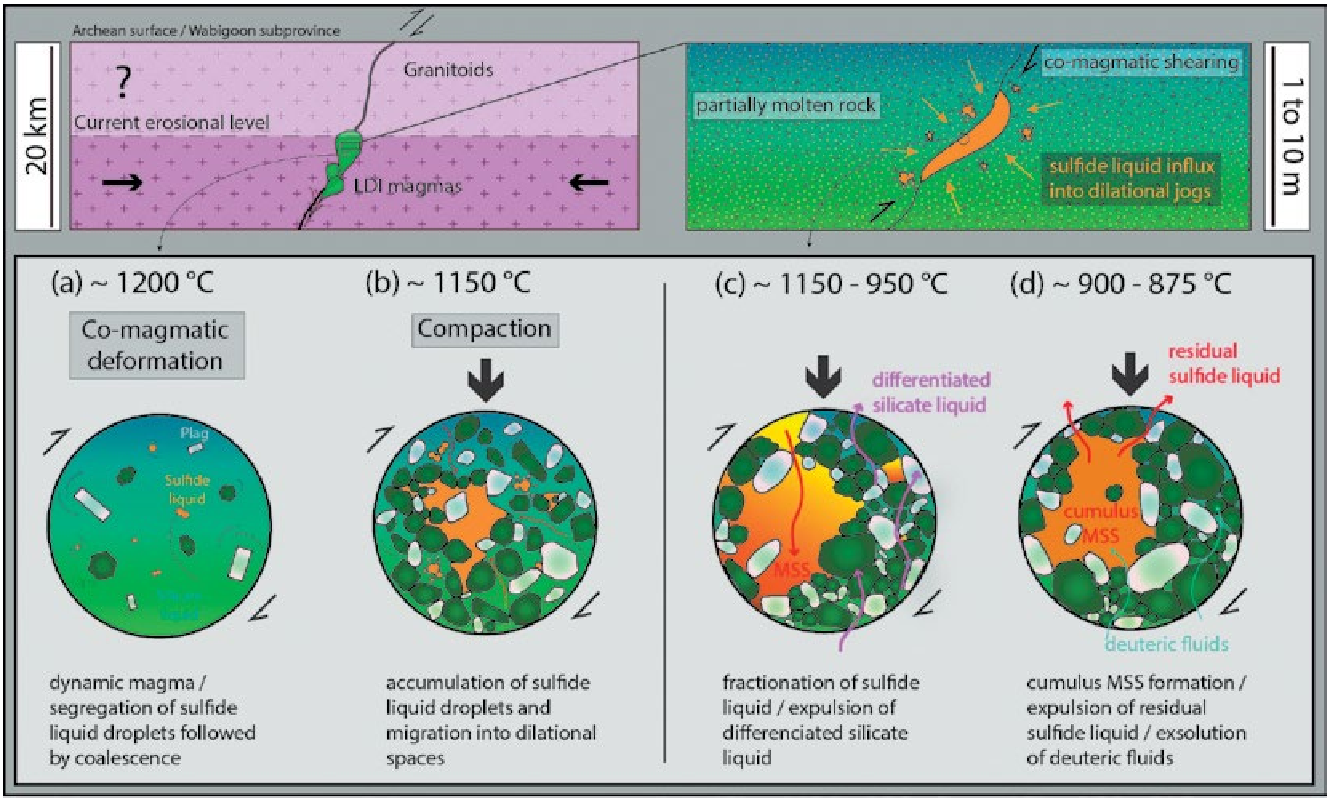

*Fig. 1.* Schematic model for the development of sulfide-rich pods at Lac-des-Iles: (a) segregation and coalescence of sulfide liquid droplets in a dynamic setting; (b) accumulation of sulfide liquid into dilational jogs during compaction; (c) fractional crystallization of sulfide liquid; (d) MSS formation and incipient alteration by deuteric fluids

of S/Se ratios and $\delta^{34}$ S values in the mantle range suggests that S was not mobile. As a result, we propose a model whereby Fe has been lost from MSS to surrounding silicates, promoting the formation of Py. However this raises the questions of how Py formed and how trace elements behaved during the formation of Py. Thus in Part 2 we discuss the implications of modifying the MSS assemblages during alteration on the distribution of PGE and the origin of PGE-bearing Py (Duran et al., 2014).

*Acknowledgements. We are grateful to North American Palladium for funding this project via the Canada Research Chair in Magmatic Ore Deposits.*

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# THE YACOUBA MAFIC-ULTRAMAFIC COMPLEX (IVORY COAST): A NEW OCCURRENCE OF Ni-Cu-PGE MINERALIZATION

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**ABSTRACT**. The Yacouba mafic-ultramafic layered complex, some parts of which were recently discovered, is a dismembered complex emplaced in the Man Archean Craton. It consists of three main rock types: peridotite and associated pyroxene peridotite, pyroxenite, and gabbronorite. Its probably Paleoproterozoic (2.1 Ga?) age of emplacement is poorly constrained,. It is characterized by rich Ni-Cu-PGE mineralization of a magmatic origin, preferentially located in the ultramafic units, virtually without a subsequent metamorphic or hydrothermal overprint. A large range of PGM has been identified, associated with base-metal mineralization and dominated by (Pt,Pd)(Te,Bi) minerals, but also complex sulphoarsenides, and Rh-bearing cobaltite-gersdorffite.

## GEOLOGY

The Yacouba mafic-ultramafic layered complex, located in the Biankouma region (western Ivory Coast) is emplaced in granulitic rocks belonging to the Man Archean Craton (3.5-2.7 Ga). The complex is interpreted as dismembered into several separate bodies that are still being explored. In the Samapleu-Yorodougou area, three mafic-ultramafic occurrences are known. Samapleu was discovered in 1976 and is now called Samapleu Main (SM); it is a small mafic-ultramafic body, about 400 m long by 350 m wide. The other two, discovered in 2010 and 2011, include Extension One (E1), a 2 km by 200 m mafic-ultramafic body with a northeast-southwest orientation, located 500 m northwest of SM, and Yorodougou (Yo), a 1.5-km-long mafic-ultramafic formation with an east-northeast to west-southwest orientation located 5 km notheast of SM. The layers plunge 70-80° towards the southeast at SM and Yo.

These mafic-ultramafic occurrences were interpreted as a dyke-like body of the Yacouba complex. The recalculated liquid compositions, in equilibrium with ultramafic and mafic cumulates, suggest basaltic to picritic parental liquids with a calcalkaline composition, typical of a continental arc magmatic signature. Calculated emplacement conditions indicate 7.5 kbar and 700-950 °C, or a depth of about 25 km, equivalent to amphibolite or granulite metamorphic conditions.

Structural and geological mapping, based on drilling and lithological studies, show that these bodies are composed of layered cumulates, each cycle being composed of dunite, pyroxene peridotite, pyroxenite, and gabbronorite. The thickness of each sequence varies from 2 to 60 m for a total thickness of the complete cycle of about 100 to 120 m.

Due to the lack of outcrops, the stratigraphic sequence has been established from numerous drill holes. Three main facies are recognized: 1) Lherzolite, dunite and harzburgite, depending on the proportion of pyroxenes; base-metal sulphides (BMS) representing about five modal percent are present in all rock types. 2) Pyroxenite (websterite, and olivine- and plagioclase-websterite), which is the most common; transition from 1) to 2) is progressive; BMS can be up to 60% in some websterite. 3) Gabbronorite where olivine is systematically absent; again, the transition from 2) to 3) is gradational and BMS are generally rare (<5%). Note also the presence of chromitite, occurring either as a sub-massive horizon, 10 to 50 cm thick, or as thin (1 to 5 cm) layers. Contacts with the host lithology (pyroxene peridotite or pyroxenite) are always sharp.

## MINERALIZATION

Disseminated base-metal sulphides occur in all three bodies. Where their content increases, they tend to occur as "net textures" (Fig. 1) and may form massive veins in pyroxenite. Brecciated textures are also observed in pyroxene peridotite and pyroxenite. The BMS assemblage is systematically composed of pentlandite, chalcopyrite, pyrrhotite, and rare pyrite, molybdenite and galena.

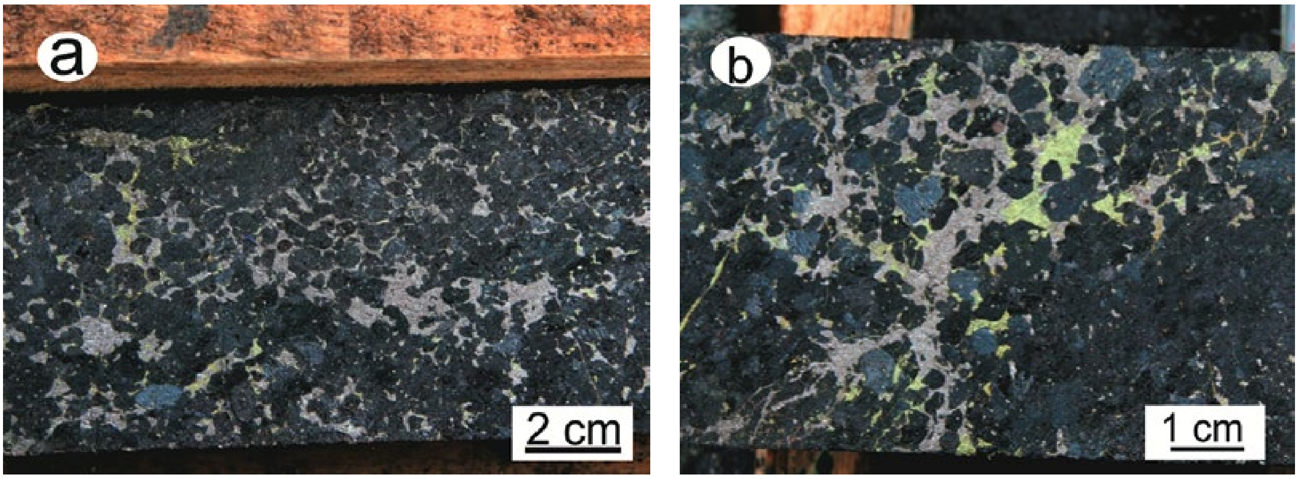

*Fig. 1.* Typical mineralization from the Yacouba Complex. a) Rich disseminated sample, b) BMS and silicates showing a net-texture

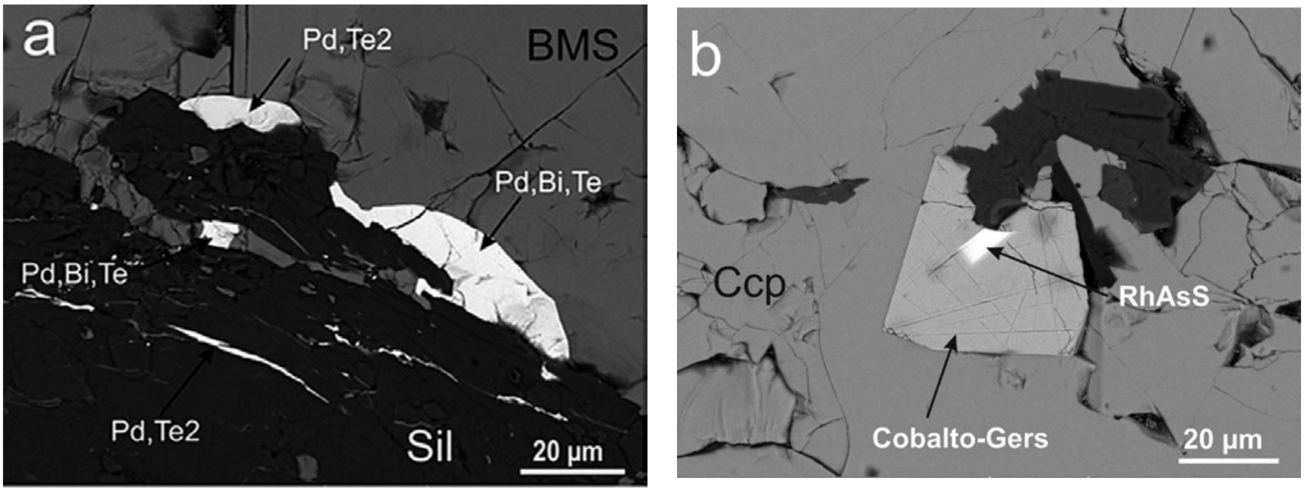

*Fig. 2.* BSE images of PGE minerals from the Yacouba complex. a) Typical PGM assemblage close to the BMS-silicate contact, b) Hollingworthite (RhAsS) exsolution in Rh-rich colbaltite-gersdorffite (Cobalto-Gers). Ccp: chalcopyrite

The Ni and Cu content varies between 0.2 and 0.6 wt.% in disseminated BMS, and up to 4% Ni and 3% Cu in massive mineralization. High PGE values have also been recorded with generally Pd>Pt. PGE take the form of PGM that are mostly included in or attached to BMS (Fig. 2). PGM include michenerite, merenskyite, moncheite, irarsite, hollingworthite, mertieite, kotulskite, laurite malanite, sperrylite, and uncommon Rh-Pd-cobaltite-gersdorffite.

## CONCLUSIONS

The discovery of the Yacouba mafic-ultramafic layered complex in the Man Archean Craton, with its Ni-Cu-PGE mineralization provides new evidence for the possibility of discovering this type of mineralization in Africa. Further studies are needed better to understand the age (probably Paleoproterozoic) of emplacement of the complex, its geodynamic environment, and the effect of deformation/dismembering. However, it seems that the Yacouba complex presents all characteristics of a “classic” Ni-Cu-PGE mineralized mafic-ultramafic layered complex, showing many similarities with the Voisey’s Bay or Jinchuan complexes.

# LIQUID IMMISCIBILITY IN MAFIC MELTS DERIVED FROM THE CONTINENTAL LITHOSPHERE: A CLUE TO THE ORIGIN OF ORE DEPOSITS

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**ABSTRACT**. The origin of Ni-Cu-PGE sulfide and magnetite-apatite orthomagmatic deposits in some continental magmatic rocks is still enigmatic, but ultimately linked to sulfide, oxide and phosphate liquids immiscible with the silicate melt. Magmatic immiscibility (unmixing of liquid phases) results in major petro- and geochemical differentiation, because the compositional divergence between unmixed phases can be extreme. The exact composition of pristine immiscible melts has proved extremely difficult to document and understand, largely because of their small quantities and ephemeral, reactive qualities during decompression, cooling and crystallization. We present two case studies (Kamenetsky et al., 2013a, b) demonstrating a novel approach to recording occurrence and compositions of immiscible liquids in large igneous provinces.

## ILICATE-SULFIDE LIQUID IMMISCIBILITY

Iron-nickel sulfide melt globules highly enriched in noble metals (Pt, Pd, Au; 120 ppm total PGE) are present within unusual high-Mg andesitic glass (8.2 wt.% MgO, 57.3 wt.% $SiO_2$, 310 ppm Ni) dredged from the southern Mid-Atlantic Ridge, near the Bouvet Triple Junction (BTJ). The composition of this unaltered glass indicates a high-temperature (>1250 °C) parental silicate melt derived from a garnet pyroxenite mantle source with pronounced 'continental' isotopic (Pb, Sr, Nd, Hf, Os, O) signatures. The sulfide globules (mostly <5 µm, largest 180 µm) have compositions consistent with being a quenched primary sulfide-hydroxide liquid. PGEs occur as alloys and reach concentrations (100% sulfide basis) ~2x higher than in sulfide globules in oceanic basalt glasses, and higher or similar to bulk sulfides in major Ni-Cu-PGE deposits (Fig. 1). The specific chemistry (high Si, high Ni, low Fe) of primary melts generated from garnet pyroxenite sources promotes sulfide saturation at low pressures, without extensive fractional crystallization and late-stage crustal contamination. The combination of high primary Ni content, sulfide saturation at low pressure, high temperature and high PGE-Au content suggests that the type of melt represented by BTJ glass may be an attractive model for the transition from magma to ore in magmatic Ni-sulfide systems, particularly those with inferred non-peridotite, lithospheric sources.

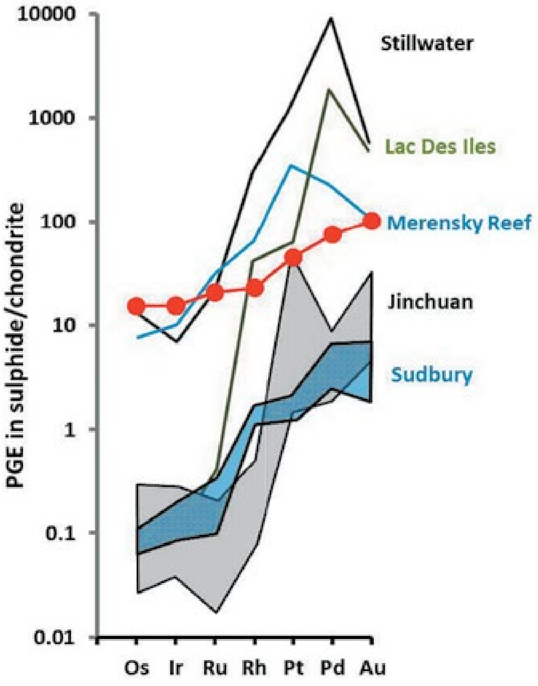

*Fig. 1.* Normalized concentrations of PGE+Au in the BTJ sulfide melt in comparison to 100% average sulfide from some major deposits (after Naldrett, 1997)

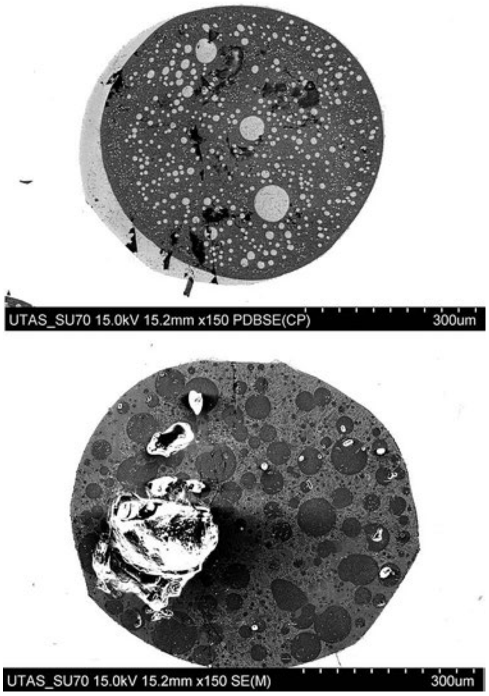

*Fig. 2.* BSE and SE images of melt pools with two immiscible phases ($L_{Fe}$ – bright; $L_{Si}$ – dark) in native iron

## SILICATE-SILICATE-METALLIC FE LIQUID IMMISCIBILITY

Silicate melt pools in native iron are found in the Khungtukun tholeiitic gabbro intrusion (Siberian Traps). The native Fe crystallized from a metallic iron liquid, which originated as disseminated globules during reduction of the basaltic magma upon interaction with coal-bearing sedimentary rocks. The silicate melts entrapped and armored by the native iron are composed of two types of globules that represent the aluminosilicate, $L_{Si}$ (60–77 wt.% $SiO_2$) and silica-poor, Fe-Ti-Ca-P-rich, $L_{Fe}$ (in wt.%: $SiO_2$ 15–46; FeO 15–22; $TiO_2$ 2–7; CaO 11–27; $P_2O_5$ 5–30) conjugate liquids (Figs. 2 & 3). Different proportions and the correlated compositions of these globules in individual melt pools suggest a continuously evolving environment of magmatic immiscibility during magma cooling. These natural immiscible melts correspond extremely well to the conjugate liquids experimentally produced in common basaltic compositions at <1025 °C. We propose that immiscibility can occur at large-scale in magma chambers and can be instrumental in generating felsic magmas and Fe-Ti-Ca-P-rich melts in the continental igneous provinces.

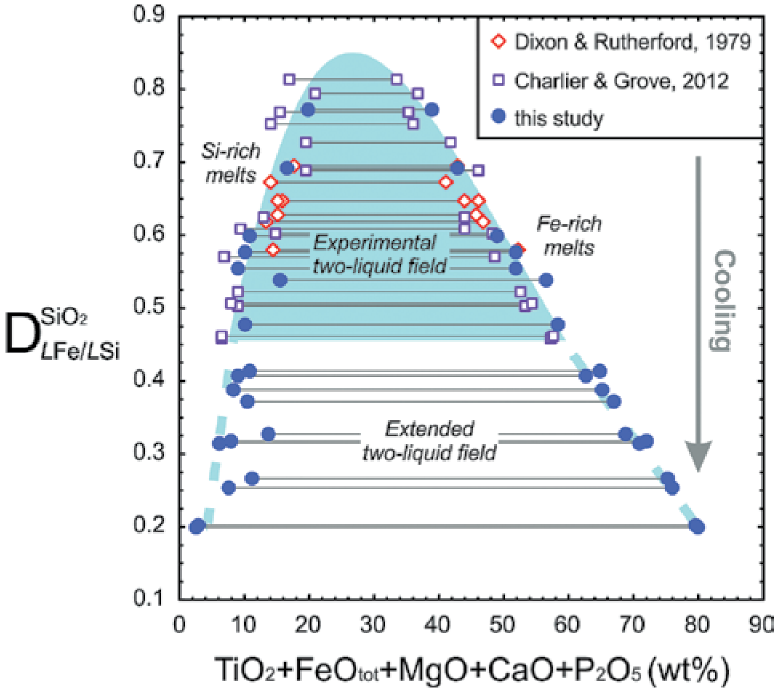

*Fig. 3.* Compositions of conjugate immiscible liquids in individual melt pools in native iron in comparison to experimental paired melts in tholeiitic systems. Horizontal tie lines indicate conjugate immiscible melt pairs

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# THE WATERBERG EXTENSION TO THE BUSHVELD COMPLEX

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**ABSTRACT**. In 2011 Platinum Group Metals (PTM) announced the discovery of PGE mineralisation in Main Zone rocks beneath Proterozoic Waterberg red bed sedimentary rocks, north of the surface outcrop of the northern limb of the Bushveld Complex. Since the discovery, extensive drilling of more than 130 boreholes, has confirmed the presence of PGE mineralisation within the first 17 km strike of a 35 km long northeast lobate arc defined by airborne geophysics. An Inferred Mineral Resource Estimate (dated September 2013) on the southern 5.4 km of strike length totals167 million tonnes grading 3.26 g/t of platinum, palladium and gold (3E) and contains 17.5 million ounces 3E with significant copper and nickel credits.

## THE WATERBERG PROJECT

The exposed northern limb forms the eastern part of what appears to be a much larger‘basin’, 100 x 130 km in sizebased on geophysical data (Kinnaird, 2005). Until the discovery of buried Bushveld rocks, it had been assumed that the exposed northern limb linked in a westward arcuate form with the Villa Nora segment of exposed Upper Zone. However, the confirmation of buried Bushveld rocks 20 km north of the exposed northern limb, refutes these earlier correlations.

The Bushveld succession in the PTM cores comprises a Main Zone (MZ) and Upper Zone (UZ). The contact between the Bushveld rocks and the Waterberg sedimentary cover is often mylonitised with a weathered reddened Bushveld gabbro below the contact, characterised by gibbsite with hematised and chloritised silicates. The footwall rocks are Archaean granite gneisses. However, commonly a granofels or agmatite forms the footwall to the Bushveld succession, which is interpreted to be re-mobilised footwall gneiss interfingered with pyroxenite.The UZ of ferrogabbro, ferronorite and gabbronorite varies between 10 and 500 m in thickness. Elsewhere in the Bushveld Complex, the base of the UZ is characterised by the appearance of cumulus magnetite, with >20 magnetitite layers within the UZ. Although cumulus magnetite occurs in UZ of the Waterberg project as observed in core samples and identified based on magnetic susceptibility, typical magnetitite layers are lacking except in one of the early cores in the south of the project area,. This contrasts to the 32 magnetitites in the UZ of the BelleVue core 60 km to the south in the northern limb (Ashwal et al., 2005). The MZ rocks are characterised by gabbronorites with thick troctolite layers and minor harzburgites, locally pegmatoidal, towards the base that are atypical of MZ rocks elsewhere in the Bushveld Complex. This package of olivine-rich rocks is at least 50 m thick and in some boreholes, the end-of-hole is within this unit. Olivine persists upwards for tens of metres in olivine-bearing gabbronorite. Commonly, a pyrrhotite-bearing pyroxenite, generally lacking any PGE grade occurs below the troctolites, which may be tens of metres in thickness.

## MINERALIZATION AT THE WATERBERG PROJECT

There are at least two “reefs” or ‘mineralized zones’, an upper T reef and a lower F reef. The T reef outlined by drilling thus far is restricted to the southern portion of the project area, whereas the F reef has been intersected with drilling for a 17 km strike to date. Exploration drilling for further strike extent is in progress. The Bushveld succession thickens northwards from the discovery hole with greater separation between the two reefs. There is a correlation between visible chalcopyrite and pentlandite abundance and grade of PGE. The T reef at its shallowest is at 130 m in depth, sub-cropping against the Waterberg. In the discovery hole the T reef is ~30 m thick but northwards thickens to <50 m thick. It comprises an upper T1 and a lower T2 unit with a middling between the two zones that varies in thickness from ~20 cm to 20 m of olivine-bearing feldspathic pyroxenite, pegmatitic gabbro or a vari-textured feldspathic-rich zone. T1 is associated with varied rock types that include a feldspar-rich pegmatoid, feldspathic pyroxenites, troctolite/harzburgite and gabbronorite and is ~20 m thick in the most northerly hole in which it occurs. T2 is mainly in a gabbronorite. Grade in both T1 and T2 is typically 3.4 g/t 3E, although locally with <14 g/t in more northerly cores. Both zones have a consistent and unusual metal ratio of ~50% Pd, ~30% Pt and anomalous 20% Au with 0.1% Ni and 0.17% Cu.

The F Reef which is hosted in serpentinised troctolite/harzburgite, is at a minimum depth of 180 m from the surface. The olivine-rich zone is 200 m thick in Hole WB99, although more typically it is 100 m in thickness. However, only part of this unit is mineralised. In the southern portion, the mineralised F zone is typically <10 m thick but in the central portion, the "Super F reef" thickens to 60 m in true thickness, with grades of 3 g/t over this interval. The metal budget differs from that of the T reef, especially in the much lower gold content. A typical drill split has 65% Pd, 30% Pt and 5% Au with 0.07% Ni and 0.17% Cu. The calculated ore resource of 17.5 million ounces Pt+Pd+Au does not include any F or T reef below 1000 m depth. Both T and F units remain open at depths below 1000 m which for initial purposes was taken as an economic depth cutoff.

The provenance of economic PGE reefs in the Main Zone of the northern limb is unclear as the Main Zone in the eastern and western limbs does not contain economic mineralization although slightly elevated PGE's occur in the Pyroxenite Marker. PGE enrichments in the Main Zone of the northern limb are also known on Moordrift, Aurora, Drenthe but links to the Pyroxenite Marker are debatable and none of these localities had troctolites associated with the PGE enrichment. The mineralized olivine-rich layers have more similarities to parts of the composite Platreef that resulted from multiple influxes (Kinnaird et al., 2005).

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# HYDROTHERMAL REMOBILIZATION AROUND A DEFORMED AND REMOBILIZED KOMATIITE HOSTED Ni-Cu-(PGE) DEPOSIT, SARAH'S FIND, AGNEW WILUNA GREENSTONE BELT, WESTERN AUSTRALIA

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**ABSTRACT**. Results from the study of the Sarah's Find nickel deposit highlight the possible remobilization of nickel by arsenic-rich hydrothermal fluids, creating a halo extending up to 1.15 km away from the ore. This NiAs geochemical halo, which is observed within the felsic volcanic footwall and can be detected using portable X-Ray Fluorescence and backed up by laboratory analyses, is associated with the presence of nickel arsenides, interpreted to form during the circulation of arsenic-rich hydrothermal fluids. High Pd and Pt concentrations, and minor gold, are also detected within this geochemical footprint. Results from a more regional scale study, combined with this Pd-Pt enrichment, suggest that the remobilised nickel is sourced from massive nickel sulfides. Combining these results with observations from other komatiite-hosted nickel sulfide deposits from the Yilgran craton, it is suggested that the presence of Pd and Pt enriched trace arsenide phases in country rocks and shear zones may be a generally applicable proximity indicator for nickel sulfides in hydrothermally altered terranes.

The remobilization of metals during post-deposition hydrothermal alteration of magmatic sulfide ores has the potential to result in geochemical haloes, whose recognition could potentially enlarge the detectable footprint of this ore type. The Sarah's Find prospect, located 4.5 km north of the Mount Keith nickel mine, Western Australia, was chosen as a case study to investigate the nature and 3D geometry of the geochemical halo created by the remobilization of base metals, gold and platinum group elements (PGEs) into the country rock surrounding massive sulfide lenses. The geometry of the main structures affecting the Sarah's Find massive sulfide lenses, their komatiitic host rock and the footwall dacite were studied in detail to identify major fluid pathways. Geochemical analyses (portable XRF and laboratory) highlight the presence of nickel, palladium and minor platinum anomalies forming a geochemical halo entirely within the footwall dacite. This halo is concentrated within a shear zone developed along the dacite-komatiite contact and extends along it up to 1.15 km away from the massive sulfides, in parallel to a prominent stretching lineation. Elevated Ni and Pd are also associated with high As, Co, Cu and S. Palladium and Pt concentrations increase with proximity to the massive sulfides. Detailed study of numerous samples containing anomalous signatures reveal the presence of nickel sulfarsenides (gersdorffite) as well as sulfides (mainly pyrrhotite, minor chalcopyrite, pentlandite, and galena) either mechanically remobilized as veinlets close to the massive sulfides, or recrystallized within the foliation. Laser ablation analyses indicate that Pd and Pt are hosted within gersdorffite. This Ni-Co-As-Pd geochemical halo is interpreted as forming syn-deformation, by deposition from arsenic-rich hydrothermal fluids migrating within the contact shear zone.

A similar pattern of Ni-Pt-Pd-As dispersion is observed at the Miitel komatiite-hosted nickel-sulfide deposit, located on the eastern flank of the Widgiemooltha Dome, Western Australia.

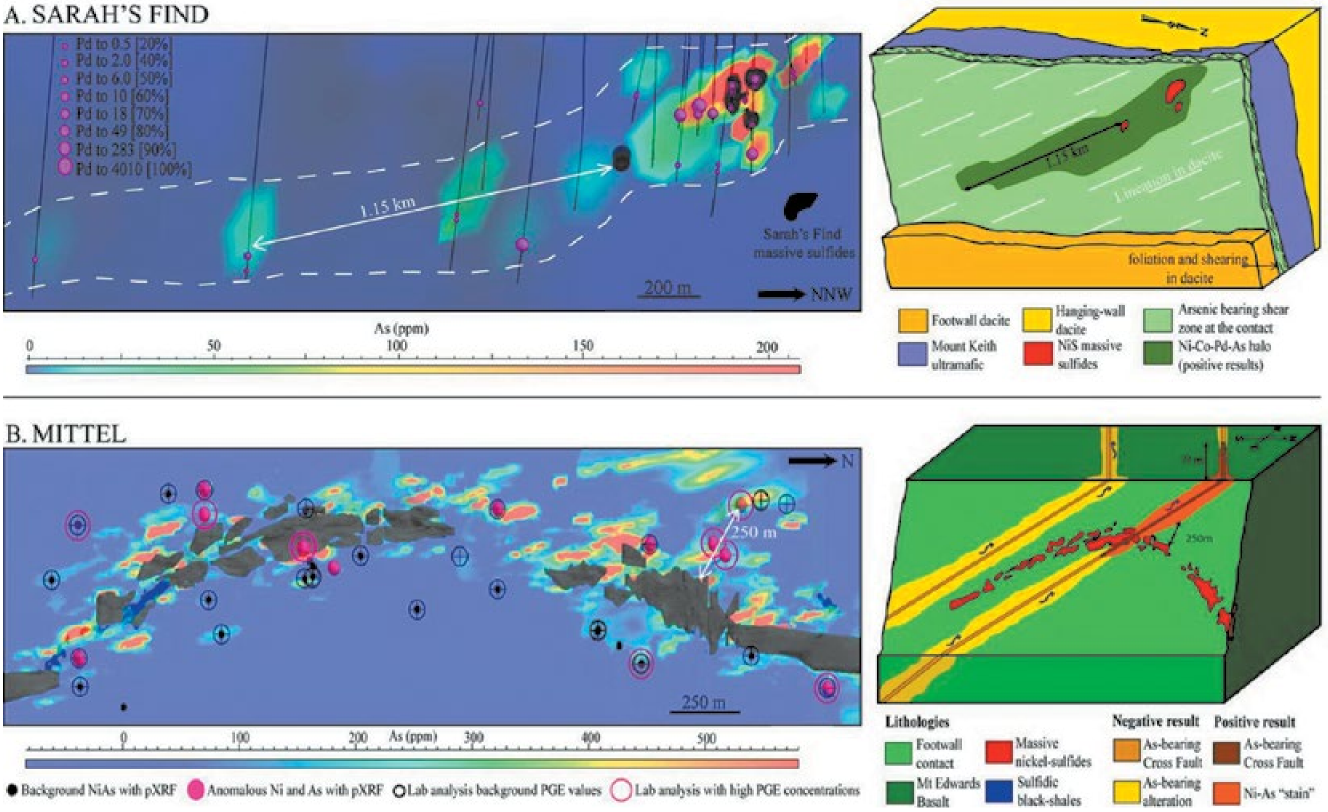

*Fig. 1.* A) Perspective view from gOcad® of a long section through the 3D model of the Sarah's Find deposit. This image combines: 1) the distribution of the arsenic in ppm at the contact between the Mount Keith ultramafic and the Mount Keith footwall dacite, and 2) the location of laboratory analyses (NiS Fire Assay) with varying size proportionally to Pd concentrations. A' 3D simplified block model of the Sarah's Find system showing the possible application of the NiAs geochemical halo to exploration targeting for nickel sulphides. B) Perspective view from gOcad® of a long section through the 3D model of the Miitel deposit. This image combines: 1) distribution of the arsenic in ppm at the contact between the basalt and the komatiites, 2) location of pXRF analyses showing anomalously high nickel and arsenic concentrations , and 3) location of lab PGE analyses highlighting samples enriched in PGEs. B' 3D block model of the Miitel system showing the possible application of the NiAs geochemical halo to exploration targeting for nickel sulfides

Pd and Pt-rich nickel sulfarsenides are observed concentrated within small quartz veins in the Mount Edwards footwall basalt, within meters of the footwall contact. At Miitel, the nickel arsenides are associated with small hydrothermal veins which cross cut the basalt; no shearing is observed, unlike around the Sarah's Find deposit. The NiAs-PGE halo around the Miitel massive sulfides extends at least 250 meters away from the mineralization, along the footwall contact. No comparable Ni-As-PGE signals were observed in other studied mineralized localities (Perseverance, northern Kambalda Dome) lacking the arsenic overprint. The presence of As-bearing fluids appears to be a necessary condition for the remobilization of nickel and PGEs along major fluid pathways and shear zones.

Geochemical haloes of Ni-As-Pd-Pt similar to those described here could potentially exist around any type of magmatic nickel sulfide mineral system that has undergone a phase of arsenic metasomatism. The presence of anomalous concentrations of Ni, Pd and As within country rocks and shear zones may be a generally applicable proximity indicator for nickel sulfides in hydrothermally altered terranes. Gradients in Pd and Pt concentrations have potential as a vectoring tool.

*Acknowledgments*. Financial support for this research was provided by MERIWA (project #M413), BHP Billiton Nickel West, Mincor Resources NL and First Quantum Minerals Ltd. Sarah-Jane Barnes and Danny Savard are thanked for their assistance with the use of the Laser Ablation (LA-ICP-MS) facility at UQAC, Canada.

# HYDROTHERMAL ALTERATION AND CHARACTERISTICS OF MINERALIZATION AT THE JINBAOSHAN Pt-Pd DEPOSIT, YUNNAN, CHINA

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**ABSTRACT**. Detailed studies on altered minerals and ores indicate that the Jinbaoshan Pt-Pd deposit is not a typical magmatic ore deposit. Ore-bearing ultramafic intrusion has been completely replaced by hydrothermal minerals, like serpentinite and talc. The strong alteration releases PGE that are originally dispersed in rock-forming minerals, and formed industrial orebodies that overlay along fracture zone

The Jinbaoshan Pt-Pd mine locates in 72 km southeast the Midu city, Yunnan, China. The deposit is the largest independent Pt-Pd deposit found in China. Detailed mineralogical studies indicate that the rocks of ore-bearing have subjected to strongly hydrothermal alteration, and mineralized characters show that it is different from the typical magmatic Pt-Pd deposits.

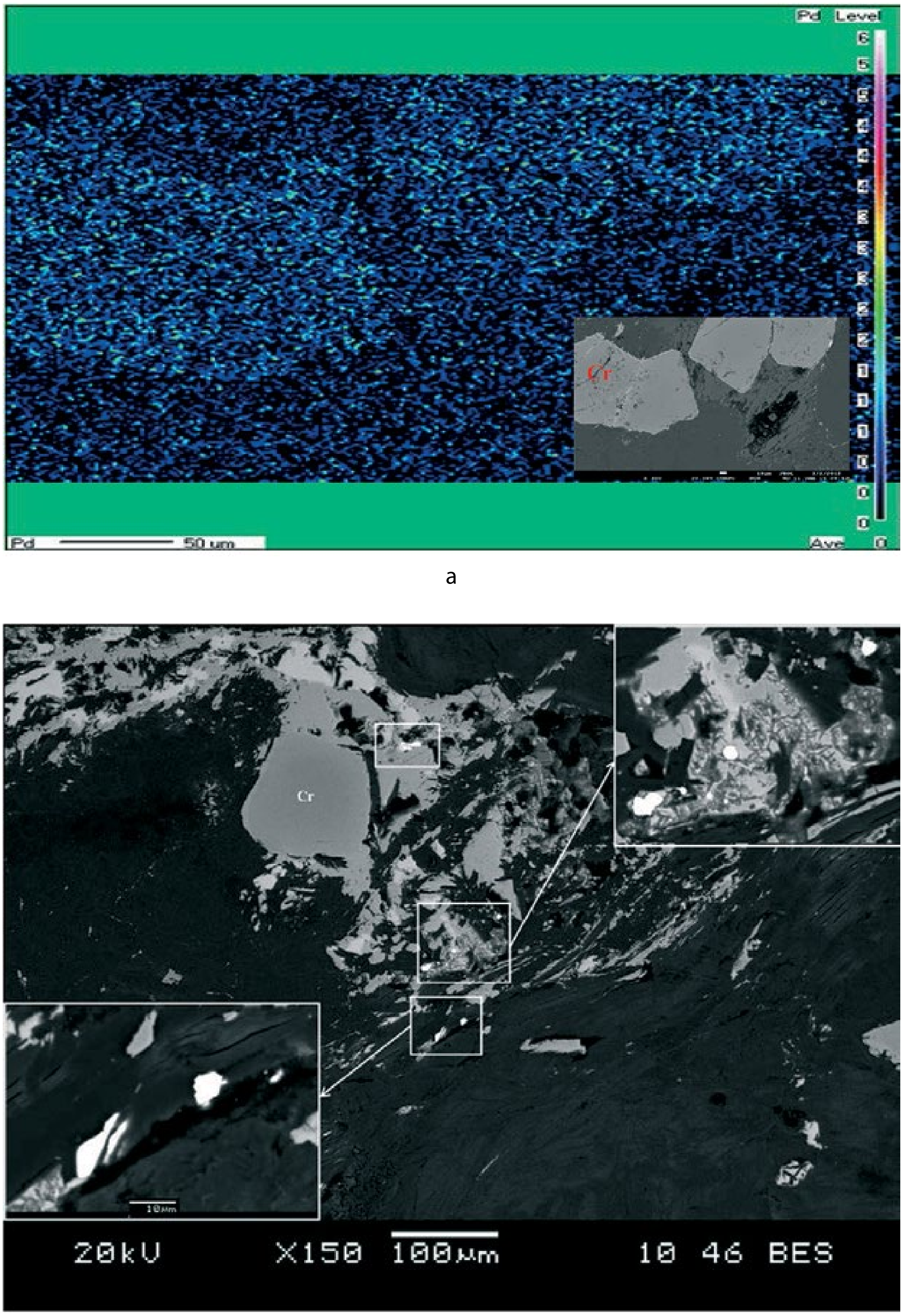
Tectonic setting of the Jinbaoshan deposit is in east side of the Red River fault. Stratiform ore-bearing ultrabasic intrusion of Hercynian (260 Ma, Tao et al., 2003) invaded in the Jinbaoshan carbonate–clastic Formation of Devonian. The ore-bearing intrusion, controlled by the Jinbaoshan anticline, is with a length of 2560 m, a width varying from 760 to 1240 m, and a thickness of 25~109 m, maximum 176 m. Ore-bearing rock is lherzolite. Crystal varies from coarse to fine grain in size from the bottom to top, and texture is from cumulative to densely fine-grained. There are more than 80 ore bodies are found in the deposit. One of the largest orebody (K12) has a size of 1754 x 500 x 20 m, and an average grade of Pt+Pd 1.90g / t, Cu 0.24%, Ni 0.20% in ores.

Ore minerals in the Jinbaoshan deposit consist of two major parts: (1) residual magmatic rock-forming minerals, including small amounts of clinopyroxene, ferrochrome spinel, magnetite, hornblende and phlogopite, and trace olivine; (2) hydrothermal and supergene minerals. The Jinbaoshan ultrabasic intrusion has been strongly serpentinized. More than 90% of minerals in the intrusion have been changed to clay minerals, like serpentine and talc. At the shallow part, rock was affected by surface water, mineral assemblage transformed to more single, and formed a serpentine-calcite zone of tens meters. On the surface, the residual serpentine is further damaged. It is transformed into chlorite with expandable layer. PGE minerals-bearing chlorite- sulphide veinlets further superimposed close to the broken parts.

Characteristics of mineralization in the Jinbaoshan deposit are different from a typical magmatic deposit. According to analysis, grades of Pt+Pd in samples, which are without late veinlets, are about 0.4~0.5 g/t. In the samples that are absence residual magmatic rock-forming minerals, Pt+Pd contents decrease to 0.2 g/t or less. In the weathering zone, Pt+Pd contents will decrease to less than 0.05 g/t.

Characteristics X-ray scanning suggests that Pt-Pd elements are generally dispersed in the magmatic rock-forming minerals (Fig. 1a). Industrial orebodies, in which PGE can be recovered, actually distributed in broken parts of the intrusion. Independent PGE minerals associated with sulfides, chlorite and dolomite occur in the late hydrothermal veinlets (Fig. 1b). The characteristics of mineralization indicate that hydrothermal fluids released PGE from the early magmatic rock-forming minerals, and enriched, re-precipitated them in fractures again.

*Acknowledgments. The research is one part of the Project of National Science and Technology No. 2008BA32B10-01B. Authors would like to thank the supporting during field by Yunnan Gold Group LTD.*



a

b

*Fig. 1.* a) Characteristic X-ray image of Pd for rock-forming minerals; residual Cr-spinels (Cr) have higher background of Pd than surrounding serpentine; b) BSE image showing fine grain Pt-Pd minerals that occur in sulfide-bearing veinlets

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# MAFIC-ULTRAMAFIC INTRUSIONS OF THE GILES EVENT, WESTERN AUSTRALIA: PETROGENESIS AND PROSPECTIVITY FOR MAGMATIC ORE DEPOSITS

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**ABSTRACT**. The Musgrave Province of central Australia hosts more than a dozen c. 1075Ma mineralized layered intrusions, hosting PGE reefs at Wingellina Hills, and V rich magnetite layers at Jameson Range. The Bell Rock, Blackstone, and Jameson-Finlayson intrusions are tectonically dismembered portions of an originally contiguous body, here named the Mantamaru intrusion that had a strike length of > 170 km and a width of at least 20 km, making it one of the world's largest layered intrusions.

More than a dozen mafic-ultramafic layered intrusions were emplaced across > 100 000 km$^2$ of central Australia at c. 1075 Ma as part of the c. 1090-1040 Ma Giles Event. The intrusions crystallized from tholeiitic magma of variable composition (<7 – 12.5 % MgO) that was emplaced at mid- to upper-crustal levels (up to ~6.5 kbar). As a result, individual intrusions show distinctive compositions. Some intrusions, such as Wingellina Hills, Pirntiri Mullari, The Wart, Ewarara, Kalka, Claude Hills, and Gosse Pile, contain significant ultramafic portions of wehrlite, harzburgite and websterite. Others, including Hinckley Range, Michael Hills, and Murray Range, are of predominantly olivine-gabbronoritic composition. Mafic intrusions containing significant troctolitic portions include Morgan Range, Cavenagh, Bell Rock, Blackstone, and Jameson-Finlayson. The latter three are tectonically dismembered portions of an originally contiguous body, here named the Mantamaru intrusion that had a strike length of > 170 km and a width of at least 20 km, making it one of the world's largest layered intrusions.

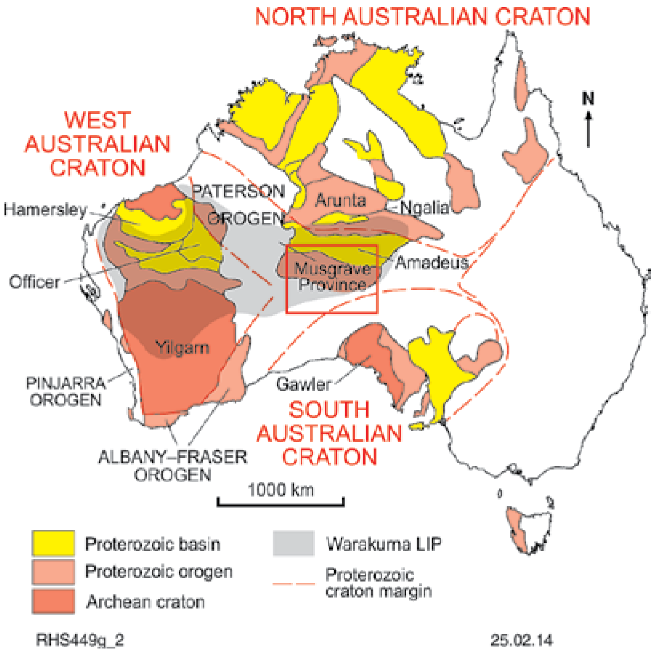

*Fig. 1.* The Musgrave Province within Australia

The Giles intrusions were emplaced into the Musgrave Province, a complex Proterozoic terrane located at the intersection between the West Australian, North Australian and South Australian cratons. The region underwent several episodes of orogeny and rifting over a timespan of > 200 Ma. The oldest event clearly affecting the entire Province was the 1220-1150 Ma Musgrave Orogeny. It arose either in an intracratonic setting or as a distal back-arc and featured early, rapid, and substantial lithospheric thinning. This allowed convecting mantle to be channeled upwards along the preserved, deep, margins of the surrounding craton keels to the newly exposed base of the Musgrave lithosphere. The result was large degree mantle melting, ponding of basalt at, and intrusion into, the base of the lithosphere, lower-crustal melting, voluminous granite magmatism and widespread mid-crustal UHT metamorphism. Magmatism largely ceased between c. 1150 and 1090 Ma,

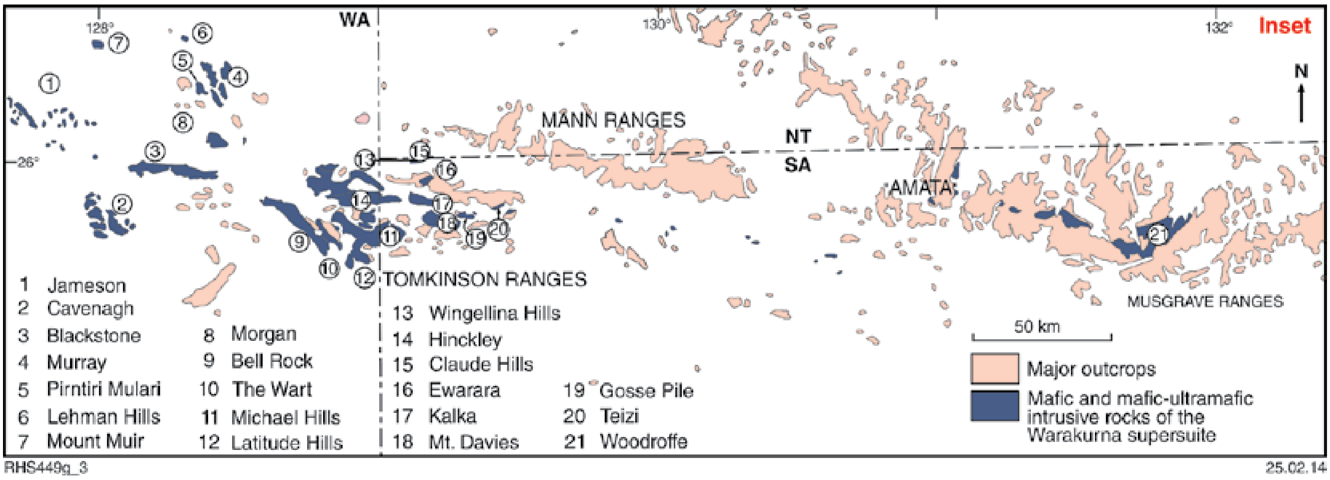

*Fig. 2.* Layered intrusions of the Giles event, Musgrave Province

possibly because the lower crust became too refractory, or because a buoyant lithospheric mantle began to form. Renewed mantle melting from c. 1090 Ma onwards led to the magmatism-dominated Giles Event (c. 1090 to 1040 Ma), comprising voluminous basic and felsic volcanic and intrusive rocks grouped into the Warakurna Supersuite. One particularly notable component of the Giles Event was the Warakurna Large Igneous Province, represented by doleritic intrusions that outcrop across ~1.5 million km$^2$ of central and western Australia (Wingate et al., 2004). The source to the Giles basic magmas was largely asthenospheric, reflected by their relatively minor crustal component (low LILE, εNd up to +2) and low Pt/Pd ratios. The long lasting magmatism and UHT metamorphism in the Musgrave Province suggests that magmatism was plate driven rather than plume driven. In many regards, the Giles Event can be viewed as an extension of the anomalous thermal regime established during the Musgrave Orogeny. Although initial extension/rifting, emplacement of the layered G1 Giles intrusions, and then significant uplift, all occurred between 1078 and 1075 Ma, mantle-derived magmatism lasted for > 50 m.y. and is also unrelated to a deep mantle plume. Periods of deformation (both extension and compression) during both the Musgrave Orogeny and the Giles Event may be related to far-field compressive influences that allowed the formation of thick sill complexes ultimately resulting in some of the world's largest layered intrusions.

The economic potential of the Giles Event includes: (i) PGE reefs in the ultramafic-mafic transition zones of layered intrusions and in magnetite layers in the differentiated portions of the intrusions, particularly in the early (G1) intrusions whose parental magmas failed to interact with abundant juvenile S of relatively late-stage felsic volcanics; (ii) Cu-Ni sulfide deposits within magma feeder conduits of late basaltic pulses that could assimilate S-rich felsic volcanics; (iii) Vanadium in the lowermost magnetite layers within the most fractionated intrusions; (iv) Apatite in the unexposed uppermost magnetite layers of the fractionated intrusions; (v) Ilmenite as granular disseminated grains in magnetite layers within the upper portions of the intrusions; (vi) Iron, particularly in tectonically thickened magnetite layers or magnetite pipes of the upper portions of intrusions; (vii) Gold and Cu, in the roof rocks and the contact aureoles of the large intrusions, and in associated granites and felsic volcanics; and (viii) Lateritic Ni in weathered portions of the olivine-rich ultramafic portions of intrusions.

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# OLIVINE, PGE GEOCHEMISTRY AND S ISOTOPES OF THE PERMIAN HUANGSHANNAN Ni-RICH SULFIDE DEPOSIT: IMPLICATIONS FOR ORE GENESIS IN THE HUANGSHAN Ni-Cu ORE FIELD

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**ABSTRACT**. The Huangshannan intrusion formed at 278 Ma and sulfides in it were segregated from Ni-rich magma. Fractional crystallization and/or assimilation of sulfide with $\delta^{34}S$ values similar to those of mantle sulfur triggered the sulfide saturation in the Huangshannan magma. Relative high PGE concentration of the Huangshannan intrusion can be attributed to a relatively higher R factor in the Huangshannan system.

The Huangshannan intrusion formed at 278 Ma, which is coeval with most Ni-Cu bearing mafic-ultramafic intrusions in Eastern Tianshan, southern margin of the Central Asian Orogenic Belt (CAOB). The Huangshan magmatic Ni-Cu ore field consists of the Huangshandong, Huangshandxi, Xiangshan and Huangshannan intrusions. The Huangshannan intrusion consists of several layers of ultramafic rocks (lherzolite and olivine websterite) in the east and a mafic unit (gabbro, norite and olivine gabbro) in the middle and west of the intrusion. Important sulfide mineralization occurs at the base of the lherzolite and olivine norite. Sulfide mineralization in lherzolite from the intrusion is characterized by strong enrichment in Ni (~18 wt.% in disseminated sulfides recalculated to 100% sulfide) and relative enrichment in platinum group elements (PGE) compared to that at the Huangshanxi and Huangshandong deposits. Because of the high Ni contents in olivine crystals (~3000 ppm), we propose that the sulfides were segregated from Ni-rich magma. The relationship between the Fo and Ni contents of olivine crystals indicates olivine norite formed from a derivative magma produced as a result of fractional crystallization of olivine. The $\delta^{34}S$ values of sulfides in lherzolite and olivine norite range from -0.4 to 0.8‰, which are similar to typical mantle values, and for this reason an evaluation of crustal sulfur addition based on $\delta^{34}S$ values alone is difficult. The data are consistent with fractional crystallization and/or assimilation of sulfide with $\delta^{34}S$ values similar to those of mantle sulfur controlling the attainment of sulfide saturation in the magma that produced the Huangshannan deposit. The decoupling of IPGEs and PPGEs and relative depletion in Pt in sulfides from the lherzolite can be explained by monosulfide solid solution (MSS) fractionation and post magmatic hydrothermal processes, respectively. Although the PGE contents of the Huangshannan deposit are markedly lower than those that characterize PGE dominated deposits, the contents are higher than those in the Huangshandong and Huangshanxi deposits. R factor modeling indicates that the differences can be attributed to a relatively higher R factor in the Huangshannan system. The modeling suggests that the pre-sulfide saturation concentrations of Ir and Pd in the magma were ~0.03 ppb and 0.13 ppb respectively. These are very low values that are suggestive of either the retention of sulfide in the mantle source or depletion due to a previous sulfide saturation event and accumulation of only a small amount of PGE-rich sulfide at depth. Olivine fractional crystallization modeling suggests that the magmas that produced the Huangshandong and Huangshanxi intrusions were Ni- depleted due to early sulfide segregation. The Ni-rich nature of olivine from the Huangshannan intrusion by comparison, together with the differemces between D-Ni and D-Pd or Ir (silicate liquid-sulfide liquid) values, indicates that if sulfide saturation occurred at depth the amount of sulfide collected could not have exceeded the cotectic proportion. The modelling is consistent with textures and sulfide distributions which suggest that the Huangshandong and the Huangshanxi deposits formed from sulfide laden magma in a dynamic conduit system.

# CONTRASTING OSMIUM, IRIDIUM, RUTHENIUM AND RHODIUM BEHAVIOR IN CHROMITE FROM VOLCANIC AND PLUTONIC ROCKS AND THE ORIGIN OF LAURITE IN CHROMITE

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**ABSTRACT**. The arrival of new LA-ICP-MS equipment at UQAC allowed us to analyse the Os, Ir, Ru and Rh contents of chromite from samples representative of different geological settings including volcanic samples (MORB, boninites, komatiites, Hawaiian tholeiite, continental flood basalt picrite) and plutonic samples (Layered intrusions chromitites – Bushveld, Stillwater, Great Dyke and Black Thor complexes – and ophiolitic podiform chromitites – Thetford Mines and Mirdita ophiolites). Our new LA-ICP-MS results confirm that chromite could act as an important phase in controlling part of the whole rock budget of Os, Ir, Ru and Rh in volcanic samples, but chromite generally shares this role with other phases such as alloys and laurite, particularly in plutonic chromite. Our results raise questions on the origin of these IPGE-rich phases.

It is well established that whole rock Cr shows positive correlations with Os, Ir, Ru, Rh in sulfide-poor volcanic and plutonic sample suites. Moreover some chromite-rich rocks from plutonic settings show enrichment in all of the platinum-group elements (PGE; Os, Ir, Ru, Rh, Pt, Pd). The PGE enrichments are commonly dominated by Os, Ir, Ru and Rh (IPGE) suggesting that the process of chromite crystallization somehow concentrates these elements over Pt and Pd. Until recently our understanding of the role of chromite in concentrating IPGE was based on correlations between whole rock Cr and whole rock IPGE which lead many researchers to propose that chromite is able to concentrate and fractionate the IPGE. It is still unclear whether the whole rock correlations observed is exclusively link to the presence of IPGE-rich phases, i.e. laurite $(Ru,Os,Ir)S_2$, entrapped in chromite during their crystallization and growth, or result from the presence of IPGE in solid solution within the chromite structure. The main difficulty in addressing this problem arose because it was not possible to carry out accurate measurements of IPGE concentration in chromite by in-situ techniques because of their very low concentrations.

The introduction of in-situ analysis of chromite by laser ablation combined with ICP-MS (LA-ICP-MS) has recently allowed the measurement of Ru content in chromites from Archean komatiitic lavas and from oxidized arc lavas from the Ambae Volcano (Vanuatu Island Arc) in which Os, Ir, Ru and Rh (≤82 ppb, ≤200 ppb, ≤162 ppb, and ≤149 ppb, respectively) have been reported (Park et al., 2012). In this contribution, we present new results for the concentrations of Os, Ir, Ru, and Rh in chromite from samples from various volcanic and plutonic settings, which confirm the role of chromite in the fractionation of PGE during early magmatic processes but raise new questions about the origin of laurite in plutonic chromite.

From our results, we see a distinction between IPGE contents of chromites from volcanic and from plutonic samples. Most of the volcanic chromites contain ΣIPGE ranging from 78 to 399 ppb except for the chromite from the MORB sample which contain ΣIPGE ~22 ppb. The plutonic chromites differ from place to place, those from chromitites from the Bushveld and Stillwater complexes have ΣIPGE < 20 ppb while ΣIPGE of chromites from Great Dyke and Black Thor chromitites range from 38 to 94 ppb. Ophiolitic chromite from podiform chromitites shows ΣIPGE from < 13 to ~ 22 ppb. On primitive mantle normalized ($PM_N$) plots, chromites from plume related lavas (Fig. 1a) have Os and Ir ranging from 5x to 10x mantle, Ru ranges from 20x to 60x mantle and Rh ranges from 3x to 27x mantle with $PM_N$ IPGE profiles showing a positive Ru anomaly. Chromites from boninites show distinctive $PM_N$ IPGE profiles (Fig. 1b) with low Os and Ir contents (from 1x to 2x mantle) while Ru and Rh range from 10x to 80x mantle, with the difference that chromite from boninites have higher $Rh_N$ than $Ru_N$. Chromites from plutonic settings are much more depleted in IPGE with concentrations generally <5x mantle (Figs 1c,d)

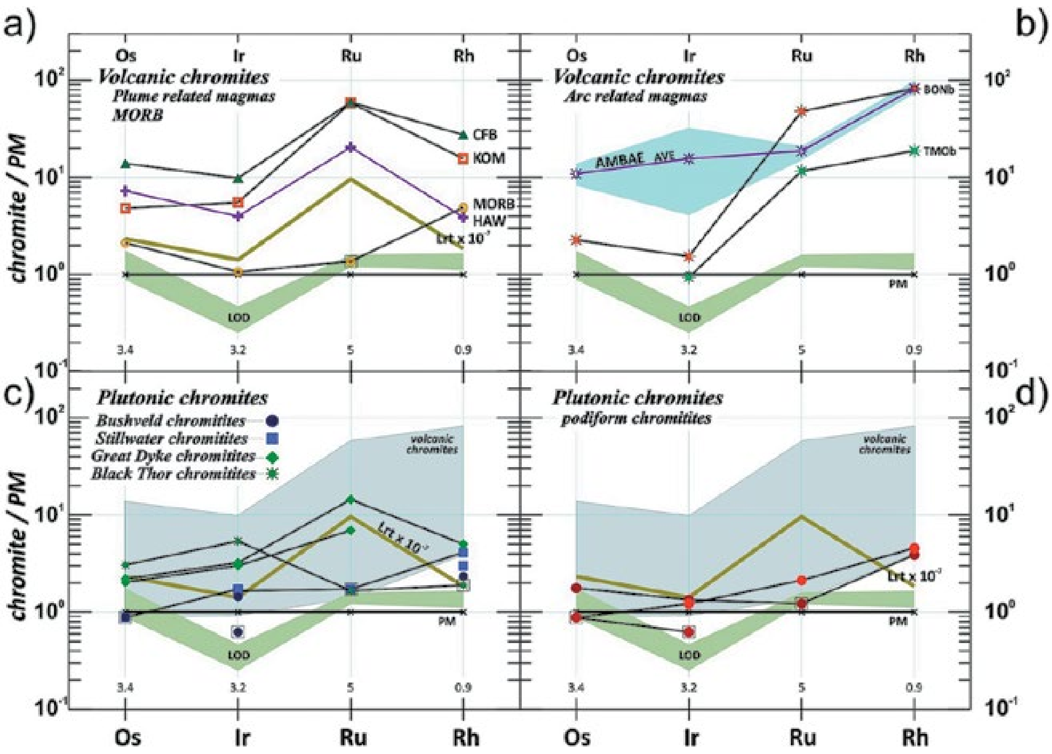

*Fig. 1*. Primitive mantle normalized IPGE profiles for chromite from volcanic settings; a) CFB=Continental flood basalt, KOM=komatiites, HAW=Hawaiian tholeiite, and MORB, b) BONb=boninite from Bonin, TMOb=boninite from Thetford Mines ophiolite, Ambae Ave=average and field for Ambae island arc volcano (from Park et al., 2012), and for chromite from plutonic settings c) from various layered intrusions, d) from mantle section of Thetford Mines and Mirdita ophiolites. For comparison, the profile of laurite (Lrt x10$^{-7}$) is added. Normalizing values (in ppb, Os=3.4; Ir=3.2; Ru=5.0; Rh=0.9) from McDonough & Sun (1995). LOD=Limit of detection

except chromites from the Great Dyke and from Black Thor chromitites which show IPGE contents ranging from 2x to 15x mantle (Fig. 1c). For comparison, the PM$_N$ profile of laurite has been added (Figs. 1a,c,d) to show its similarity with the PM$_N$ IPGE profiles of the chromite from plume related lavas.

Since plutonic chromites are known to contain laurite inclusions, there is maybe a link between IPGE poor plutonic chromite and the presence of these inclusions. Our results raise the question about the origin of these laurite inclusions, are they simply early magmatic phases entrapped in chromite? or the result of chemical exchange between base metal sulfide inclusions and host chromite during cooling, i.e. diffusion of Ni and Fe from sulfide into the chromite and diffusion of IPGE from chromite into the base metal sulfide to form laurite?

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# PGM IN THE STILLWATER CHROMITITES AND IMPLICATIONS FOR THE MAGMATIC PROCESSES THAT FORMED THE ULTRAMAFIC PART OF THE STILLWATER COMPLEX

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**ABSTRACT**. The distribution of PGM provides insights into the processes forming PGE deposits. PGM have been located in 8 chromitite layers from basal layer A to top layer K in the ultramafic units below the economic PGE-rich JM reef in the Stillwater complex, USA. Within chromite grains most PGM are laurite, with rarer, smaller PPGM including malanite [CuPtRh(+/-Ir)S] and Pt-Pd-sulfides. Interstitial to chromite grains PPGM dominate including Pd-Pb, PtPd-tellurides, sperrylite, platarsite, minor laurite and one grain of Pd-Ge. The laurite shape reflects formation and varies from mainly round in lower and upper layers, to euhedral in the thicker middle G layer. The Os content of laurite is lowest and silicate inclusions with laurites are most abundant in layer G. Rutile inclusions are most abundant in layer B. Trace Rh in laurite and PPGM with laurite are most abundant in the uppermost layer K and laurite size increases upwards. Each layer has a distinct PGM assemblage. Within chromite grains IPGE- and PPGE-PGM are greatest in the upper layers suggesting increasing PGE content in the magma upwards whereas interstitial PGM associated with BMS indicate sulphur saturation occurred between chromite grains in the lower layers.

## INTRODUCTION

The Stillwater Complex in Montana USA is a layered intrusion of 2705+/–4Ma, is divided into Basal, Ultramafic, Lower, Middle and Upper Banded series (Zientek et al., 2002). The lower part of the Ultramafic series contains harzburgite with chromitite layers numbered from the base upwards A to K. The aim of this study was to examine the PGM in these chromitite layers and determine whether there are any systematic differences between the layers that may lead to an increased understanding of the processes that concentrate PGE in these chromitites.

## RESULTS

Out of 145 PGM observed within chromite grains 136 are laurite ranging from 1x1 to 9x18 µm in size with a total area in 2D of 2234 µm$^2$. PPGM within chromite grains are always associated with laurite, with a total area of only 19 µm$^2$ and consist of Pt-Pd-Rh-Ni-Cu-Fe sulphides including malanite. Laurites are largest in the upper layers J and K and average 7.5% Os. These are mostly subhedral with a few perfect spheres in layer K. PPGM associated with laurite and traces of Rh (approximately 2%) in laurite are both most abundant in the uppermost layer K. The middle layer G contains smaller laurites that are often euhedral and average only 5.4% Os. Silicate inclusions associated with these laurites are most abundant in this layer. The middle chromitite G is devoid of PPGM both within and interstitial to the chromite. The laurites in the lowest chromitite layers A and B are smallest and are round with an average of 8.5% Os. Most of the rutile inclusions associated with laurites occur in layer B. The Rh-poor PPGM interstitial to the chromite grains are most abundant in the lowest chromitite layers A and B. This assemblage consists of Pd-Pb+/–Hg, Pt, Pd tellurides, sperrylite, minor laurite and one grain of platarsite and one of Pd-Ge. These PPGM are tiny, only 0.1-4 µm in diameter, whereas the largest interstitial laurite is 14 µm in diameter.

## DISCUSSION AND CONCLUSIONS

The presence of composite grains of PGM in the chromite grains suggests that some PGM crystallized prior to chromite formation and sulfur saturation. The systematic changes in PGM morphology, size, and composition within the chromitite layers record PGE magma composition just prior to formation of each chromitite layer and show that the crystallization occurred in an evolving magma that became richer in all 6 PGE towards the top of the chromitite layers. The interstitial PPGM in the lower layers may have formed from exsolution from the associated BMS that was As- Te- and Bi-bearing and records crystallization and sulfur saturation post chromite crystallization. The predominance of euhedral laurite in the middle G chromitite may be due to this being the thickest chromitite where subsolidus recrystallization and annealing was most prominent. Each chromitite layer has a distinct

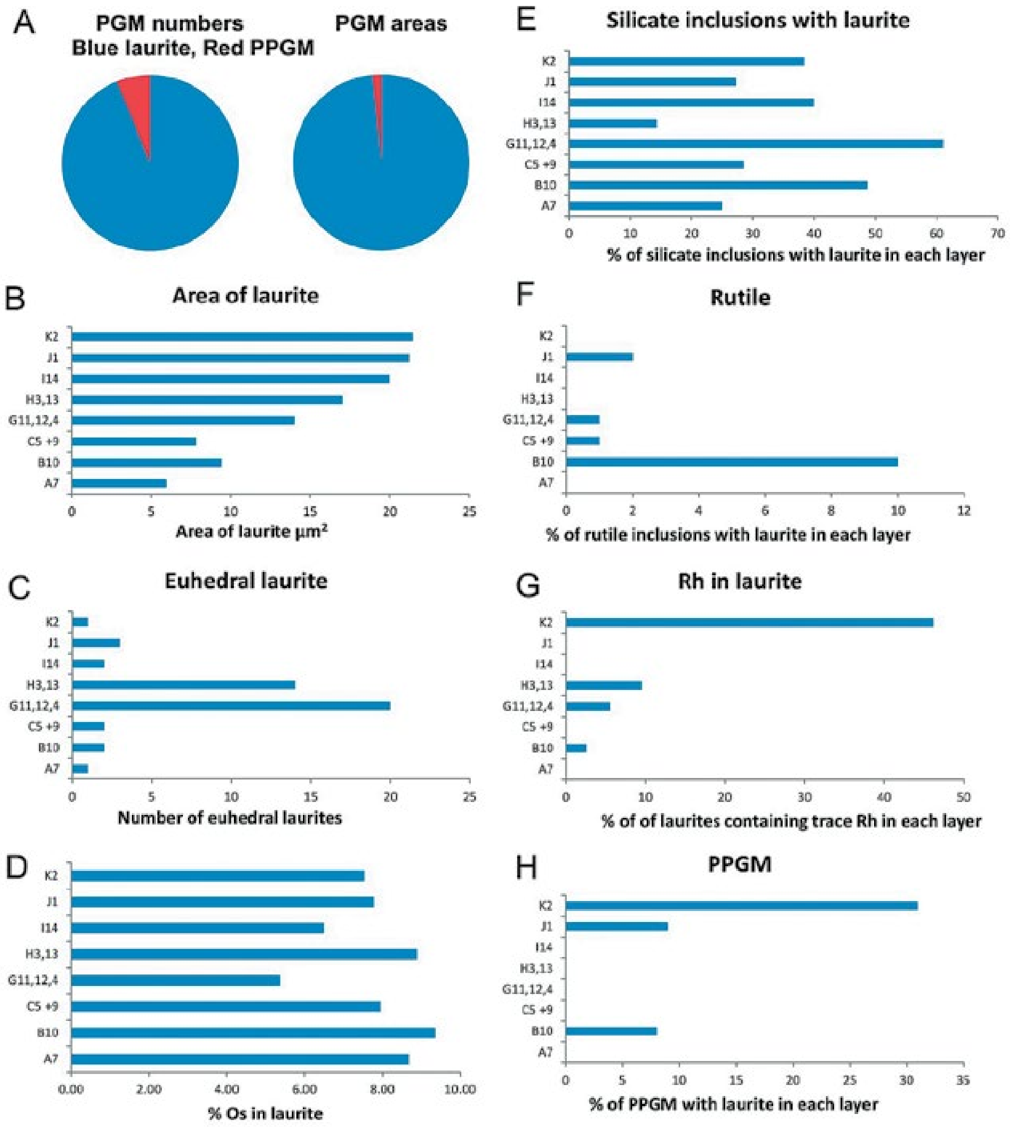

*Fig. 1*. Characteristics of the PGM within the chromitites. A) PGM types by number and area, B-F) variations in PGM with stratigraphic height through layers A to K), B) Laurite size, C) Laurite shape, D) Os content in laurite, E) % of laurite with silicate inclusions, F) % of laurite with rutile inclusions, G) % of laurite containing Rh, H) % of laurite with PPGM in composite grains

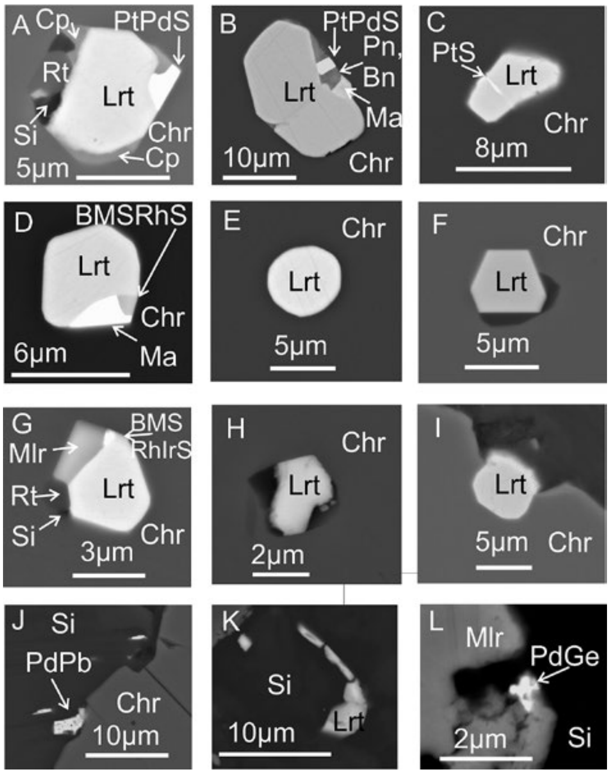

*Fig. 2.* Backscattered scanning electron microscope images of PGM A) Composite grain from chromitite J, B) largest laurite in a composite grain from chromitite K, C) Pt-S infilling a crack in laurite from chromitite K, D) Composite grain of laurite and PPGM from chromitite K, E) Rounded laurite from chromitite K, F) Euhedral laurite with a silicate inclusion from chromitite G, G) Composite grain of laurite from chromitite B, H) Corroded laurite from chromitite layer G, I) Laurite on the edge of a chromite grain from chromitite G, J) Interstitial Pd-Pb-Hg in serpentine on the edge of a chromite grain from layer B, K) Laurite [Ru(Os,Rh)$S_2$] in silicate from layer A, L) Pd-Ge on the edge of millerite and in contact with silicate from layer B. Symbols Cp=chalcopyrite, Mlr=millerite, Pn=pentlandite, Bn=bornite, Si=silicate, Chr=chromite Rt=rutile, Lrt=laurite, PtPdS=Pt-Pd-S, Ma=malanite, PdPb=Pd-Pb-Hg, PtS=Pt sulfide, BMSRhS=Ni-Fe-Cu-Rh-S, BMSRhIrS=Ni-Fe-Rh-Ir-S

PGM assemblage suggesting that there was no mixing of the different chromitite layers by slumping.

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# MAGMATIC Ni-Cu-PGE DEPOSITS IN SMALL INTRUSIONS: PROCESSES AND FUTURE RESEARCH DIRECTIONS

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**ABSTRACT**. As a result of ongoing field, analytical, experimental and geochemical studies our knowledge of the genesis of Ni-Cu-PGE deposits continues to increase. Closed system processes that may have controlled the evolution of relatively thin, strongly differentiated, intrusions provide an end-member for the study of PGE-enrichment in mafic to ultramafic systems. Although we have reached a stage where the enrichment of metals and the attainment of sulfide saturation in a mafic intrusion is predictable, our knowledge of the physical processes that control sulfide liquid accumulation and the formation of compositionally and mineralogically distinct layers in such intrusions is inadequate and limits accurate predictive models for ore genesis.

Exploration for PGE deposits has been and continues to be a particularly difficult undertaking. This is not a result of a lack of capable field and analytical techniques; the mobility of the PGEs in low-temperature environments is well-understood and exploration geochemical methods are sound. The extreme difficulty lies in that we have so few operating deposits, and the best occur in very large igneous bodies, only a few of which are known in continental settings. Despite many years of excellent research on reef-type occurrences in the Bushveld Complex, Stillwater Complex, and the Great Dyke, there remains considerable uncertainty as to how theses deposits formed. We know more about smaller reef-type occurrences in much more spatially restricted intrusions such as the Platinova Reef in the Skaergaard (Holwell & Keays, 2014), and PGE enriched layers in intrusions such a Stella (Maier et al., 2003) and Sonju Lake.

The Sonju Lake intrusion in Minnesota occurs as a ~ 1200 m thick sheet located within the ~ 1.1 Ga Midcontinent Rift System. Olivine –rich rocks occur in the lower portion of the intrusion, grading upwards through oxide-rich gabbro and apatite-bearing diorite (Miller & Ripley, 1996). The intrusion provides a natural laboratory for the study of differentiation processes and metal distribution that appear to have occurred *in situ*. Miller (1999) has shown that a ~ 100 m thick zone of PGE enrichment occurs at the level of the ferrogabbro. Unfortunately, grades only locally exceed 1 ppm Pd and much less Pt. Cu also peaks near the PGE enrichment, but Ni has been sequestered by early-forming olivine. Ni contents drop to values less than 20 ppm at and above the level of the PGE concentration. The occurrence is an excellent example of PGE, Cu and Au enrichment as a result of fractional crystallization, and illustrates several important aspects of magmatic Ni-Cu-PGE ore formation. Perhaps first is the clear need for the relatively early attainment of sulfide saturation in an intrusion if Ni-rich sulfide mineralization is to result. A corollary to this is that for intrusions the size of Sonju Lake, early sulfide saturation driven by a process such as Si-contamination will not produce economic sulfide-rich accumulations. This is the case even though orthopyroxene may be produced instead of olivine, and due to its lower D (Ni) value will deplete the magma in Ni to a lower degree than would olivine. The cotectic proportion of sulfide (i.e., that amount controlled by the sulfide saturation surface) is produced by such a process, and even with very efficient collection of sulfide sufficient tonnages of Ni-rich mineralization cannot be produced. Whether or not an immiscible sulfide liquid will separate once saturation is achieved is difficult to predict, but with cooling and crystallization immiscible sulfide liquid will normally form, but in insufficient quantities to generate Ni-rich ore. The problem is not one of relative Ni abundance, but is related to the amount of sulfide that can possibly be collected through physical processes. The attainment of sulfide saturation via the addition of externally derived sulfur provides a method by which sulfide supersaturation may be attained, and potentially economic tonnages of Ni-rich sulfide produced. With the early attainment of sulfide supersaturation Cu and PGE enrichment will accompany that of Ni. However, the attainment of early sulfide supersaturation generates a potential deterrent for possible PGE enrichment. In the simplest terms this is a mass balance (R-factor) dilemma; too much sulfide in the system (lower R-factors) will dilute the PGE grade. The balance is a relatively delicate one if Ni- and PGE-rich occurrences are to be produced.

In the absence of external sulfur addition, the level at which sulfide saturation would have been attained in the Sonju Lake intrusion is predictable using codes such as MELTS (Ghiroso & Sack, 1995) and an equation for sulfide solubility such as that of Li & Ripley (2009), or COMAGMAT (Ariskin et al., 1993). For a reasonable parent magma composition sulfide saturation in the Sonju Lake intrusion is predicted to have been attained when magnetite began to crystallize; the drop in iron content of the magma strongly impacts its ability to dissolve sulfide. At this point the Ni content is predicted to have dropped significantly due to olivine crystallization, as observed. Although the level at which PGE enrichment related to sulfide saturation is predictable, the width of the enriched zone is not. Clearly, if the PGEs were not dispersed over 100 m but rather concentrated within a 1 to 5 m thick reef a very different profitability prospectus emerges. Although it appears that the PGEs, Cu and Au were concentrated in residual liquid, we do not understand if immiscible sulfide liquid separated from the entire mass of residual liquid or from only a boundary layer above the collection of solidified crystals, and what processes governed the thickness of the anomalous PGE enrichment. Topics such as these that pertain to physical processes in magmatic systems are key directions for future research. In truth, this is a problem that is inherent in the interpretation of all layered intrusions, and not specific to horizons of potential metal enrichment. However, if widely dispersed zones of PGE enrichment are the norm in systems where fractional crystallization appears to have occurred in a closed system, the formation of much thinner and more concentrated reefs, such as the Merensky Reef of the Bushveld Complex and the J-M Reef of the Stillwater Complex, is likely to have involved the emplacement of discrete magma pulses whose enrichment in PGEs is not related to an *in situ* process.

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# ACCESSING TEMPERATURE AND MANTLE SOURCE LITHOLOGY OF THE ORE FORMING MAGMAS

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**ABSTRACT**. The paper demonstrates significantly higher potential temperatures of mantle plumes and LIPs compared to MORB and suggests significant role of olivine-free hybrid lithologies in origin of magmas forming PGE, Ni, and Cu ores.

The composition of source and formation conditions of mantle derived magmas play crucial role in their ore potential. It is widely accepted that the incorporation of subducted material into the mantle, the ascent of hot plumes from the mantle core boundary or within the mantle, and melting and reaction between different lithologies have modified the mantle mineralogy and chemistry in a way that has a profound effect on its partial melts (Hofmann & White, 1982; Sobolev et al., 2007, Herzberg, 2011). Because the hybrid lithologies (garnet pyroxenite) resulted from reaction of partial melts of recycled crust (eclogite) with mantle peridotite are essentially olivine-free, they are melted out at a much earlier stage and to significantly higher extent than an unreacted peridotitic mantle (Sobolev et al., 2007). Because pyroxenite-derived melts do not leave olivine and sulphide in their restites one should expect their enrichment in Ni, Co, PGEs and Cu. In addition, such melts are expected to be severely sulphur undersaturated and thus should accumulate chalcophile elements during their fractional crystallization. All these illustrate importance to understand whether olivine-free hybrid lithologies were involved in the source of ore forming melts and what were their melting conditions.

In this paper I will overview new developments in estimating source lithologies and potential temperatures of mantle derived melts using compositions of their liquidus assemblages of olivine and spinel. I will present the new formulation of olivine-spinel Al-Cr geothermometer (Wan et al., 2008; Coogan et al, 2014) based on our recent high-temperature experiments with controlled oxygen fugacity and will use it to estimate potential temperature of mantle sources of different OIBs, LIPs and MORBs (Sobolev et al., 2013). I will demonstrate significantly higher potential temperatures of mantle plumes and LIPs compare to MORB. I will review usage of Ni, Mn, Ca contents of olivine to estimate proportions of hybrid pyroxenite (Sobolev et al., 2007; Herzberg, 2011; Matzen et al., 2013) in the sources of mantle derived magmas and will discuss usage of other trace elements in olivine (Cr, Co, Zn, Sc) for this task. Finally, I will demonstrate significant role of olivine-free hybrid lithologies in origin of magmas forming PGE, Ni, and Cu ores.

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# IS CRUSTAL CONTAMINATION CRUCIAL FOR SULFIDE IMMISCIBILITY? IMPLICATIONS FROM PGE-DEPLETION OF THE LAYERED INTRUSIONS IN THE EMEISHAN LARGE IGNEOUS PROVINCE, SW CHINA

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**ABSTRACT**. Most of the layered intrusions in the central Emeishan Large Igneous Provence represent magma chambers of magma plumbing systems. Extensive fractional crystallization of silicates rather than crustal contamination in deep-seated magma chambers resulted in sulfide segregation and PGE depletion in the residual magma. When the PGE depleted magma entered the layered intrusion, crystallization of Fe-Ti oxides triggered secondary sulfide segregation and the sulfide liquids may by upgraded in PGE via reaction with new injected magma. Thus, the samples of the intrusions have large variation in PGE.

A series of Permian mafic-ultramafic layered intrusions in the central zone of the Emeishan large igneous province (ELIP), SW China, were considered associated with the high-Ti basaltic magma resulted from partial melting of a ~260 Ma mantle plume (Zhou et al., 2008; Song et al., 2005). These layered intrusions, including Panzhihua, Baima, Taihe and Hongge, are characterized by unusually thick stratiform massive Fe-Ti oxide layers (up to 60 m thick) and magnetite gabbro (up to 200 m thick) in the lower or middle zones (Panxi Geological Unit, 1984). Although thin PGE-reefs have been discovered in the lower zone of the Xinjie intrusion (Zhong et al., 2011), the other layered intrusions are characterized by PGE depletion (Zhang et al., 2013; Bai et al., 2013). Recent studies indicated that the layered intrusions represent the magma chambers in magma plumbing systems (Song et al., 2013; Zhang et al., 2012; She et al., 2014; Luan et al., 2014). The parental magmas had been variable Fe-Ti enriched due to different degrees of silicates fractionation in deep-seated magma chambers. To demonstrate the PGE geochemistry of the layered intrusions in the central ELIP, we collected recent published and unpublished data of PGE, trace elements and Nd isotope of the layered intrusions and the Emeishan high-Ti basalts (Zhong et al., 2003; Song et al., 2009; Howarth & Precev, 2013; Zhang et al., 2013; Bai et al., 2013).

As shown in Figure 1, the samples of the layered intrusions except some of the Hongge intrusion have a very small variation in Nd isotope, demonstrating compositional variation dominantly controlled by fractionation rather than crustal contamination. However, the layered

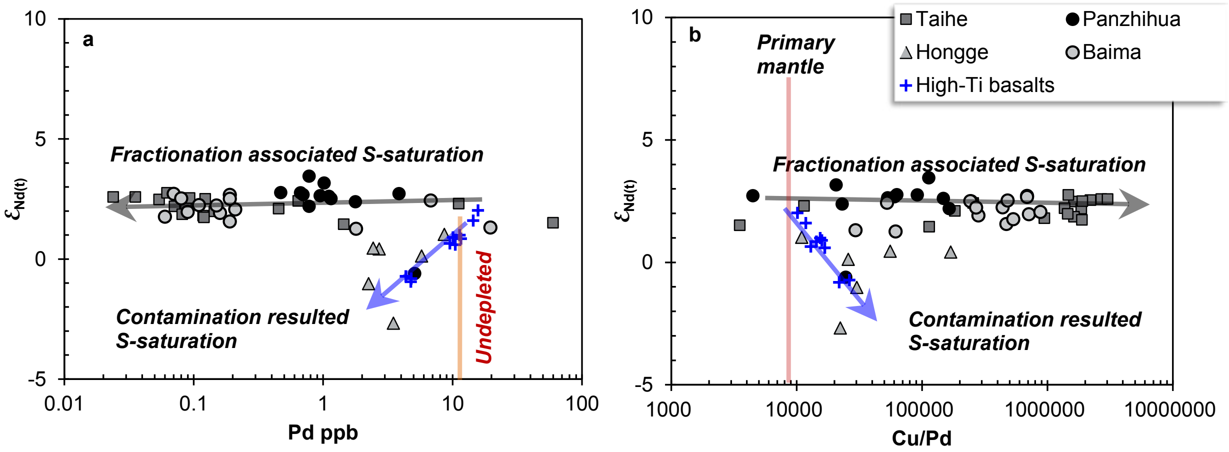

*Fig. 1.* Binary plot of $E_{Nd(t)}$ versus Pd concentration (a) and ratio of Cu/Pd (b)

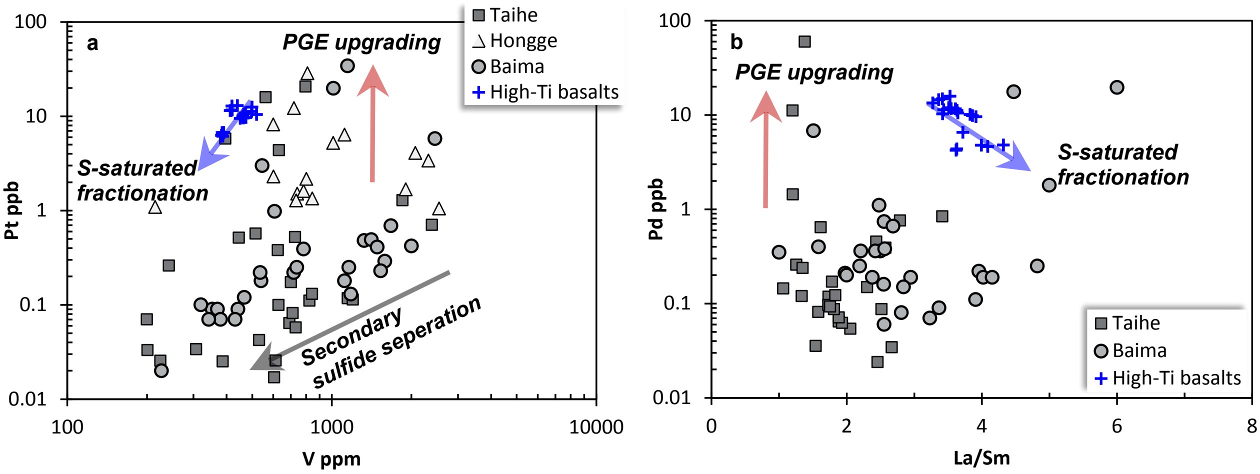

*Fig. 2.* Binary plot of V versus Pt (a) and La/Sm versus Pd (b)

intrusions display large variation in Pd concentrations and Cu/Pd ratios (Fig. 1). Particularly, Pd concentrations of most of the samples are less than 1 ppb, evidently lower than those of the high-Ti basalts. Correspondingly, the samples have Cu/Pd ratios much larger than that of the primary mantle (Fig. 1), indicating that their parental magmas were S-saturated and Pd-depleted before entering the intrusions. Although the samples of the Hongge intrusion show a negative correlation between Pd and $E_{Nd(t)}$ along with the high-Ti basalts, their weak Pd depletion and low Cu/ Pd ratios relative to the other intrusions suggest that crustal contamination is not the critical factor for the PGE depletion in the rocks. Thus, we propose that the sulfide immiscibility and segregation most likely occurred in magma chambers at depth during fractional crystallization of olivine, pyroxene and plagioclase. A problem is why the layered intrusions have so large variation in PGE concentrations.

Petrographic observations have indicated that the Fe-Ti oxide ore layers contain up to 2-3 modal % sulfides. Consistently, Pt is positively correlated with V for most of the samples from the intrusions (Fig. 2a). This implies secondary sulfide segregation was triggered by the crystallization of Fe-Ti oxides during fractionation of the PGE-depleted parental magmas. Thus, there is not a correlation between Pd concentration and La/Sm ratios, which become larger as fractional crystallization of pyroxene (Fig. 2b). Plots of Figure 2 also appear that some samples of the layered intrusions are richer in Pt and Pd than the high-Ti basalts. The PGE enrichment in some samples, which have large ranges of La/Sm ratios and V concentrations, can be attributed to upgrading of PGE due to the reaction of the sulfide liquid and new magmas.

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# Ni-Cu-PGE TARGETING USING LITHOGEOCHEMISTRY

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**ABSTRACT**. Lithogeochemistry can be a powerful tool when used for Ni-Cu-PGE targeting in mineral exploration at both the regional and project scale. It can be used to identify prospective magmatic events, and to identify main magma conduit pathways and prospective intrusions.

Ni-Cu-PGE sulfide mineralization is typically hosted in ultramafic-mafic magmatic systems, including extrusive (flows) and intrusive (sills, dykes and chonoliths) environments. A majority of these events are associated with large igneous provinces, typically Proterozoic or Archean in age, but not always (e.g., Permian age for Noril'sk). During targeting, it is important to identify favourable magmatic events. The most favourable events are associated with major lithospheric breaks, in particular those adjacent to rigid Archean lithosphere. Such locations are important because it is believed that rigid lithosphere aids in focusing higher flux, more effusive, and more dynamic magmatic systems (e.g., Begg et al., 2010). Exploration targeting for Ni-Cu-PGE mineralization is a multidisciplinary process involving geophysical surveys, geological and, structural interpretation, lithogeochemistry and surficial geochemistry, and occurs in multiple stages and at multiple scales. In this contribution we focus on the role of lithogeochemistry during targeting.

Delineation of Ni-Cu-PGE prospective from non-prospective magmas and intrusions is very important during evaluation for both terrain-scale targeting and project-scale targeting. A number of lithogeochemical investigating methods are employed. These include:

1. Identifying magmas with high background metal contents *[Terrain scale targeting]*

An unpublished CAMIRO study of 110 mafic-ultramafic intrusions in Ontario (Sproule et al., 2005) noted that the background chalcophile element abundances of PGE mineralized intrusions possessed significantly higher background PGE abundances than those of PGE unmineralized intrusions. Similar observations of published and unpublished data sets from other economic Ni-Cu-PGE mineralized intrusions reveal similar features. This is particularly evident in intrusive conduit and chonolith-hosted of komatiitic basaltic to high MgO basaltic magmatic affinity.

Interpretation of Ni abundances in magmas is complicated by its dual lithophile and chalcophile nature. Cu can be successfully utilized, however Cu abundances are strongly controlled by fractionation. Thus, an anomalous Cu abundance in a gabbro differs strongly to that of a peridotite. In contrast, interpretation of PGE abundances is far simpler. Background abundances are determined using log normal probability plots to identify populations. Typically, background abundances of >50 ppb Pt+Pd in unmineralized rocks are considered anomalous and may indicate a fertile, potentially prospective system. It is very important to note that this work must exclude high S rocks (max 2% S).

2. Identifying the most primitive areas of magmatism in a suite of intrusions *[Terrain to project scale targeting]*

It is important to look for the most primitive or rocks derived from the highest MgO portions. These primitive portions can represent the main magma pathway in complex "plumbing" systems in conduits and chonoliths, and the most effusive, metal-rich portions. This does not just imply searching for the highest MgO rocks, as cumulate processes can result in accumulation of phases such as olivine increasing MgO. The highest MgO parental magma portions can be identified using the following processes:

Identification of preserved little-altered chilled margins (rare).

Identifying the highest forsterite in preserved olivines. Preserved olivine is rarely observed in most Proterozoic to Archean magmatic systems.

Identification of high forsterite modal olivine from whole rock geochemical data using Niggli norms (this can be calculated using freeware such as GCD Kit: http://www.gcdkit.org/). This method is very effective, particularly in Archean and Proterozoic magmatic systems.

3. Localized areas with enrichment in chalcophile elements *[Project Scale Targeting]*

The elements of interest, in order of importance, are Pt, Pd, Au, Cu and Ni. Pt and Pd are preferentially utilized for this assessment as they are less affected by alteration and/or metamorphism, and the scale of difference between mineralized and unmineralized intrusions is far more marked. Cu can be successfully utilized, however Cu abundances are strongly controlled by fractionation, and are typically affected by alteration and/or metamorphism particularly in Archean and Proterozoic rocks. Ni is both lithophile and chalcophile so interpretation of abundances can be complicated, however values >3,500 ppm Ni are an indicator of enrichment as such abundances are mostly not possible from lithophile elements alone (assuming that there has been no development of surficial phases such as garnierite). It is redundant to search for complimentary depletion in chalcophile elements. Furthermore, solely using chalcophile element depletion as an indicator of Ni-Cu-PGE mineralization can be misleading.

4. Higher tenor portions *[Project Scale Targeting]*

Tenor is the amount of metal in 100% sulfide (not to be confused with R factor which is the mass ratio of silicate magma with which a segregated sulfide *l*iquid has equilibrated). Intrusions or flows with high tenor sulphides are usually associated with the most dynamic portion of a magmatic system representing a conduit zone or magma pathway and is considered most prospective.

High tenors are marked by elevated chalcophile element/sulfide ratios. It is preferred to use Pt and Pd as the chalcophile elements (e.g., Pd/S and/or Pt/S) as their partition coefficients are high (Kd > 10,000 between sulfide and silicate melt), thus these elements are more sensitive to changes in R factor. Importantly, these elements are less affected by alteration and/or metamorphism compared to Cu. In many data sets, S data is unavailable and can also be affected by redistribution of S during alteration and/or metamorphism. In this case, Cu can be used as a proxy, e.g., Pd/Cu or Pt/Cu as a tenor proxy. Se can also be used a proxy for S, e.g., Pd/Se or Pt/Se as a tenor proxy. However, most commercial laboratories provide poor Se data as the detection limits are too high.

5. Crustal contamination *[Project Scale Targeting]*

This is not a requirement for Ni-Cu-PGE deposits (and is not observed in some major Ni-Cu-PGE deposits such as Jinchuan or Nebo Babel), but is commonly observed in most significant deposits (e.g., Noril'sk, Voisey's Bay). Methods for identification of crustal contamination include:

Trace element lithogeochemical indicators (commonly used) such as enrichment in large ion lithophile elements relative to high field strength elements, coupled with depletion in Nb relative to elements such as Th.

S/Se ratios (rarely used). This method is less reliable for altered and metamorphosed rocks, and most commercial laboratories do not provide sufficiently low level detection limits for Se.

Stable and radiogenic isotopic indicators (rarely used). These methods are expensive and too slow in the time frame of most exploration programs.

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# PARENTAL MAGMA CHARACTERISTICS OF THE XIANGSHANZHONG MAFIC-ULTRAMAFIC INTRUSIONS RELATED MAGMATIC Cu-Ni SULFIDE DEPOSIT IN JUELUOTAGE, XINJIANG, NW CHINA

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**ABSTRACT**. Several sulfide ore-bearing mafic-ultramafic intrusions occur along the southern margin of the Late Paleozoic Central Asian Orogenic Belt (CAOB) in north Xinjiang, NW China. Their origin and relationship with the Permian basalts in the region remain equivocal. In this study, we investigate the olivine clinopyroxenite of Xiangshanzhong mafic-ultramafic in eastern Tianshan, and therefore speculate the parental magmas genesis of the Xiangshanzhong intrusion.

The Eastern Tianshan region in NW China represents a complex Paleozoic orogen, located between the Junggar and Tarim blocks, and form part of the CAOB. During the prolonged orogenic events associated with the collision between the Junggar and Tarim blocks in the Paleozoic, a suite of mantle-derived mafic-ultramafic rocks, which typically host magmatic copper-nickel platinum ore deposits, were emplaced along the east-west axis of the Tianshan Mountains (Wang et al., 2006; Mao et al., 2008). These mafic-ultramafic complexes have Permian formation ages, ranging from 279 to 285 Ma (Han et al., 2004; Zhou et al., 2004; Wu et al., 2005; Zhang et al., 2008). Mineral exploration work in recent years has led to the discovery of several Permian mafic-ultramafic intrusions with associated magmatic Cu-Ni sulfide deposits in the Eastern Tianshan region. The scale of these deposits mostly reached to big/medium-size. Furthermore, many studies have also documented coeval basalts in the adjacent areas. The relationship between the Permian basalts, which cover large areas in the Eastern Tianshan and the Tarim region, and the formation and emplacement of the Eastern Tianshan mafic-ultramafic intrusions remain unclear.

The magmatic Cu-Ni sulfide deposit in the southern margin of CAOB located in different tectonic unit can be divided into four main metallogenic belts from north to south: Altai, Jueluotage, Central Tianshan and Beishan metallogenic belts. All the sulfide-bearing mafic-ultramafic intrusion in above four belts can be divided into single intrusion, multiple small complex, and large complex according to the area of the outcrop. The profile shape of large complex is basin shaped, multiple small complex are mostly basin shaped, and the profile of single small rock as dykes. We attempt to reveal the characteristics of source, and further indicted the parental magma of the Xiangshanzhong sulfide-bearing mafic-ultramafic intrusion in Jueluotage.

We founded the occurrence of olivine clinopyroxenite in the Xiangshanzhong intrusive complex with visible pyroxene cumulate structure, high Mg, low Cr, Na, and Ti contents, and characterized by distinctively low trace element contents. Our data suggest that the clinopyroxene in the olivine clinopyroxenite probably crystallized from an earlier batch of magma. The rare earth element (REE) patterns and εNd values of the Xiangshanzhong mafic-ultramafic units suggest that these rocks represent cumulates of basaltic composition that were likely co-genetic and derived from the same magmatic source. The presence of phlogopite and amphibole, occurrence of Zr, Hf, Nb, and Ta negative anomalies, the trace element abundances of the parental magma, and the Nd isotopes (+5.9 –+8.3) of whole-rocks suggest that the source of the Xiangshanzhong complexes may be a depleted mantle metasomatized by subducted slab-derived fluid or melt. Furthermore, the ($^{87}$Sr/$^{86}$Sr)i ratios, εNd(t) values and trace element geochemistry of whole-rock and clinopyroxene grains are consistent with those of the Permian Tuha basin basalts. As well as the closest position in space, we propose the Permian Tuha basin basalt and Eastern Tianshan intrusions are the products of the same magma. The major oxides compositions of the Tuha basin basalts show the trend of hydrous basaltic magma crystallization frication, so the parental magma of intrusive rocks should also be hydrous. The trace and REE primitive mantle and chondrite pattern of melt inclusion in olivine phenocrysts of Tuha basalts display MORB characteristics. The above hydrous, Nb and Ta deplete, MORB magma characteristics of Eastern Tianshan intrusions reveal the source subducted metamorphism. Further model indicted that the addition of subduction fluid and oceanic sediment in Jueluotage and Altay is lower than that of Central Tianshan and Beishan. The Xiangshanzhong intrusion has characteristics of both plume and subduction-related origin and we therefore speculate that the partial melting of subduction-related depleted mantle triggered by Permian plume activity during the post-collision extension regime generated the parental magmas of the Xiangshanzhong intrusion. The occur of subduction fluid, reduce the melting point, increase the partial melting degree of magma source, and formation Cu and Ni rich parental magma, which is conducive to form magmatic Cu-Ni sulfide deposit in Jueluotage, Xinjiang.

*Acknowledgments. This study was financially supported by the Natural Science Foundation of China (Nos. 41002026 and 41030424) and China Postdoctoral Science Foundation funded project to Dr. Dong-Mei Tang.*

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# PGE GEOCHEMISTRY AND METALLOGENESIS OF THE NEWLY-DISCOVERED TAMARACK MAGMATIC Ni-Cu-(PGE) DEPOSIT, MINNESOTA, USA

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**ABSTRACT**. The Tamarack Ni-Cu-(PGE) deposit is hosted in the Tamarack Intrusive Complex (1105.6±1.2 Ma) within the Paleoproterozoic Animikie Basin and associated with the Midcontinent Rift System, Minnesota. The sulfide mineralization has a typical magmatic pyrrhotite-pentlandite-chalcopyrite assemblage. Variations in PGE characteristics are modeled by R-factor estimates (disseminated sulfides) and by a sulfide liquid fractionation calculations (semi-massive and massive sulfides). The disseminated sulfides are suggestive of equilibration at R-factors between 100 and 10,000, most likely representing "effective" R-factors. Metal enrichment in semi-massive and massive sulfides likely resulted from extensive sulfide liquid fractionation.

The Tamarack Ni-Cu-(PGE) mineralization is hosted in the mafic-ultramafic Tamarack Intrusive Complex (TIC, 1105.6±1.2 Ma) within the Paleoproterozoic Animikie Basin and associated with the early stages of development of the Midcontinent Rift System (MRS) in NE Minnesota. Mineralization appears to have formed in a dynamic magmatic conduit system. The northern portion of the TIC, in a form of an irregular funnel, contains two main intrusive units that host the bulk of disseminated and net-textured mineralization in the system. The wide top portion (referred to as the FGO Intrusion), composed of fine grained peridotite, feldspathic peridotite, feldspathic pyroxenite, and melagabbro, hosts mostly disseminated and patchy net-textured sulfide mineralization. The FGO mineralization appears to occur in discrete layers more concentrated toward the bottom on this intrusion. The narrow, dike-like, bottom portion (the CGO Intrusion) is composed of coarse-grained peridotite, feldspathic peridotite, melatroctolite and melagabbro, and hosts disseminated and semi-massive (net-textured) sulfide mineralization localized at the core of the intrusion. Massive sulfides have been emplaced into the country rocks – slates and metagraywackes of the Upper Thomson Formation. The sulfide mineralization is characterized by a typical magmatic pyrrhotite, pentlandite, chalcopyrite and minor magnetite assemblage.

Modal proportions are similar in all sulfide types. In addition to variations in textures and host lithologies, PGE characteristics are distinctive. Nickel has a strong positive correlation with S in all sulfide types, while Cu and the PGE (except Pt) show strong correlation with S in semi-massive sulfides only. The disseminated sulfides in the FGO Intrusion show good correlation between the PPGE, Au and S but poor correlation between the IPGE and S. They are subdivided into two groups: relatively IPGE enriched and relatively IPGE depleted. Disseminated sulfides in the CGO Intrusion show good positive correlation between PGE, Au and S and PGEs and are strongly PPGE enriched. Semi-massive (net-textured) sulfides are Cu- and IPGE-enriched relative to PPGE except for one Pt-undepleted sample. Massive sulfides are subdivided into three groups: IPGE depleted – the only group where Cu positively correlated with S, one Pt-enriched but slightly IPGE depleted sample, and one PPGE depleted sample. Ni and Cu poorly correlate with the PGE in the disseminated sulfides, and do not correlate in the other sulfide types. Relatively good positive correlation between IPGE and PPGE is found for the disseminated sulfides in the FGO Intrusion, but not for any other sulfide type.

Variations in PGE characteristics are modeled by R-factor estimates for the disseminated sulfides and by a fractionation of an MMS from sulfide liquid calculations for the semi-massive and massive sulfides using accepted partition coefficients of the PGEs between sulfide and silicate liquids. Both the FGO and CGO disseminated sulfides are all suggestive of equilibration at R-factors in the 100 to 10,000 range. These values most likely represent “effective” R-factors which reflect the effects of varied processes occurring in the conduit system, including possible cannibalization of pre-existing sulfide. Variations in the semi-massive and massive sulfides associated with the CGO are representative of different amounts of MSS fractionation from a sulfide liquid of a primary composition consistent with an R-factor of ~400. The textural and spatial characteristics, along with the R-factor estimates and sulfide liquid fractionation modeling, suggest that several sulfide liquids were involved in the formation of sulfide mineralization in the TIC. The low initial concentrations of Ir, Os, Pt and Pd (0.1 ppb, 1 ppb, 2 ppb, and 1.5 ppb respectively) may be related to fractional crystallization of olivine and chromite, possible crystallization of IPGE minerals that saturated in the silicate liquid, and local fractionation of MSS. Enrichment of Ni, Cu and PPGEs in massive sulfides is thought to be produced as a result of extensive fractional crystallization of a sulfide liquid. Immiscible sulfide liquids are thought to have been transported via multiple pulses of magma within the conduit system. The sulfides were emplaced in the core of the conduit and in the wide bottom portion of the FGO as the velocity of the magmas dropped. The addition of crustal S is thought to have been the principal process which drove the early attainment of sulfide supersaturation in the magmas at depth.

# FORMATION OF NKOMATI MASSIVE CHROMITITE BODY VIA CRYSTALLIZATION WITHIN A MAGMATIC CONDUIT

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**ABSTRACT**. The general upward decrease in the Cr/Fe and Mg/Fe ratios of Bushveld chromite which is observed through the Lower and Critical Zone is consistent with a trend of magmatic differentiation of the whole complex (Hulbert & von Gruenevaldt, 1985; Scoon & Teigler, 1994; Naldrett et al., 2012). However, no zonal distribution of the major oxides or upward fractionation of chromite composition has been described in a particular layer that adds an additional argument in a favor of the Eales's model (Eales, 2000) that invokes crystallization of chromite in the staging chamber or conduit with the consequent injection of a chromite slurry. Here we report for the first time on a primary reverse zoning of a chromite composition preserved in the Nkomati thick chromitite body of Bushveld affinity, revealing its crystallization in situ from magma currents.

The layered mafic-ultramafic Uitkomst Complex, which hosts the Nkomati deposit, is an elongate tube-shaped body, at least 12 km long, that concordantly intruded sedimentary rocks of the Early Proterozoic Transvaal Supergroup (Gauert et al., 1995). The Complex is composed of several persistent stratigraphic units from the base upwards: Basal Gabbro 3-6 m thick, Lower Harzburgite 60-90 m thick, Chromitiferous Harzburgite and Massive Chromitite units with a total thickness of up to 60 m, Main Harzburgite up to 400 m thick, a Pyroxenite unit less than 100 m thick, and Main and Upper Gabbronorite units with chilled and quenched zones at the top contact (Gauert et al., 1995). The Complex is intruded into quartzite of the Black Reef and Oaktree Formations, Malmani Dolomite and shales and ironstones of the Timeball Hill Formation.

An unusual feature of the Uitkomst Complex is the occurrence of two types of mineralization that make up the Nkomati deposit: Ni-Cu-PGE sulfide ore, and massive chromitites together with the discontinuous chromitite seams and disseminated chromites. Uitkomst chromitites are located within the ultramafic sequence of olivine-rich rocks and carry accompanying sulfide and PGE mineralization. In this study, we analysed chromite from the thickest chromitites in the mining area intersected by the SHM022 borehole. The $Cr_2O_3$ content in chromite increases from 44 to 54.5 wt.% upwards in the upper massive chromitites showing an opposite trend to the differentiation. The general increase is not continuous but it is composed of five cycles which are separated by minor reversals (Fig. 1). The cyclic patterns are observed in the distribution of all major oxides with Al and $Fe^{3+}$oxides correlating negatively with $Cr_2O_3$ whereas MgO demonstrates a positive correlation. In the lower part of chromitiferous zone the $Cr_2O_3$ content in chromite decreases from 48 to 36 wt. % with height associated with a general decrease in chromite content down to 1-5 vol. % (Fig. 1).

We conclude that the changes in the chromite composition coupled with the cyclicity of textural changes in the chromitites and host harzburgite indicate the dynamic nature of their formation and multiple magma influxes into yet unconsolidated resident cumulates in the channel. Such a model is consistent with that suggested earlier by Gauert (1995). Evidence on the new influxes is also observed in the overlying harzburgite-dunite unit where brecciated chromitites and chromitiferous harzburgite are cemented by later chromite-poor harzburgite.

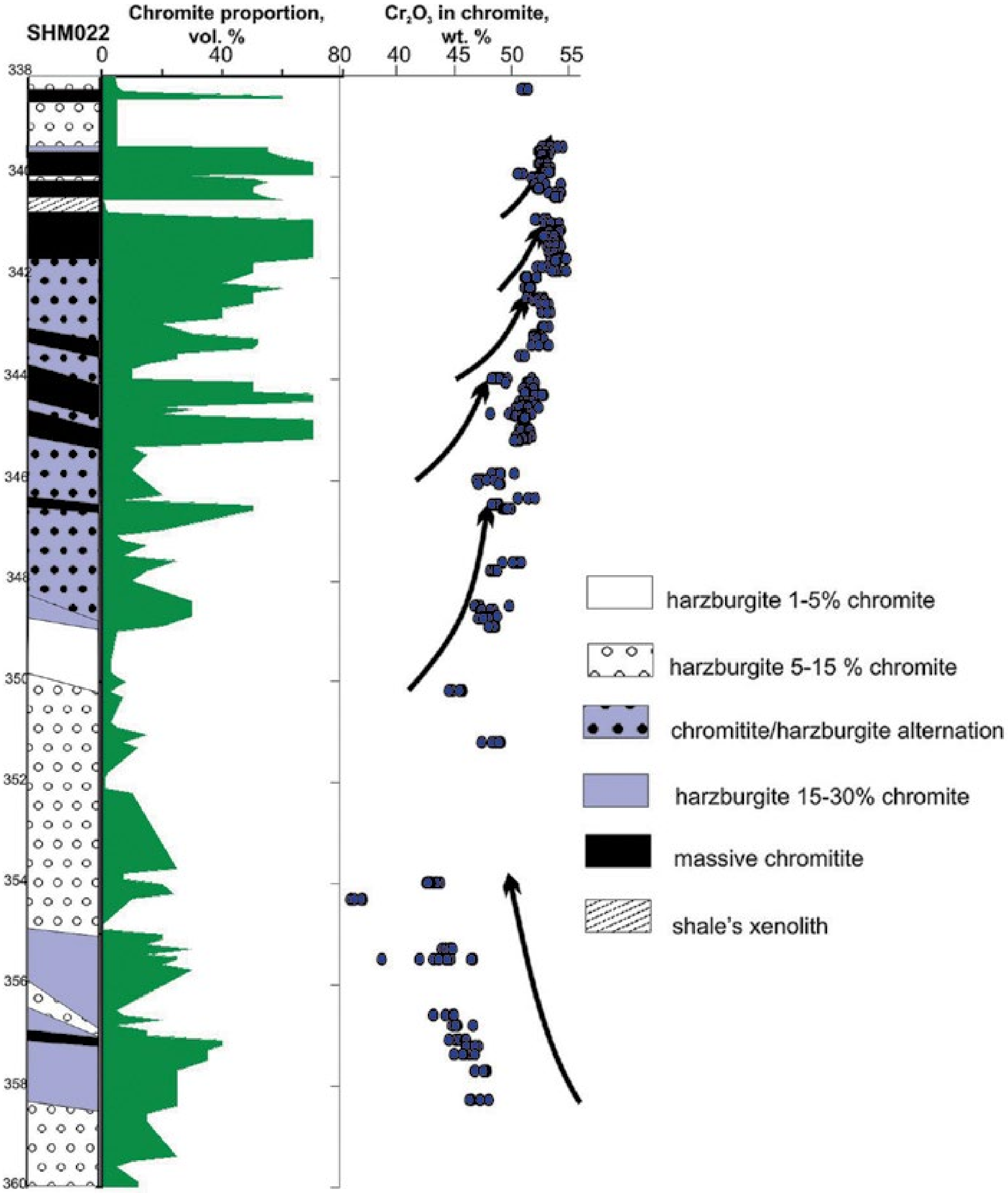

*Fig. 1.* Distribution of chromite and $Cr_2O_3$ content of chromite in the main Nkomati chromitite body through borehole SHM022

*Acknowledgements. The study is partially supported by the RFBR grant 14-05-00448a and SAR NRF through THRIP.*

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# STRUCTURAL SEQUENCE AND THE RELATIONSHIP WITH Cu-Ni SULFIDE DEPOSIT IN THE JINCHUAN AREA, GANSU, CHINA

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**ABSTRACT**. Ore-controlling structures have their own characteristics in the Jinchuan area. A deeper nappe fault of the Luliang stage, which occurs between the Bajiazuizi and Tamazigou Formations, made the hanging strata of Baijiazuzi Formation reversing and fragmentizing that created a chance for penetrating of ore-bearing magma which associated with later extensional structures. The Jinchuan area had been developed into a typical metamorphic core complex and accompanied by large-scale mafic-ultramafic magma intrusion during Middle and Late Proterozoic. Qilian orogeny is the major movement after forming of the Jinchuan ore deposit. A series of thrust and strike-slip faults made the Longshoushan metamorphic core complex gripping and bulge because of the collision. It composes a palm tree structure that builds the main regional structure framework. The Qilian-orogeny movement also led to the original stratiform ore-bearing magmatic intrusions rupture, strike-slip and tilt. Due to the uplift of the Tibetan Plateau, the new tectonic movement further pushed the ore-bearing magmatic intrusions to the Cenozoic alluvial layer.

The Jinchuan Cu-Ni sulfide deposit, which occurs in Precambrian metamorphic rocks, has extremely complex geological background. In this paper, authors report some new understanding for structural framework and its evolution in the area based on a systematic analysis about the features of stratum, major faults, basic-ultrabasic magmatism and regional metamorphism.

Tectonic setting of the Jinchuan area is in the Longshoushan, southwest margin of the Alashan block. A regional fault ($F_1$) locates in north side where is adjacent to the Chaoshui Basin, and another regional faults ($F_2$) is located in the south side near by the Hexi Corridor Basin (Fig. 1). Strata in the area consist of four major parts: (1) Achaean deep metamorphosed base (Baijiazuizi Formation); (2) Lower Proterozoic middle metamorphosed base (Tamazigou Formation); (3) Middle or Upper Proterozoic to Lower Paleozoic (Sinian-Cambrian) less metamorphosed cover (Shaohuotong Formation); (4) almost no metamorphosed Upper Paleozoic (mainly Devonian) cover. The major stratigraphic units show a zonal distribution of monoclinic layers which strikes to northwest, and trends to southwest. From northeast to southwest, the formation is from Baijiazuzi Formation → Tamazigou Formation → Shaohuotong Formation → Devonian, and that shows a metamorphic zonation from upper amphibolite facies to partial melting → lower amphibolite facies → greenschist facies → almost not metamorphosed Devonian calcareous sandstone.

Folds are not developed in the area, but faults. All of the four stratigraphic units have a fault contacting between each other. Series northwest-west, northwest-striking nappe faults, eastwest-striking extensional faults and northeast-striking slip faults form the structural framework in this area. All these indicate a complex structural background of superposition of multiple levels and multiple episodes.

According to a systemic survey of cross-sections in the area, the degree of migmatization increases from north to south in the Baijiazuzi Formation because an old and deeper nappe fault ($F_{3,}$ about 1.8 billion) is in contact between the Baijiazuzi Formation and the Tamazugou Formation. The fault also made the hanging strata of Baijiazuzi Formation fragmentizing. Pebbly carbonate-clastic sediments in the Shaohuotong Formation indicate the accumulation of orogenic collapse ($F_8$) and the presence of the structural basin. It may suggest that there was continental separation during late Proterzoic, and associated with large-scale mineralized basic-ultrabasic magma invasion. As one part of the Qilian orogenic belt, the Jinchuan region in the late Paleozoic orogeny accepted a strongly squeeze, and formed a series of relatively shallow and tightly NWW folds, thrust faults ($F_1$, $F_2$, $F_4$) and strike-slip faults

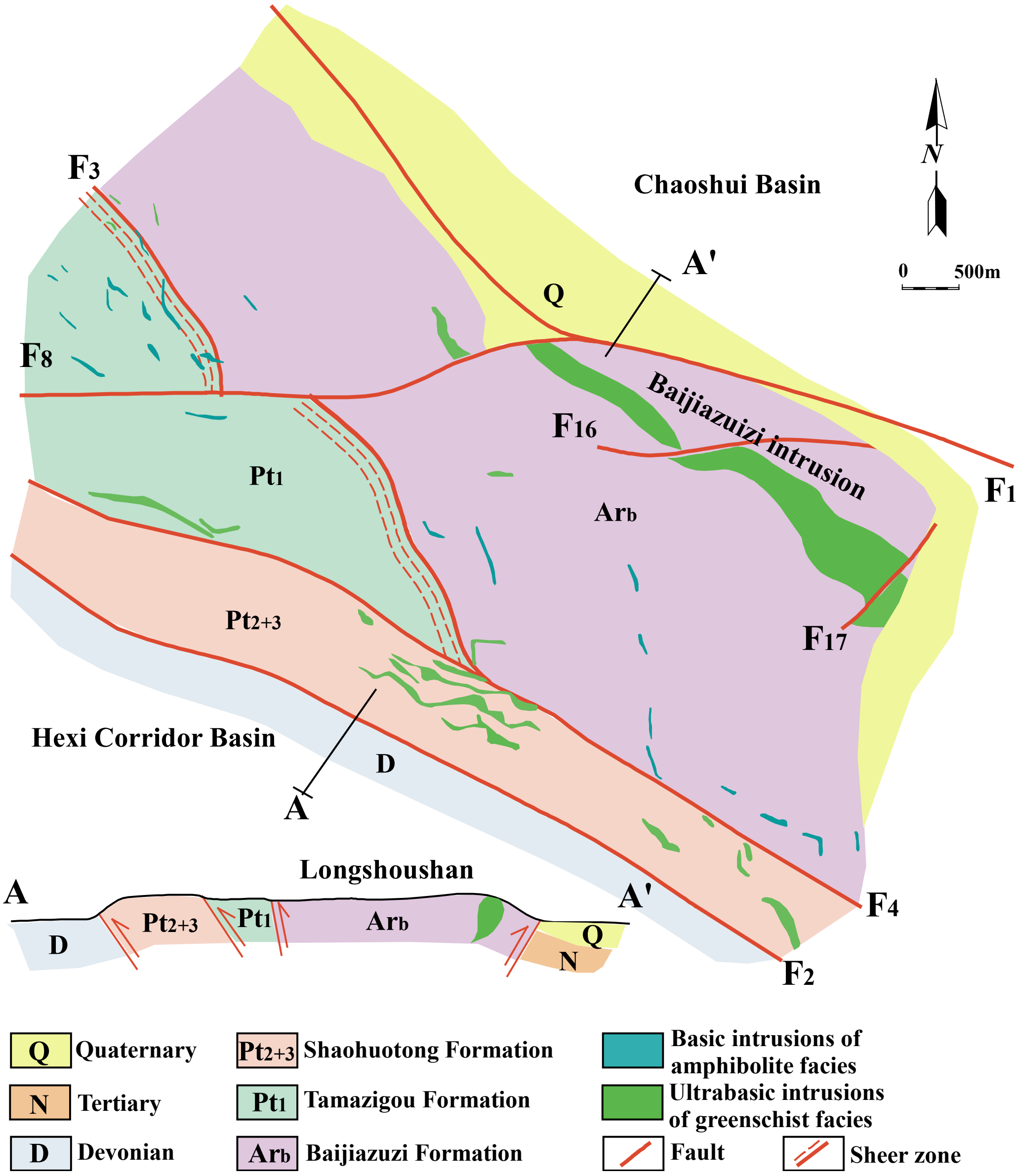

*Fig. 1.* Simplified geological map of the Jinchuan area

(F$_{16}$, etc.). These faults made the Longshoushan metamorphic core complex gripping and bulge because of the collision, and thrusting it to above the Devonian strata. They made the region to compose a palm tree structure that builds the main regional structure framework.

Because of the strong tectonic movements, we believe that the mineralized Bajiazuzi ultrabasic intrusion actually is not a dyke as recognized by the early researches. All characteristics of structures, rocks, and ores are pointing to that the Baijiazuzi mineralized intrusion is oblique because of crushed. The intrusion was probably a horizontal sheet which invaded along fragmentizing strata. The Qilian-orogeny movement led to the original stratiform ore-bearing magmatic intrusion rupture, strike-slip and tilt. Due to the uplift of the Tibetan Plateau, the new tectonic movement further pushed the ore-bearing magmatic intrusions to the Cenozoic alluvial layer.

# SESSION 5

## Ophiolites and Ural–Alaskan–type intrusions: traditional and innovative looks on the PGM formation

**Conveners: Evgeny Pushkarev & Edward Ripley**

The session will focus on the PGE enrichment and platinum-group minerals formation in chromitites and ultramafites of ophiolite complexes and Ural-Alaskan-type intrusions. Potential topics include:

1) Chromite and PGM formation in ophiolite and Ural-Alaskan intrusions – why do the huge chromite deposits in ophiolites contain relatively low concentrations of PGEs relative to the Pt-rich chromitites from Ural-Alaskan intrusions.
2) Geological, mineralogical, geochemical and experimental studies on the association between chromite and PGMs.
3) The role of high- and low-temperature fluids in the formation and distribution of PGEs in chromitites and ultramafic rocks.
4) The genesis of unusual sulfide-rich PGE mineralization in Ural-Alaskan intrusions.
5) PGMs are from source to placer – only accumulation or transformation? The unique PGMs placers of the World.

# INSIGHTS INTO ORE GENESIS OF ZONED URALIAN-TYPE MASSIFS USING OSMIUM ISOTOPES: EVIDENCE FROM LAURITE AND Os-RICH ALLOYS FROM THE NIZHNY TAGIL MASSIF, MIDDLE URALS, RUSSIA

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**ABSTRACT**. The Nizhny Tagil zoned-type massif located in the Middle Urals is associated with world-class platinum-group elements (PGE) placer deposits. The Os-isotope results identify a restricted range of $^{187}Os/^{188}Os$ values of laurite, Os-rich alloys and chromitite. Similarly 'unradiogenic' $^{187}Os/^{188}Os$ values are indicative of a common near-to-chondritic source for the PGE. The compositional and isotope-geochemical results provide new insights into ore genesis and temporal evolution of ultramafic rocks of the Uralian Platinum Belt.

The 47-km$^2$ Nizhny Tagil massif forms part of the 900-km-long Uralian Platinum Belt (UPB) and represents an undisputable example of a zoned Uralian-type clinopyroxenite-dunite complex (Efimov, 1998). It consists of a pipe-like dunite core ($Fo_{88-92}$), surrounded by a narrow zone of wehrlite and rimmed by an outer zone of clinopyroxenite. It is famous for platinum deposits; over 160 tonnes of platinum have been mined from associated placer and load deposits in the past.

Major cluster of U-Pb and Sm-Nd isotope ages defined the range for Uralian-type complexes between 540 and 425 Ma. Geochronological data for dunite of the Nizhny Tagil massif remains scarce (Malitch et al., 2009; Krasnobaev et al., 2010). This investigation forms part of a more extensive study that aims to place constraints on the origin and isotopic signatures of platinum-group minerals (PGM) typical of subcontinental and oceanic mantle.

Analyzed samples of chromitite with podiform texture have been identified in dunite of the Alexandrovsky Log located in the central part of the Nizhny Tagil massif. The majority of PGM are represented by Pt-Fe alloy grains with sizes ranging from 10 to 2000 microns (Fig. 1). These alloys show significant compositional variations. The dominant PGM are iron-platinum alloy, having compositions close to $Pt_2Fe$ (e.g., Pt=PGE; Fe=[Fe+Cu+Ni]), tetraferroplatinum PtFe, unnamed Pt(Fe,Cu) and/or tulameenite ($Pt_2FeCu$) (Fig. 2). Os-Ir(-Ru) alloys, Ru-Os sulphides and Rh-Ir sulpharsenides are also present occurring as small inclusions in Pt-Fe alloy grains in subordinate amounts (Fig. 3). Os-Ir(-Ru) alloys correspond to minerals of osmium and iridium. Laurite, besides ruthenium and sulfur, contains minor concentrations of osmium and iridium, varying in the range 0.38-1.24 at.% and 0-0.98 at.%, respectively. PGE sulpharsenides are represented by hollingworthite (RhAsS) – irarsite (IrAsS) solid solution series.

*Fig. 1.* Pt-Fe alloy grains from dunite in Alexandrovsky Log. Yellow scale bar equals to 1 mm

Laurite inclusions have $^{187}Os/^{188}Os$ values between 0.12256±0.00006 and 0.12284±0.00009, with a weighted mean of 0.12269±0.00012 (2 sigma, $n=4$), and $^{187}Re/^{188}Os$ lower than 0.00006, whereas Os-Ir alloys have $^{187}Os/^{188}Os$ values ranging from 0.12164 to 0.12259 with a mean of 0.12221 and a standard deviation of 0.00040, $n=4$. The osmium isotope results identify a restricted range of similar $^{187}Os/^{188}Os$ values for laurite and Os-Ir alloys (Fig. 3) that are consistent within uncertainty with 'unradiogenic' $^{187}Os/^{188}Os$ values defined for the chromitite (0.1217-0.1260, Malitch et al., 2011). The observed Os-isotope similarity between PGM and chromitite suggests that the osmium isotope budget of chromitite is largely controlled by laurite and Os-rich alloy. The average $T_{RD}$ ages of laurite and Os-rich alloys from the Nizhny Tagil massif correspond to the late Riphean (ca. 870±50 Ma).

Frequently the Uralian Platinum Belt has been considered as a chain of in situ gabbroic intrusions, where dunite was assumed to represent a cumulate of gabbroic magma. Contrary opinion considers the UPB as a complex tectonically integrated structural unit, which comprise distinct in origin formations (e.g. mantle residual material, products of its abyssal transformation, crystalline metabasites of problematic nature, material of abyssal crystallization of tholeitic magma, products of prograde metamorphism of volcanic crust and later granitoids). The new Os-isotope data support the concept of the genetic autonomy of the Uralian dunite ‘cores’ (Malitch et al., 2009; Krasnobaev & Anfilogov, 2014) and allow considering them as the most ancient formations, tectonically integrated in the structure of the Uralian Platinum Belt.

*Acknowledgments. This study supported by RFBR and Government of the Sverdlovsk Region (grant 13-05-96044-r-ural-a), and Ural Branch of Russian Academy of Sciences (project 12-P-5-2015).*

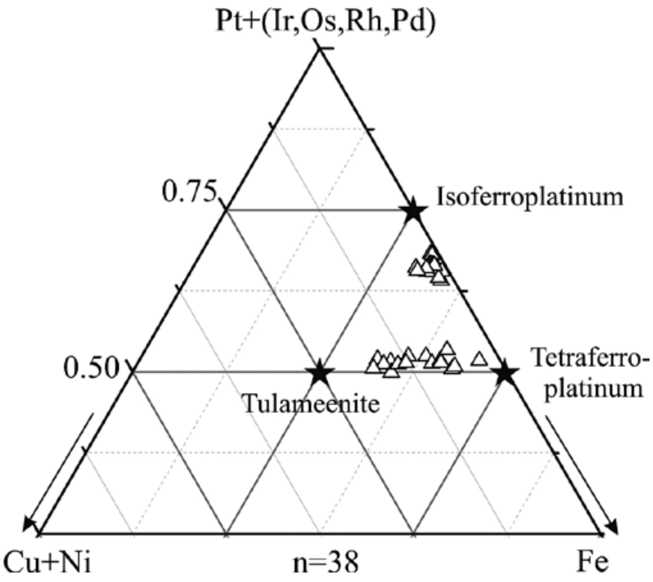

*Fig. 2.* Chemical composition of Pt-Fe alloys from chromitite of the Nizhny Tagil massif in the ternary diagram (at.%.) Pt+(Ir,Os,Rh,Pd) – Cu+Ni – Fe

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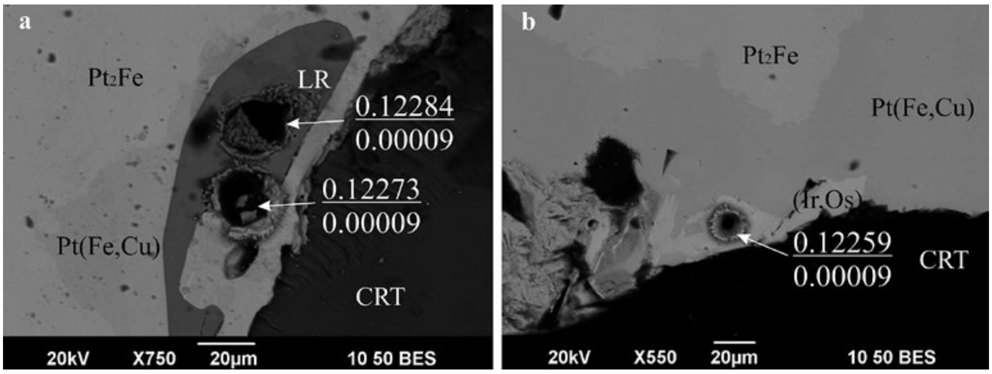

*Fig. 3.* Back-scattered electron images of internal texture of PGM from chromitite of the Nizhny Tagil massif. Holes denote laser ablation MC-ICP-MS analyses. $Pt_2Fe$ – ferroan platinum, Pt(Fe,Cu) – solid solution series tetraferroplatinum (PtFe) – tulameenite (PtFe0.5Cu0.5), LR – laurite, (Ir,Os) – osmian iridium, (Os,Ir) – iridian osmium, CRT – chromite, numbers in numerator and denominator correspond to $^{187}Os/^{188}Os$ value and the measurement error, respectively

# CRUST-MANTLE INTERACTION IN THE TUMUT REGION OF THE LACHLAN FOLD BELT, SOUTHEASTERN AUSTRALIA: A SYNTHESIS OF NEW ISOTOPIC INFORMATION (Re-Os, U-Pb, Lu-Hf and O)

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**ABSTRACT**. An increasing number of studies are reporting U-Pb ages of zircons recovered from rocks of the mantle sections of ophiolitic complexes. Were these zircons crystallized in the mantle from percolating metasomatic fluids or are they xenocryst of crustal material recycled during subduction? Their significance in the genesis and evolution of ophiolites and exhumed mantle rocks is controversial. The deciphering of this complexity requires integrated datasets that are not confined to zircon U-Pb data alone. Equally importantly, these data must be integrated within a comprehensive geological framework. This study of zircons from the Tumut region in southeastern Australia sends a cautionary message to researchers who use ophiolitic zircon to study the past geodynamics of Earth's lithosphere and convecting mantle.

This study focuses on the ophiolitic rocks of the Tumut region, located in the Lachlan fold belt of southeastern Australia, where two subvertical linear belts strike NNW-SSE and crop out discontinuously over a strike length of 140 km. The more deformed and metamorphosed rocks are in the western Wambidgee serpentinite belt, part of which has undergone upper amphibolite-facies metamorphism. In contrast, the eastern Coolac serpentinite belt contains a high proportion of massive (unfoliated) rocks and has only undergone greenschist-facies metamorphism. On its eastern contact, it is either faulted against, or intruded by, the S-type Young Granodiorite (Graham et al., 1996 and references therein).

Until now, constraints on the timing and evolution of the ophiolitic rocks in the Tumut region have been restricted mainly to the U-Pb isotopic information obtained on zircons from leucogabbro and plagiogranites. These limited data led to the conclusion that the ophiolitic rocks and the granitic magmas of the Lachlan fold belt were both generated as part of the same major tectonothermal event (Graham et al., 1996). Here we present new isotopic evidence that integrate the Re-Os systematics of platinum-group minerals recovered from chromitites and U-Pb, Lu-Hf and O-isotope information on zircons recovered from a range of mantle and crustal rocks of the Tumut region.

During this study several small, up to 10-20 μm, laurite ($RuS_2$) grains have been found in massive (high-Cr) chromitites from the Quilter's open cut in the Coolac Serpentinite Belt. A range of 'unradiogenic' $^{187}Os/^{188}Os$ values (0.1146-0.1220) collected on the laurite gives Re-depletion model ages varying between 0.84 and 1.89 Ga with a maximum at around 1.18 Ga and a shoulder at ca 1.64 Ga. These data imply that the age of the mantle beneath southeastern Australia is at least Mesoproterozoic.

New U-Pb, Hf- and O-isotope and trace-element data were obtained for zircons from a range of rocks from both serpentinite belts of the Tumut region. These rocks include two (high-Al and high-Cr) massive chromitites, leucogabbro, plagiogranite and rodingite in the Coolac belt, and a plagiogranite sample of the western Wambidgee belt. Detrital zircon grains have been recovered from gullies draining outcrops consisting of mainly weakly serpentinised massive porphyroclastic harzburgite of the Coolac belt. Zircons from the Young granodiorite collected at the contact with the Coolac serpentinite belt were also studied to refine the tectonic relationships and timing of the granitic magmatism.

U-Pb dating of zircons from the plagiogranite of the western Wambidgee belt defined a single age population with a Concordia age of 483.5±2.3 Ma. These zircons show a relatively homogeneous Hf-isotopic composition with a narrow range of strongly positive εHf (from+11 to +14), consistent with their crystallisation from mantle-derived melts. In contrast, the origin of zircons from the Coolac belt is complicated by the large proportion of zircons with negative εHf and heavy (>6) $\delta^{18}O$ indicative of a crustal origin. Furthermore, the similarity of the Coolac ophiolite-derived zircons with those from the Young granodiorite may indicate that they were introduced into the Coolac peridotites during the voluminous granitic magmatism that occurred in the region ca 430 Ma ago. In this case, the zircons carry no information on the origin of the Tumut ophiolite and only suggest that emplacement of the Coolac rocks had most likely preceded granitic magmatism of the Lachlan Fold Belt.

*Acknowledgements. Funding for this study has been provided by Australian Research Council (ARC) FT110100685 grant and funding to the ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS).*

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# REDOX STATE OF DUNITE-CLINOPYROXENITE COMPLEXES OF URAL–ALASKAN–TYPE

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**ABSTRACT**. A comparative study of the redox state of the dunite-clinopyroxenite complexes in Russia was performed using current methods of oxythermobarometry (Ballhaus et al., 1991). A total of 87 samples from the Ural massifs: Nizhny Tagil, Kytlym, Denezhkin Kamen, Zheltaya Sopka, Svetly Bor, Gladkaya Sopka, Uktussky, Khabarninsky and also from Kondyor (Aldan shield) and Galmoenan (Koryak) massifs were studied.

To obtain correct results, the iron oxidation state of chrome spinel was evaluated using Mossbauer spectroscopy. When calculating the temperature of olivine-chrome spinel equilibrium, amendments for the occurrence of titanium in chrome spinel structure were empirically determined.

All studied massifs can be divided into two non-overlapping groups of statistics according to the temperature of olivine-chrome spinel equilibrium ($T^{ol-sp}$). The high-temperature group consists of ultramafic rocks of the Uktus, Nizhny Tagil, Kondyor and Galmoenan massifs. The chromite-dunite series of the Uktussky massif is characterized by the greatest values of $T^{ol-sp}$ (1100-1200°C). The dunites of the Nizhny Tagil massif are the least homogeneous according to $T^{ol-sp}$. The highest levels of $T^{ol-sp}$ (1050-1150°C) were recorded in the fine-grained rock facies of the marginal part of the massif. The temperature of the coarse-grained dunite of the central part was 180 °C lower. Still lower (another 70-150°C) was $T^{ol-sp}$ of epidunite chromitites associated with primary platinum deposits. The temperature values of the natural rock groups do not overlap. Dunite-clinopyroxenite complexes located in close association with gabbro have a 300°C lower $T^{ol-sp}$ compared with similar rocks of the Nizhny Tagil massif. This group includes all the dunite bodies of the Kytlym massif, Gladkaya Sopka, Zheltaya Sopka and minor dunite-clinopyroxenite-gabbro bodies of Denezhkin Kamen.

The calculations of oxygen fugacity ($fO_2$) showed a large range of variations in the redox state of the studied samples of ultramafic rocks. The $fO_2$ value was one to four orders of magnitude higher than that of the FMQ buffer. Spatial variations of $fO_2$ were observed within a belt, massifs, and its individual units. They were expressed most clearly by comparing $fO_2$ and the iron content of chrome spinel (#*f*). The chromite-dunite series in these coordinates formed subparallel ellipses with relatively small, comparable to analytical errors, $fO_2$ variations, attesting to the redox state constancy within the series (Fig. 1). For easy reference, the similar angle of inclination of long ellipse axes allows the calculation of $fO_2$ value reduced to a constant #*f* value. The massifs have the following sequence according to oxygen fugacity at 60% #*f* : Galmoenan (3.2 units log $fO_2$ relative to FMQ buffer), Svetly Bor and Konder (3.1 units), Kosva dunite body and Gladkaya Sopka (3.0), Nizhny Tagil and Denezhkin Kamen (2.7), Sosnovsky Uval (2.6) Iovskoe body (2.2), East Khabarny Association and Uktussky massif (2.0). Due to the fact that the iron content variations of chrome spinel and olivine in dunites are induced by their close association with clinopyroxenites, the $fO_2$ values can be extended to the whole chromite-dunite-clinopyroxenite series in this massif.

The value of oxygen fugacity in chromitites, syngenetic with dunites with background concentrations of platinoids, is virtually identical to that of host dunites, while it is 1.5-2 orders of magnitude higher in platinum-bearing chromitites. This, along with geothermometric data, indicates the existence of a geological gap between the formation of these types of chromitites and highly

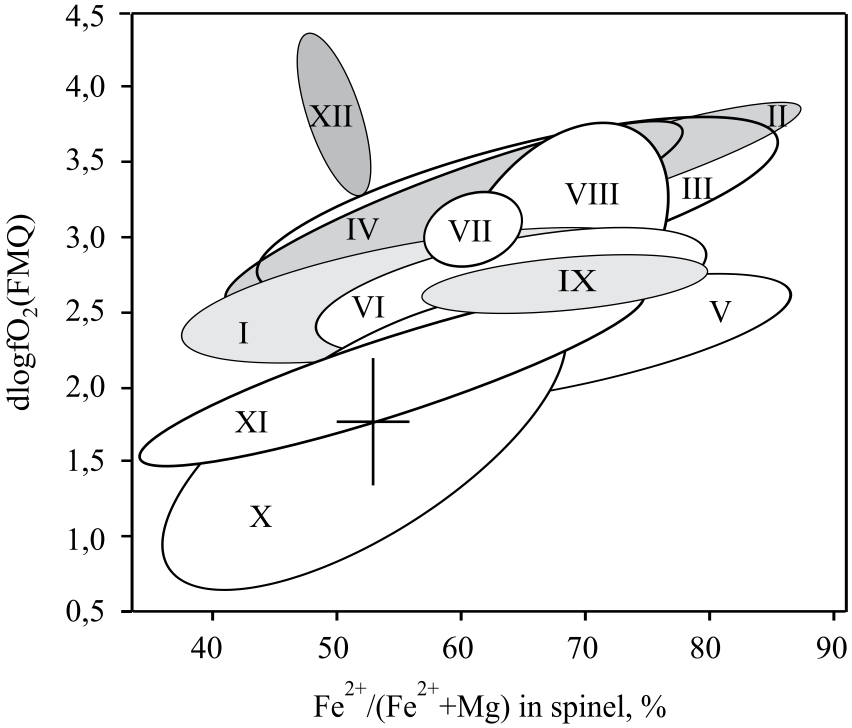

*Fig. 1.* Dependence of oxygen fugacity in ultramafic rocks of the Ural-Alaskan type from the iron content of chrome spinel. Massifs: I – Nizhny Tagil, II – Svetlobor, III – Kondyor, IV – Galmoenan, V – Iov body, VI – Sosnow Uval, VII – Gladkaya Sopka, VIII – Zheltaya Sopka, IX – Denezhkin Kamen, X – Uktus, XI – East Khabarny Association, XII – Pl-chromitites

oxidized fluid compositions, responsible for generating platinoid mineralization.

Conspicuous is the similarity of the material composition, platinum mineralization, redox state and temperature of olivine-chrome spinel equilibrium of dunite-clinopyroxenite complexes of the Nizhny Tagil massif in the Platinum Belt of the Urals with Kondyor massif of the Aldan Shield. The "Ural" era of these complexes is association with gabbro accretion that took place at a lower temperature and in more reducing conditions. Later, fragmentarily, at 550-600°C and oxygen fugacity+3÷+4 units log $fO_2$ (FMQ), gabbro-ultramafic associations underwent high temperature aqueous metamorphism ending in early serpentinization.

*Acknowledgements. This investigation was supported by the Ural Branch of the Russian Academy of Sciences (grant 12-P-5-1020 and 12-C-5-1004), RFBR–Ural 13-05-96031.*

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# THE CHROMITITE-PGE ASSOCIATION OF THE URALS: AN OVERVIEW

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**ABSTRACT**. Chromitites of the Urals vary in size from world-class giant deposits restricted to the depleted mantle tectonite of ophiolites, down to small, sub-economic deposits associated with supra-Moho ophiolitic cumulates or the dunite core of concentrically zoned complexes of the Alaskan Type. Four major groups of chromitite have been recognized and, based on the chromite mineral chemistry, morphology, host rock association, and type of parental magma, they have been assigned to specific tectonic settings of formation (Garuti et al., 2012, and references therein).

Overview of more than 130 published and unpublished analyses of chromitite indicate the existence of significant differences in PGE distribution among the various groups of deposits, reflecting differences in parental melt composition and fertility of the source (Table 1). The high-Cr, low-Ti chromitites (group 1) contain up to more than 800 ppb of total PGE. They have negative PGE patterns (low Pd/Ir ratio) typical of chromitites hosted in the mantle section of ophiolites, and are enriched in Ru-Ir-Os with respect to their mantle host. However, massive chromitite from the giant deposits of Kempirsai and Ray-Iz display distinctive modal and geochemical enrichment in Os and Ir (Fig. 1A) compared with other chromitites of the Urals (Kraka, Kluchevskoy, Voykar-Syninsky) and most chromite deposits in Mesozoic-Cenozoic ophiolites of the Mediterranean, Himalayan and Caribbean regions, which display a Ru positive anomaly with relatively low Os-Ir content. Since group-1 chromitites formed by metasomatic interaction between percolating melt (boninite, high-Mg tholeiite) and residual-mantle harzburgite, the observed fractionation among the IPGE must be a feature inherited from one or both the reactants, possibly related with partial melting conditions of their sources. The high-Al, low-Ti chromitites of the Urals (group 2) mainly occur in supra-Moho cumulates of ophiolites, more rarely they are found as podiform bodies within residual mantle. Chromite deposition is triggered by fractional crystallization and mixing of MORB-like melts, or their metasomatic interaction with residual mantle. In general, these chromitites tend to be PGE depleted (up to 250 ppb of total PGE) compared with the high-Cr types, and characterize for less fractionated PGE patterns (high Pd/Ir ratio), and local enrichment in Pt-Pd relative to the IPGE (Fig. 1B) possibly determined by segregation of magmatic sulphides during the chromitite event. Extremely high PGE contents (up to 26 ppm) are found in small, high-Al chromitites associated with supra-Moho cumulates in continental margin ophiolite complexes of the Urals (Fig. 1C). Chromitite occurring close to the base of the cumulus sequence is Ti-poor (group 3a) and has negative sloping PGE pattern (Pd/Ir= 0.02-0.29), with 26 ppm of total Os+Ir+Ru. A second chromitite horizon possibly located in the upper part of the cumulus sequence (group 3b) is Ti-rich. It has positive sloping PGE pattern (Pd/Ir=3.85-19.73) and contains a PGM+Fe-Ni-Cu sulphide assemblage. The complementary trends of the PGE patterns is striking, and suggests evolution from S-undersaturated to S-saturated conditions during the chromitite event. However, such a contrasting geochemical signature cannot be the result of fractionation of a single batch of magma, more likely, it reflects successive injections of melts derived from different sources, during the early stages of ocean opening. The PGE geochemistry and other geochemical and mineralogical evidence indicate high degree of partial melting of almost undepleted sources, notably: 1) the subcontinental lithospheric mantle, or 2) the underlaying, upwelling asthenosphere, producing PGE-rich magmas varying from MORB-type to continental Fe-tholeiite.

Chromitite in Alaskan-type complexes has high-Cr, high-Ti composition and characterizes for high $Fe^{3+}$substituting for Cr at relatively low Al content, reflecting crystallization under high $fO_2$. The parent melt has calc-alkaline affinity with hydrous, Fe-rich and high-K composition. It was generated by second-stage partial-melting of a fluid metasomatized mantle source. Chromitite varies from PGE rich up to several tens

Table 1

**Typification of the Uralian chromitite and chromite-bearing massifs**

| *Massifs* | *Chromitite type* | *Ultramafite host* | *Parental melt* |
|---|---|---|---|
| ***1) High-Cr, low-Ti chromitite in subduction-related setting*** | | | |
| Ray-Iz | podiform | depleted mantle-tectonite | Island-Arc boninite |
| Voykar-Syninsky | podiform | depleted mantle-tectonite | Island-Arc boninite |
| Kempirsai | podiform | depleted mantle-tectonite | Island-Arc boninite |
| Kraka | podiform | depleted mantle-tectonite | Island-Arc tholeiite |
| Kluchevskoy | podiform | depleted mantle-tectonite | Island-Arc tholeiite |
| ***2) High-Al, low-Ti chromitite in subduction-unrelated setting( Mid-ocean ridge, Back arc)*** | | | |
| Voykar Syninsky (low-Ti) | stratiform-podiform | supra-Moho cumulates | MORB |
| Kempirsai (low-Ti) | stratiform-podiform | supra-Moho cumulates | MORB |
| ***3) High-Al, low-Ti and high-Ti chromitite in subduction-unrelated setting(Ccontinental-margin)*** | | | |
| a) Nurali (low-Ti) | stratiform | supra-Moho cumulates | MORB |
| b) Nurali (high-Ti) | stratiform | supra-Moho cumulates | Fe-tholeiite? |
| ***4) High-Cr, high-Ti chromitite in Ural-Alaskan-type complexes*** | | | |
| *a) concentrically-zoned dunite-clinopyroxenite-gabbro-hornblendite emplaced at the root of Island Arc* | | | |
| Kachkanar | pod-veinlet | dunite | ankaramite |
| Kytlym | pod-lense | dunite | ankaramite |
| Kytlym Butyrin vein | | | ? |
| Nizhny Tagil | pod-lense | dunite | ankaramite |
| Uktus | vein-lens | dunite | ankaramite |
| *b) layered dunite-clinopyroxenite-gabbro-hornblendite associated with mantle tectonite* | | | |
| East Khabarny | stratiform | dunite-websterite | ankaramite? |

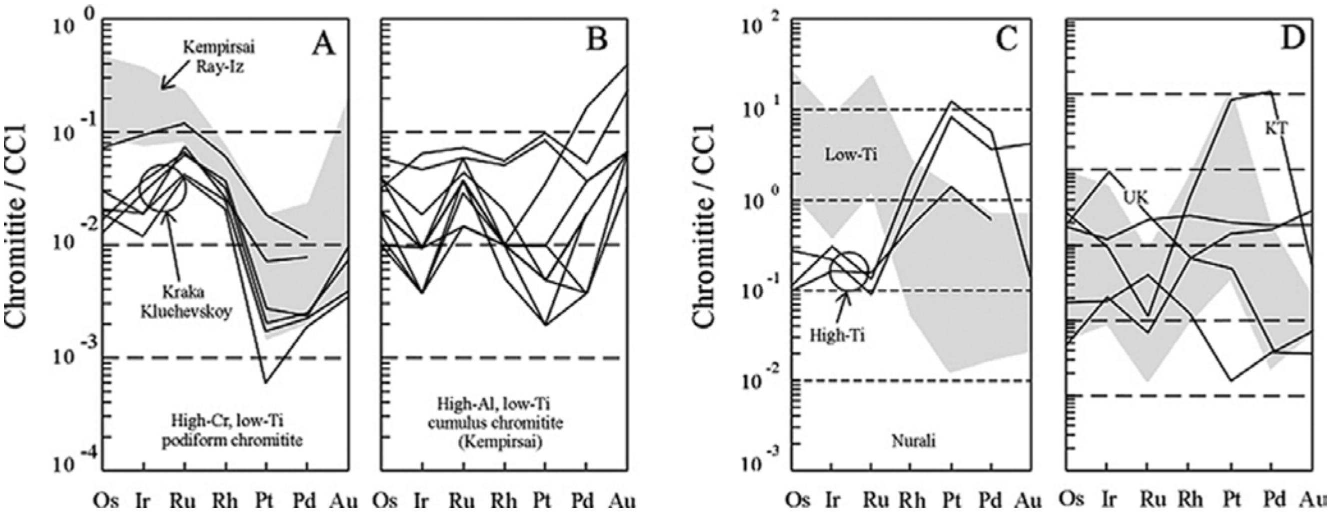

*Fig. 1*. Chondrite-normalized PGE patterns for chromitites of the Urals. Compilation of literature data and unpublished analyses of the authors (see references in Garuti et al., 2012)

of ppm (group 4a) to almost PGE barren (group 4b). They display modal and geochemical enrichment in Pt and Ir resulting in PGE patterns with a typical M-like shape (Fig. 1D). Fractionation between IPGE and PPGE is suggested by comparison of PGE profiles in Fe-poor magnesiochromitite (Pt/Ir=0.10) from the Uktus complex (UK) and Cr-rich magnetite (Pt/Ir=651) from Kytlym (KT). Profiles from chromitite in the East-Khabarny complex (Fig. 1D) are not consistent with an Alaskan-type affinity, possibly implying a different mechanism for PGE fractionation (S-saturation of the parent melt?). The Pt-Ir signature of the Urals Alaskan-type chromitite may indicate that the depleted mantle undergoing re-melting contained a residual PGE fraction probably consisting of refractory Ir-Os and Pt-Fe alloys.

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# SOURCE OF PGM AND GOLD FROM THE CEMPAKA PALAEOPLACER DEPOSIT, SE KALIMANTAN, INDONESIA

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**ABSTRACT**. The Cempaka palaeoplacer diamond deposit is located in SE Kalimantan, approx. 40 km SE of the main city of Banjarmasin. Diamonds have been known from SE Kalimantan since at least 600 A.D. (Spencer, 1988) and exploration by western companies began in 1965, largely as a result of the discovery of a gem-quality 166.85 carat diamond known as the 'Tri Sakti'.

The region comprises a belt of Late Jurassic to Cretaceous metasedimentary and metavolcanic rocks (Manunggal Formation), deposited in a pull-apart basin following emplacement of the Meratus Ophiolite (Sikumbang, 1986). These are surrounded by Cenozoic sedimentary basins and overlain by Late Cenozoic fanglomerates deposited at the base of the Meratus Mountains. The Cempaka palaeoplacer deposit is immediately contained within and derived from, erosion of the laterised fanglomerates. The diamonds appear to have been initially derived from the Meratus Mountains to the NE and then reworked through several sedimentary cycles into Cenozoic and Quaternary depocentres under low-lying coastal plains. The host sediments for the diamonds, PGM and gold are the upper unit of an alluvial facies, consisting of coarse gravels, sandy gravels and gravelly sands. Associated phases are zircon, magnetite, chrome spinel, corundum and diaspore.

The PGM grains range in size from 200 um to 1.5 mm, are mostly subrounded to rounded, and moderately pitted and etched. Similarly, the gold grains range in size from 75 um to 1.7 mm, are mostly subrounded to rounded, and extremely pitted, etched and commonly folded (Fig. 1). EMP analysis of the PGM clearly show that they mostly consist of Pt-Fe alloys with high Pt:Fe (>5). Some of these contain pure Os inclusions while others contain Ru- and Ir-rich grains (Fig. 2). The gold consists of a core of Au-Ag, surrounded by a narrow rim of pure Au. Gold fineness averages 898 for the cores and 985 for the rims. Importantly, no other elements were detected in the gold grains.

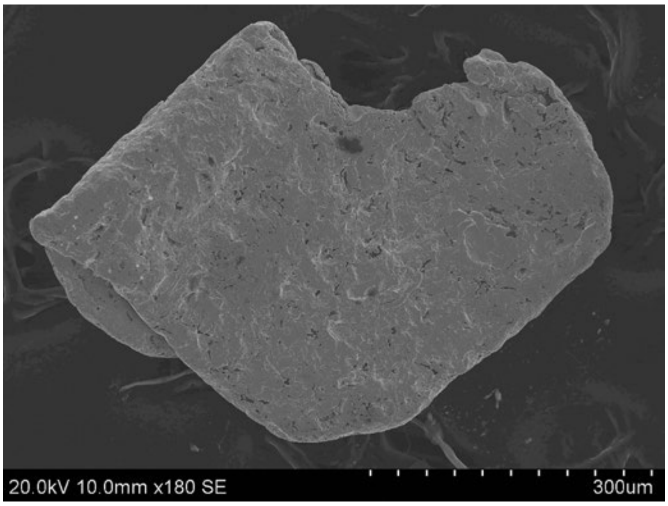

*Fig. 1.* SEM image of gold grain showing significant folding

Based on morphological studies, both the PGM and gold appear to have been transported at least 10 km from their source and additionally, have most likely been recycled several times within the fluvial environment. The PGM mineralogy suggests derivation from a bimodal source, ophiolites (either the Meratus or Bobaris ophiolites) and as yet undiscovered Alaskan-type complexes. On the other hand, the chemistry of the gold suggests that it is derived from an epithermal environment, with the closest source for this being uneconomic epithermal gold mineralization within the Sumatra-Meratus Arc.

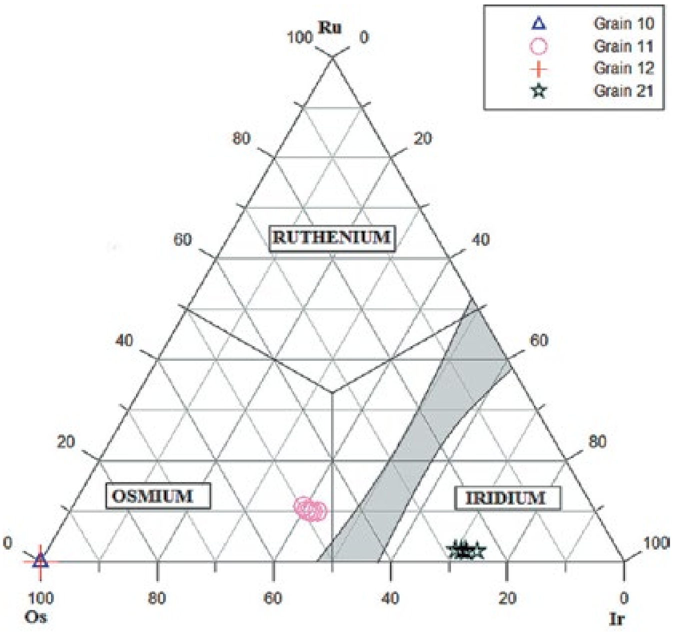

*Fig. 2.* Ternary plot of alloy trends in PGM (adapted from Tolstykh et al., 2005)

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# TRANSITION-ZONE MINERAL ASSEMBLAGES IN “OPHIOLITIC” CHROMITITES: IMPLICATIONS FOR COLLISION-ZONE DYNAMICS AND OROGENIC PERIDOTITES

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**ABSTRACT**. The diamonds and other UHP phases, including cubic MG-silicates, in Tibetan “ophiolites” reflect subduction of typical SSZ-type chromitites and peridotites, probably derived ultimately from continental lithospheric mantle, into the Transition Zone >200 Ma before the India-Asia collision. The exhumation and emplacement of the depleted peridotites are related to the tectonics of slab roll-back during that collision.

Diamonds have been reported from Tibetan “ophiolites” for ≥30 years, but have been widely dismissed as contaminants, because their unusual morphology and light C ($\delta^{13}C$=-18 to -27) are unlike those of kimberlitic diamonds. However, the diamonds have now been found *in situ* in both the chromitites and the peridotites of “ophiolites” along the Yarlung-Zangbo suture (Tibet) and the Polar Urals (Yang et al., 2014). These massifs are dominated by depleted spinel harzburgite; some yield whole-rock Re-Os $T_{RD}$ ages back to 3.4 Ga (Shi et al., 2012), suggesting that they represent ancient SCLM.

LA-ICPMS analyses of the diamonds show LREE-enriched trace-element patterns parallel to those of kimberlitic fibrous diamonds; the “ophiolitic” diamonds thus appear to be natural. However, the Tibetan diamonds also have: negative anomalies in Sr, Sm, Eu, Yb; very low Fe; high Ta and inclusions of $Ni_{70}Mn_{20}Co_5$ alloy. The diamonds are accompanied by a range of alloys, native metals, carbides and silicides, implying $fO_2$ down to IW=-8. Exsolution of coesite, diopside and enstatite from chromite implies the former existence of the CF ($CaFe_2O_4$) structure, stable at P≥12.5 GPa (380 km) (Yamamoto et al., 2009). The recent discovery of a cubic Mg-silicate (essentially “anhydrous antigorite” with an inverse-ringwoodite structure) suggest P≥18 GPa. The highly-reduced assemblage and the diamonds appear to reflect interaction of the chromitites with low-$fO_2$ fluids in the Transition Zone (TZ).

The presence of these super-reducing ultrahigh pressure (SuR-UHP) assemblages in “orogenic peridotites” raises many questions. Some have suggested that the chromitites crystallised in the TZ, and rose to be emplaced in suboceanic mantle. However, the trace-element signatures of the chromites are identical to those of typical ophiolitic chromitites, and imply primary crystallisation at shallow depths; this is consistent with the inferred UHP metamorphism of antigorite inclusions (to baiwenjiite) in the chromitites. *In situ* analyses of PGE sulfides give $T_{RD}$=290-630 Ma, peaking at 325 Ma. Euhedral zircons separated from the chromitites give U-Pb ages of 376±7 Ma, and εHf= 9.7±4.6 ($T_{DM}$ ca 2 Ga), suggesting some crustal input. However, $T_{RD}$ model ages of Os-Ir nuggets in the chromitites are much younger: 234±3 Ma (Shi et al., 2007). We interpret the sulfide+zircon ages as dating the shallow formation of the chromitites, while the Os-Ir model ages may record the timing of intense reduction and chromite recrystallisation in the TZ following deep subduction. This subduction clearly preceded the India-Asia collision, and would be related to early events in the paleo-Tethys. Dynamic modeling suggests that the rise of the peridotites from the TZ to the crust during the Early Tertiary/Late Cretaceous was rapid (ca. 6 Ma), and probably was driven by the rollback of the Indian slab after it had stalled in the TZ.

Mantle samples from the TZ thus may be present in other collision zones; how should we recognize them? One striking feature is the *absence* of eclogites or similar UHP crustal rocks in or around the peridotite massifs, or along the 3000 km of the Yarlung-Zangbo suture. If these massifs represent oceanic mantle, or ancient SCLM that became seafloor before being subducted during an earlier plate collision, their deep subduction was driven at least partly by the negative buoyancy of an eclogitic crust. If that detached from the slab in the TZ, it would sink deeper into the mantle, while the buoyant harzburgites would try to rise. These SuR-UHP massifs carry unique information on the tectonics of collision zones, and the physical and chemical makeup of the TZ.

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# PRIMARY PLATINUM MINERALIZATION IN THE OWENDALE INTRUSION NEW INSIGHTS INTO THE GENESIS OF PLATINUM MINERALIZATION IN URAL-ALASKAN-TYPE INTRUSIONS

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**ABSTRACT**. A total of 639 kg of Pt was recovered from placer deposits in the Fifield region of Australia; it is presumed that this Pt was derived from nearby Ural-Alaskan-type intrusions such as the Owendale intrusion. Primary Pt mineralization in the Owendale intrusion, comprises two styles of mineralization, namely (1) Pt-rich but Cu-S-Pd-Au-poor and (2) Cu-Pt-Pd-Au sulphides. We suggest that the PGE were originally hosted by PGE-rich sulphides, some of which underwent partial to complete destruction during serpentinization of the hosting dunites and wehrlites and also through reaction with high temperature $K_2O$-rich hydrothermal fluids.

## GEOLOGY AND PGE MINERALIZATION OF THE OWENDALE INTRUSION

The Owendale Intrusion, which is one of a series of Ural-Alaskan-type intrusions in NSW, consists of 80% mafic rocks (diorites and monzonites) and 20% ultramafic rocks (clinopyroxenites, wehrlites and dunites). Three distinct types of PGE mineralization occur at Owendale, viz: (1) Pt-rich, but Cu-S-Pd-Au-poor, mineralization in "P" units that are pegmatoidal clinopyroxenites that form irregular lenses and veinlike bodies in olivine pyroxenites and have grades up to 14 g/t Pt over 1.4 m (Elliot & Martin, 1991; Johan et al., 1991); (2) Cu-Pt-Pd-Au sulphides that occur mainly as disseminated sulphides over broad zones in the dunites/wehrlites but also as irregular veins and segregations in both dunites/wehrlites and clinopyroxenites: and (3) a Cu-S-Pd-Au-poor but Pt-rich association with grades up to 24 g/t Pt over 1 m; this style of mineralization is dominated by Pt-Cu and Pt-Fe alloys that are disseminated over broad intervals within partially to totally serpentinized dunites and wehrlites (Brill & Keays, 1990). An important feature of the Pt mineralization is it is often associated with large amounts of phlogopite that may have formed during interaction of high temperature, $K_2O$-rich fluids with primary magmatic sulfides in the rocks.

Mineralization in the P units is dominated by Pt-Fe alloys together with minor Os, Pd, Ir and Rh alloys, sulfides, antimonides, and arsenides (Johan et al., 1989). The Pt-rich, Cu-S-Pd-Au-poor mineralization consists of Pt-Fe and Pt-Cu alloys within serpentinized dunites and wehrlites (Fig. 1). These alloys always occur in the serpentine mesh lines of the partially altered ultramafic rocks and never within the olivine (Fig. 1). Virtually all the Cu in the S-poor, but Pt-rich, dunites and wehrlites is hosted by Pt-Cu alloys. Zones of disseminated Cu-Pt-Pd-Au sulphides in the dunites/wehrlites are interdigitated with zones of Pt-rich, but Cu-S-Pd-Au poor mineralization. Despite the large differences in their Cu, S, Pd, and Au contents, the Cu-S-Pd-Au rich and Cu-S-Pd-Au-poor assemblage, have very similar Pt:Rh:Ir ratios.

These data provide strong evidence that the Pt (along with Rh and Ir) in the disseminated Pt-Cu and Pt-Fe alloys within serpentinized dunites and wehrlites were initially hosted by PGE-rich sulfides that were co-magmatic with Cu-S-Pd-Pt-Au-rich sulfides present as disseminations, veins and segregations in dunites/wehrlites and clinopyroxenites. During serpentinization, most of the S and the majority of the Cu, Pd and Au in the disseminated primary PGE-bearing sulfides within these dunites and wehrlites were driven off, resulting in the formation of Pt-Cu and Pt-Fe alloys.

## IMPLICATIONS

This study has a number of significant implications for our understanding of Alaskan-type intrusive complexes and the processes that form secondary PGE mineralization. The data presented here indicate that the characteristically low S contents of PGE mineralization and predominance

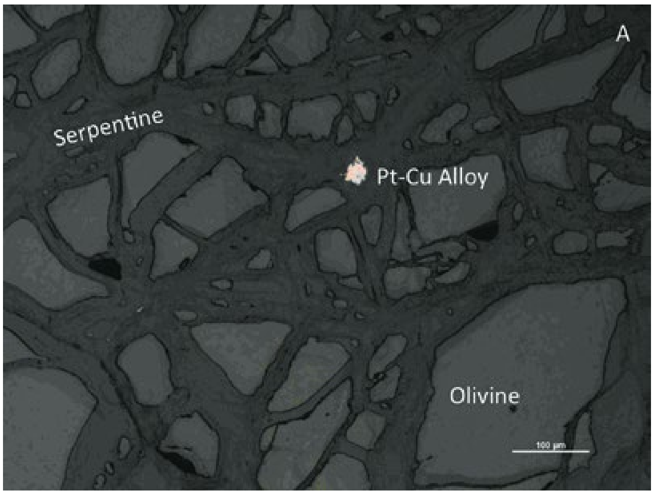

*Fig. 1.* Pt-Cu alloy in serpentine "veins" developed during serpentinization of dunites

of Pt alloys in Alaskan-type intrusions are likely to be a product of post-magmatic rather than primary processes. This study has demonstrated that the PGE in the Owendale intrusion were carried into the system as PGE-rich magmatic sulfides that were subsequently destroyed either during reaction between these sulfides with $K_2O$-rich fluids derived from monzonitic magmas that intruded the ultramafics, or during serpentinization of the dunites and wehrlites. If the PGE in the Owendale intrusion were carried into the system as PGE-rich sulfides in olivine-dominated slurries, with some of the PGE-rich sulfides lagging behind these slurries, then there may be significant quantities of PGE-rich sulfides, possibly at shallow depths, below the Owendale intrusion. If this hypothesis is correct, then other Alaskan-type intrusions also have the potential to have PGE-rich sulfides associated with them. Finally, serpentinization of PGE- (and Au-) rich sulphide-bearing ultramafic rocks may provide an important source of Au for Au-forming hydrothermal fluids.

*Acknowledgements. Platina Resources is gratefully acknowledged for their support of this project and for granting permission to publish these results.*

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# PLATINUM GROUP MINERALS IN OPHIOLITIC CHROMITITES OF TIMOR LESTE

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**ABSTRACT**. The possible ophiolitic origin of the Hili Manu peridotites, located in the Manatuto District on the north coast of Timor Leste, ~50 km east of the capital Dili, has been a topic of considerable debate over the last three decades (e.g. Berry, 1981; Harris & Long, 2000; Falloon et al., 2006). These ultramafic rocks were identified within two massifs (Be Heda and Kerogeol Hills in the east and Subao Highway in the west) separated by an amphibolite block of undefined origin. The peridotites range from unaltered to completely serpentinised dunites, harzburgites and lherzolites associated with rare rodingites and gabbros. This is the first detailed study on the textures, mineralogy and geochemistry of the Hili Manu chromitites, and their platinum-group elements mineralisation.

At Hili Manu the chromitites bodies are hosted in completely serpentinised dunites and harzburgites in the eastern massif and in fresh olivine-rich harzburgites in the western massif. The western massif differs from that in the east, in that the peridotites have a distinctive high-T layering and foliation. The shapes of the chromitites are also distinct between the two massifs, tabular in the east and distinctively vein-like morphologies in the west. In addition, the chemistry of chromite within the chromitite bodies (high-Cr) and surrounding host peridotites (low-Cr) are distinctly different.

Chromitites at Hili Manu have total PGE concentration between 73 and 1295 ppb, while the host peridotites have total between 28 and 364 ppb. Both of them are characterised by enrichment in IPGE (Os, Ir, Ru) over PPGE (Rh, Pt, Pd), typical of an ophiolite setting (Fig. 1). The wall rock of the chromitite body at Be Heda Hill has a slightly different PGE distribution, with higher contents of Pt and Pd than the wall rock from Kerogeol Hill and Subao Highway.

Chromites from the chromitites at Hili Manu contain several grains of Os-rich laurite (Table 1). The laurite grains are euhedral and sub-rounded solid inclusions (3-10 μm) fully embedded within unaltered grains of chromite (Fig. 2). The morphology of the PGMs and their mode of occurrences suggest that they crystallised at the same time as the chromite grains. Preliminary Re-Os model ages range from 0.05 $T_{RD}^{ECR}$ (Ga) (Subao Highway) to 0.21 $T_{RD}^{ECR}$ (Ga) (Kerogeol Hill).

Table 1

**EMPA results of PGM inclusions within the chromitite pods in Hili Manu**

| *Sample ID* | *GRN* | *Wt %* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *Os* | *Ir* | *Ru* | *Rh* | *Pt* | *Pd* | *S* | *Total* |
| AL17A | GRN 1 | 21.34 | 10.565 | 31.97 | 0.41 | BLD | 1.14 | 31.61 | 99.92 |
| AL21-1 | GRN 1 | 24.35 | 6.03 | 34.89 | 0.385 | BLD | 1.285 | 32.41 | 101.65 |
| AL21-1 | GRN 2 | 23.67 | 7.97 | 34.11 | 0.465 | BLD | 1.185 | 32.68 | 102.18 |
| AL21-3 | GRN 1 | 22.44 | 9.215 | 32.205 | 0.57 | BLD | 1.13 | 31.95 | 100.07 |
| AL21-3 | GRN 2 | 23.94 | 6.14 | 35.02 | 0.37 | BLD | 1.125 | 32.34 | 101.16 |

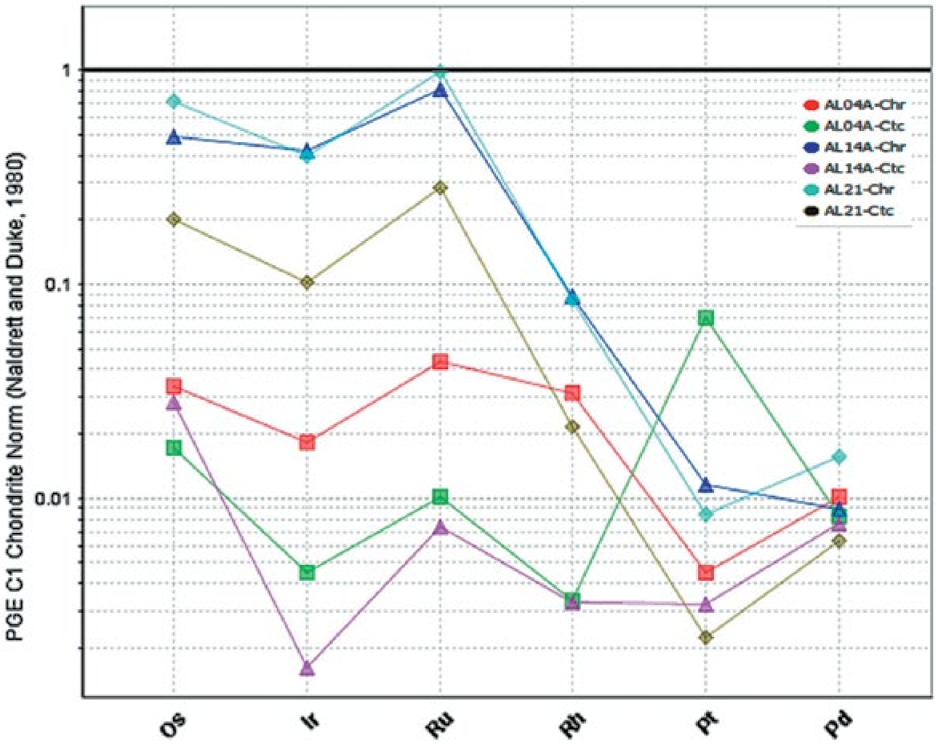

*Fig. 1*. CN-PGE graph for chromitites from Be Heda Hill (AL04A), Kerogeol Hill (AL14A) and Subao Highway (AL21). Note: Chr – chromite pod, Ctc – contact wall rock

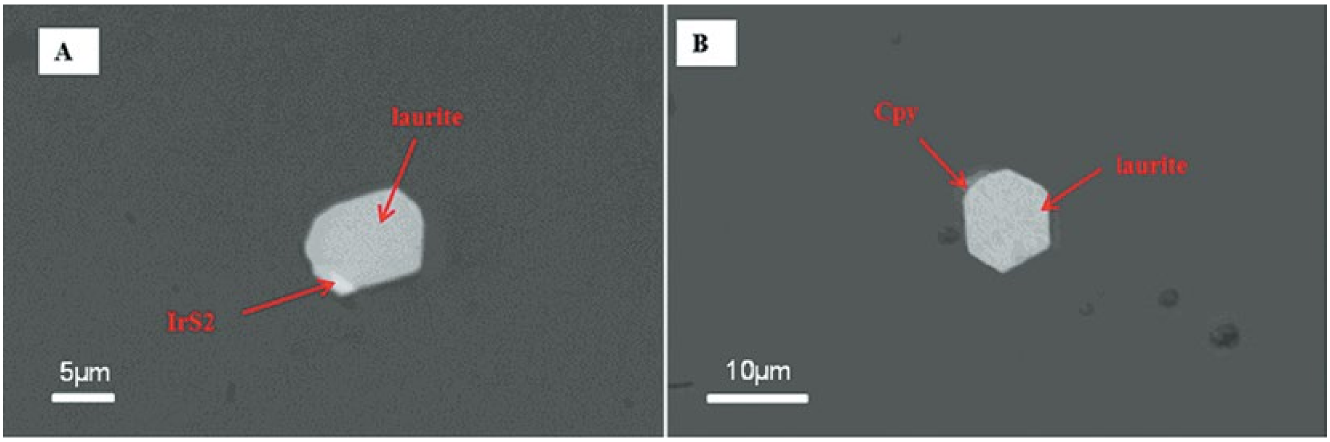

*Fig. 2*. (A) BSE of euhedral laurite (~10 μm) coexisting with unidentified $IrS_2$ within unaltered chromite (ID21 – Subao Highway) (B) BSE of euhedral laurite (~10 μm) coexisting with chalcopyrite (Cpy) within unaltered chromite (AL21 – Subao Highway)

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# DISTRIBUTION OF PLATINUM-GROUP ELEMENTS, GOLD AND SILVER IN THE CHROMITES OF THE NIZHNY TAGIL MASSIF, PLATINUM BELT OF THE URALS

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**ABSTRACT**. The paper presents data on the distribution of trace elements in chromites from different petrographic chromitite types of the Nizhny Tagil massif. Increased amounts of gold and silver are identified. According to the research it was revealed that the migration of PGE, together with other trace elements, was imposed on chromite possibly overlapping with it in time.

The problem of prospecting and exploration of primary platinum deposits in zonal massifs of the Alaskan type involves researches dealing with chemical differences in composition of chromites of various chromitite petrographic types. Moreover it is necessary to study the possible use of these differences for understanding the genesis of platinum mineralization and development of geochemical criteria for its exploration and forecasting. Certain prerequisites for raising this question were outlined by Malakhov et al. (1995), Lazarenkov et al. (1995), Fershtater et al. (1999), Pushkarev et al. (2007) & Volchenko et al. (2007), who studied the distribution of platinum-group elements (PGE) in different types of chromites.

To solve these issues we identified contents of PGE, Au, Ag and a wide range of trace elements in chromites of the Nizhny Tagil massif. Analyses were performed in the Central Laboratory VSEGEI by Laser ablation ICP-MS.

Chromites in chromitites of the Nizhny Tagil massif are divided into two polar groups: the rich massive veined type (PGE 47.42-59.02 ppm) and the PGE-poor type (PGE 0.02-0.49 ppm). Almost all types of chromites are characterized by relatively significant amounts of silver and sometimes noticeable content of gold. The presence of silver, whose amount usually exceeds the concentration of platinum, is a remarkable feature of chromites from the Nizhny Tagil massif.

Analysis of the relationship of precious metals in Nizhny Tagil chromites with other groups of chemical elements among themselves, as well as their relationship with the Nizhny Tagil dunite and primitive mantle (McDonough, 1990), reveals that the geochemical migration of PGE, gold and silver in this massif is accompanied by the geochemical migration of the following elements: Cr, Zn, Co, Cu, Zr, Pb, Nb, Sn, Sb, Cd, Bi, Y, Th, Tl, U. This migration seems to be quite independent, but it can spatially and temporally overlap with the formation of chromite segregations in dunites of the Nizhny Tagil massif.

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# STRUCTURE AND MINERALOGY OF PERIDOTITE FROM BAER OPHIOLITE, YALUNG ZANGBO SUTURE ZONE, TIBET: RECORDS OF TWO STAGE EVOLUTION FROM MID-OCEAN RIDGE TO SSZ

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**ABSTRACT**. The Yarlung Zangbo Suture Zone (YZSZ), including the ophiolite complexes, the ophiolitic mélange, and metamorphic and sedimentary sequences, is thought to be the geological feature of the most important collision event to have happened on Earth since the Cretaceous-Tertiary and marks the most important boundary between India and Eurasia.

Rosaries of ophiolitic massifs in YZSZ outcropping from Namche Barwa syntaxis in the east to Ladakh area in the west can be subdivided into several ophiolitic complexes: Namche Barwa syntaxis ophiolites, Luobusa ophiolites, Xigaze ophiolites, Yungbwa ophiolites, Dongbo ophiolites, Karzog-Spontang ophiolites and Sapat-Jijal ophiolites.

The Baer ophiolite crops out in the Dongbo ophiolites. The tectonites in the Baer ophiolite are mainly made of Cpx-bearing harzburgite and no crustal section was found. According to the texture and structure of the peridotites, the mineral assemblage can be divided into three generations:

1) the first generation mineral assemblage of the residual mantle includes olivine, orthopyroxene and clinopyroxene porphyroclast;

2) the second generation includes olivine, orthopyroxene, clinopyroxene and spinel showing variable Cr# of 0.12-0.5. They have representative features of magmatism and along the first generations porphyroclast, and are products of partial melting and melt-peridotite reaction;

3) the third generation amphibole display low $Na_2O$ (1.35%~2.08%) and $TiO_2$ (0.26%~0.28%), indicating that they recorded the event of mantle metasomatism during subduction. The petrography and mineralogy of peridotites from Baer are interpreted to suggest that the peridotites in Baer experienced a two-stage evolution: they were formed at a slow spreading mid-ocean ridge and subsequently entered a subduction zone setting.

# A POSSIBLE CONTINENTAL MARGIN-TYPE OPHIOLITE IN THE WESTERN YARLUNG ZANGBO SUTURE ZONE, TIBET, CHINA

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**ABSTRACT**. The ophiolites located in the western Yarlung Zangbo Suture zone (YZSZ) consist from bottom to upward of peridotite, mafic dikes, massive basalt and basaltic hyaloclastites, silty shale, radiolarian chert and siliceous to massive limestones. The geochemistry and isotope of 120~130 Ma mafic dikes and Late Jurassic to Early Cretaceous radiolarian chert show that they formed in a continental margin environment; 137-140 Ma OIB-like basalt reflect a seamount volcanism. Associated with the similar fossil and sedimental characteristics on both sides of the YZSZ, we infer that the peridotites represent blocks of oceanic mantle formed in the ocean-continent transition environment.

The Yarlung Zangbo Suture zone (YZSZ), extending more than 2000 km across southern Tibet and into Myanmar, is thought to mark the tectonic boundary between India and Asia. Several large ophiolitic massifs which crop out discontinuously in the western part of this zone, e.g., the Dongbo, Purang, Dangqiong and Xiugugabu bodies (Fig. 1), are considered to be fragments of Neo-Tethyan ocean lithosphere emplaced during subduction of the Indian plate beneath Eurasia. Those ophiolites show a seamount-like stratigraphy, consisting from the base upward of peridotites, mafic dikes, massive basalt and basaltic hyaloclastites, mudstone and silty shale, radiolarian chert locally containing discontinuous basaltic lava flows, and siliceous to massive limestones with minor oolites. The peridotites, which are composed of depleted harzburgite, minor lherzolite and dunite, experienced high degrees of partial melting and then were enriched by later fluids/melts. Mafic dikes intruding into the peridotites have zircon U-Pb ages ranging from120.2 ± 2.3Ma to 130 ± 0.5 Ma (Li et al., 2008; Xiong et al., 2011), and exhibit N-MORB-like chondrite-normalized REE patterns, with negative Nb anomalies in spider diagrams. These geochemical features are similar to those of volcanic-rifted margin basalts (Dilek & Furnes, 2011; Pearce, 2008). Some OIB-like basalts occurring between the silty shale and peridotites have a zircon U-Pb age of 140Ma. These basalts have much higher $TiO_2$ (aver. 3.27 wt.%) contents than the MORB-like lavas and are thought to reflect limited seamount volcanism. Sparse E-MORB-like basalts also crop out within the radiolarian cherts in the upper part of the seamount sequence. They have a zircon U-Pb age of 137 Ma, in agreement with Late Jurassic to Early Cretaceous ages of radiolarian fossils in the host cherts of (Liu et al., 2013). Geochemical evidence suggests that the cherts were deposited in a continental rifted margin environment. Similar Cenozoic fossil fauna and flora have been reported on both sides of the YZSZ, and have been interpreted to indicate a narrow Neotethyan ocean basin (Hu et al., 2008; Xiao & Wang, 1998). We infer that the peridotites outcropping in the western part of the Yarlung Zangbo Suture zone represent blocks of oceanic mantle derived from a transition environment between the northern rifted margin of the Indian block and the adjacent ocean basin.

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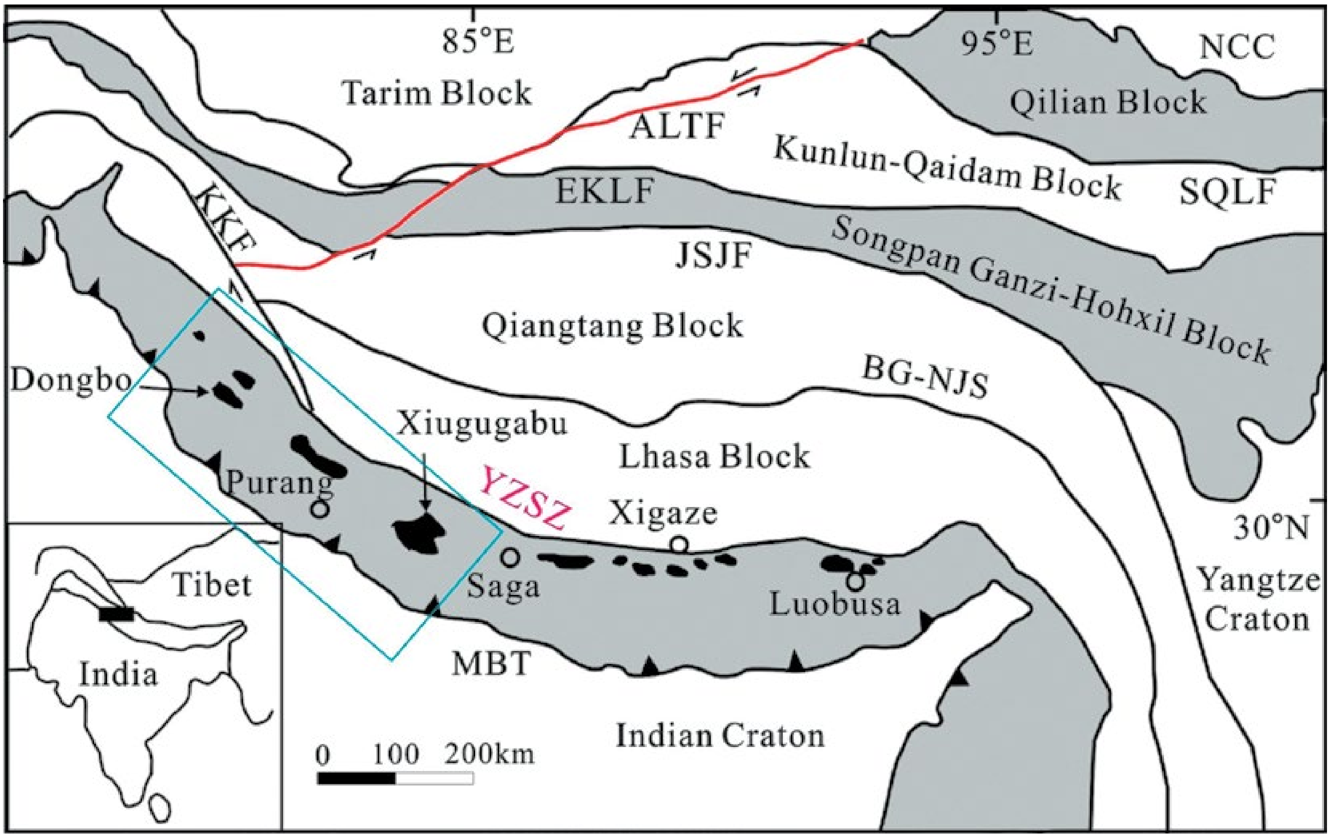

*Fig. 1*. Sketch map of the Tibetan plateau showing major tectonic units and study area (modified after Liu et al., 2010). ALTF: Alkin strike-slip fault; BG-NJS: Bangong – Nujiang suture; EKLF: East Kunlun fault; KKF: Karakorum strike-slip fault; JSJF: Jinshajiang fault; MBT: Main boundary thrust fault; NCC: North China Craton; SQLF: Southern Chilien strike-slip fault; YZSZ: YarlungZangboSuture Zone.

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# THE FINAL SILICATE MAGMA APPROACHES AN "AMPHIBOLIC" COMPOSITION IN THE AMPHIBOLE-RICH PERIDOTITES OF THE BUTYRIN VEIN, KYTLYM MASSIF (URALS) AND THE HUDSON HIGHLANDS (NEW YORK)

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**ABSTRACT**. We describe two examples, one in the Kytlym ultramafic massif, Ural Platinum Belt, Russia, and the other in the Hudson Highlands in southeastern New York State, U.S.A., that involve a late magmatic amphibole considered to approach a melt composition. Both indicate that the latest melts in environments of tectonic relaxation following a series of major continent-continent collisions may well involve an "amphibolic" melt, possibly coexisting with a felsic silicate magma, an oxide magma, a carbonate magma, and a sulfide melt.

The Butyrin veins of amphibole-bearing clinopyroxenite with a chromian spinel cut the Kosva dunite in the Kytlym ultramafic massif, Ural Platinum Belt (UPB), Russia. The thin veins have a border zone of orthopyroxene; their main part consist of clinopyroxene, chromian spinel, zoned calcic amphibole and sparse fresh olivine. The augite, Mg# ≈ 0.95, is homogeneous. The grains of the clinopyroxene contain a strikingly patchy distribution of xenomorphic domains of calcic amphibole, here interpreted as melt inclusions. The larger the domain, the more likely is the evidence of multiple centers of nucleation and growth. Each domain or subdomain is zoned from a tremolitic border to magnesiohornblende, with the magnesiohornblende richer in Cr, Fe and Ti than the tremolitic rim. The amphiboles are richer in Cr, Fe and Ti than their augite host; both F and Cl are negligible at the W site. The textures are not affected by deformation. Augite and the chromian spinel may well have crystallized from coexisting silicate and oxide melts, and the calcic amphibole crystallized soon thereafter, at or near the solidus of the silicate melt. By implication, that melt converged to a magnesiohornblende composition. Interestingly, PGM and sulfide grains are located at amphibole – chromian spinel interfaces (Zaccarini et al., 2011). In other complexes of the UPB, such an ultrabasic melt may well have coexisted with an iron oxide melt, as a sideronitic texture involving magnetite has been documented in the literature.

Unusual alkali-rich amphibole-dominant peridotites were emplaced in upper-amphibolite- to granulite-facies rocks of Grenvillian (Proterozoic) age in the Hudson Highlands in southeastern New York State. These intrusive rocks are Neoproterozoic [1001±2 Ma (Wilks mine), 1009.5±1.9 Ma (Hogencamp mine), U/Pb on zircon], coarse-grained, undeformed, and cut their host rocks with a sharp contact. They are spatially associated with small deposits of magnetite. Magnetite and sulfides (pyrrhotite±pentlandite with chalcopyrite) locally define a sideronitic texture. Also present are fresh magnesian fayalite, phlogopite, almandine and calcite. The amphibole is hastingsitic, and rather unusual in being enriched in K, the halogens and the light rare-earths. At some localities, Cl is dominant, whereas at others nearby, fluorine is dominant at the W site. Along with accessory phlogopite, an amphibole is the last phase to crystallize, and constitutes the intercumulus phase in Cpx+Ol cumulates. Compositionally, such an amphibole approaches a magma of OIB type. It is probably for this reason that an unusually coarse grain-size is typical of the amphibole. Oxygen-isotopic evidence suggests that the amphibole and calcite both contain a mixture of crustal and mantle components. The oxide, sulfide and silicate melts are considered to be related to an asthenopheric source heating the overlying metasomatized lower crust at the very end of the Grenville event, at a stage of tectonic relaxation. We attribute to a mixed hydrothermal and carbothermal fluid the efficient transfer of heat needed for the anatectic reactions in the lower crust, leading to a coeval syenitic melt of likely anatectic origin.

These two examples involve very different amphiboles, but both indicate that the latest melts in environments of tectonic relaxation following a series of major continent-continent collisions may well involve an "amphibolic" melt, possibly coexisting with a felsic silicate magma, an oxide magma, a carbonate magma, and a sulfide melt.

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# A GENETIC MODEL OF PGM HOSTED IN CUMULATIVE GABBRO-PYROXENITE-DUNITE COMPLEXES OF THE KORYAK HIGHLAND, RUSSIA

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**ABSTRACT**. A new genetic model of platinum group minerals (PGM) from gabbro-pyroxenite-dunite (GPD) plutonic complexes has been developed. The genetic types of PGM resources make up a multifactor system of ore-forming processes with the participation of PGE contained in PGD complexes. The defined genetic types of PGM and criteria of their evolution are regarded as self-dependent attributes of mineral deposits, their prospecting, exploration, and mining.

The gabro-pyroxenite-dunite (GPD) plutons of the Olyutorka accretionary complex in the Koryak Highland are comparable with similar island-arc rock associations of southeast Alaska and other segments of the Pacific Fold Zone. These plutons are formed by dunite body and by wehrlite-clinopyroxenite and then gabbroic coat. The GPD plutons are comagmatic to picrite-basalt lava flows of the Late Cretaceous-Paleocene Achaivayam island arc. The formation of large dunite bodies is explained by multifold supply of primary picritic magma to the conduit chamber and periodical crystallization of Cr-spinel-olivine and olivine-clinopyroxene cumulates owing to removal of the residual melt. Pyroxenite and gabbro consecutively crystallized from the melt. Dunites of the GPD massifs show regularly zonal deformational structures caused by synmagmatic recrystallization, long-term transportation, and cooling (Batanova et al., 2005). The placer PGM deposits in areas adjoining the GPD plutonic complexes of the Olyutorka accretion arc complex of the Koryak Highland are analogs of the world's largest placers of the Platinum Belt in the Urals.

A genetic model has been developed for PGM hosted in plutonic GPD complexes of the Koryak Highland (Mochalov, 2013). The following mineralogical-geochemical and genetic PGM types have been distinguished: (1) magmatic platinum (Pt), (2) magmatic-fluid-metasomatic platinum (Pt) and osmium-platinum (Pt > Os), (3) fluid-metamorphic iridium-platinum (Pt > Ir), and (4) hydrothermal metasomatic platinum-copper (Pt-Cu).

PGM of the magmatic Pt type were formed under conditions of monocyclic petrogenesis of Cr-spinel-olivine and olivine-clinopyroxene cumulates as products of picritic magma fractionation in the "canal-chamber" (Fig. a).

The magmatic-fluid-metasomatic platinum Pt and osmium-platinum Pt > Os types were formed by interaction of these early cumulates with magma. The abundance of these types is proportional to injections of picritic magma into the "canal-chamber" (Fig. 1 a, b).

PGM of the fluid-metamorphic iridium-platinum Pt > Ir type accumulated as a result of synmagmatic recrystallization of GPD cumulates. Their development depends on (1) mono- or polycyclic GPD cumulative complex and (2) the degree of GPD cumulate recrystallization from partial to complete and the degree of transformation of PGM pertaining to the magmatic and magmatic-fluid-metasomatic Pt types (Fig. 1 c).

The monocyclic GPD complexes are not favorable for prospective magmatic Pt deposit formation (Fig. a). The polycyclic GPD complexes differ in their prospectively from ore occurrences to unique magmatic-fluid-metasomatic Pt and Pt > Os deposits, as well as deposits of the fluid-metamorphic Pt > Ir type (Fig. 1 b, c).

The genetic types of PGM accumulation imply a multifactor system of ore-forming processes with the participation of platinum-group elements in GPD complexes. The genetically different PGM accumulations in GPD complexes should

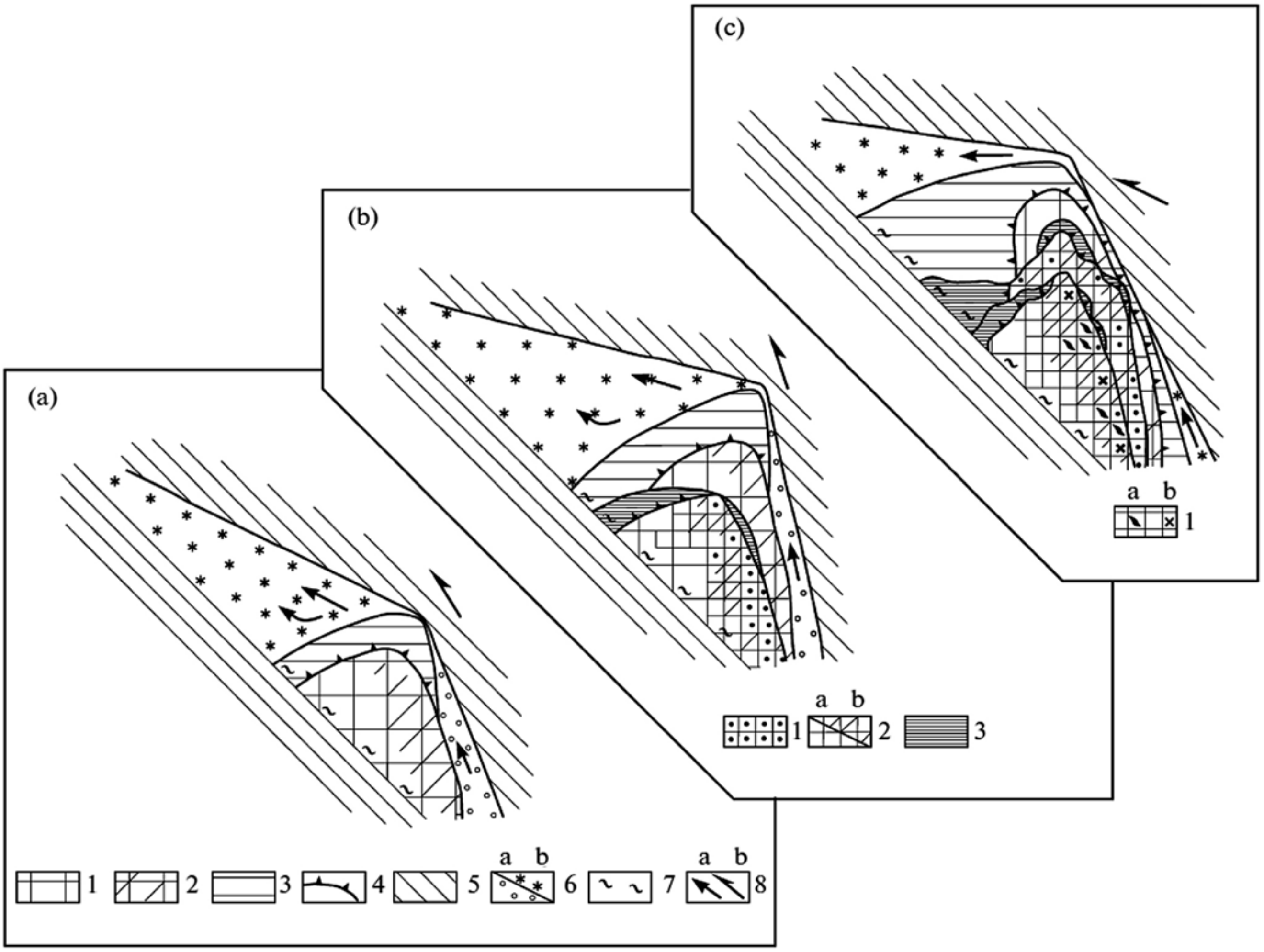

*Fig. 1.* Conceptual schemes of PGM evolution in GPD plutonic complexes: (a) monocyclic GPD cumulative complex with PGM of magmatic Pt-type, (b) polycyclic GPD cumulative complex with synmagmatic metasomatic and metamorphic recrystallization of PGM in dunites, (c) polycyclic GPD cumulative complex with multiple synmagmatic recrystallization of dunite. Legend to panel (a): (1, 2) cumulates of primary picritic melt: (1) olivine-pyroxene and (2) Cr-spinel-olivine; (3) magmatic Pt type in pyroxenite of residual melt; (4) magmatic fluid-metasomatic Pt > Os type at the contacts between dunite and clinopyroxenite; (5) country rocks; (6) melts: (a) primary picritic and (b) residual; (7) zone of the highest abundance of hydrothermal metasomatic Pt-Cu type in ultramafic rocks enriched in kink bands up to the almost mylonite structure; (8) directions of (a) melt flow and (b) dynamic stress. Legend to panel (b): (1) magmatic fluid-metasomatic Pt type in polygonal coarse-grained to pegmatoid black dunite with abundant µm-sized inclusions of Cr-spinel and Cr-magnetite in olivine; (2) fluid-metamorphic Pt > Ir type in (a) fine-grained porphyroclastic dunite, wehrlite, and pyroxenite; (b) dunite with Cr-spinel disseminations; (3) porphyroclastic clinopyroxenite. Legend to panel (c): (1) zone of fluid-metamorphic Pt > Ir type with nuggets in chromitite (a) schlieren and (b) veins hosted in magnesian dunite with the medium-sized and large porphyroclasts

be regarded as self-dependent geological objects of local forecasting. In this connection, it is necessary to renew mineralogical and geochemical criteria for prospecting and exploration of PGM genetic types in GPD complexes as well as their mining conditions.

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# GENESIS FEATURES OF PLATINUM MINERALS IN ULTRAMAFIC COMPLEXES OF KORYAK HIGHLAND OPHIOLITES

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**ABSTRACT**. The mantle and cumulative complexes of Koryak ophiolites were formed in different tectonic settings: from early rifting to mature island arcs. Partitioning aspects of platinum group minerals (PGMs) from these complexes are well studied by now. Rare earth elements (REE) partitioning, as a relic of solar protoplanetary matter, persistently correlate with Ca and between light (LREE) and heavy (HREE) rare earth elements within. Thereupon, studying the REE geochemistry in rock-forming upper mantle minerals may help to understand the genesis of PGM during the global evolution of chondrite material.

Peridotites from mantle complexes are lherzolites, fertile diopside-bearing harzburgites and properly harzburgites. The main difference between fertile and depleted peridotites is a morphology of accessory Cr-spinel: spinel from lherzolites and diopside-bearing harzburgites is always xenomorphic, but in ordinary harzburgite spinel is represented by mainly octahedral individuals (OI-Spl) with negative inclusions of amphibole, serpentine and chlorite. Clinopyroxene REE patterns indicate three transformation stages of primary harzburgite-lherzolite substrate:

- lherzolite passive depletion, possibly along with long-term fluid interaction, as clinopyroxene occurs only locally with LREE depletion;
- harzburgite-lherzolite matrix transformation to properly harzburgite by the partial melting, leading compositional shift of clinopyroxene and spinel to “refractory” values and more intensive LREE depletion in clinopyroxene. Due to the partial melting chemical composition of clinopyroxene from plagioclase-bearing lherzolites compatible to clinopyroxene from harzburgite in a following systematics: HREE–LREE, Y–LREE, Y–Gd, Y–Eu, Y–Sm, Gd–Eu, Gd–Sm, and Y–Zr, Gd–Zr as well;
- new formation of harzburgite with different amounts of spinel octahedral individuals, in a setting of active mantle fluid interaction and the prevalence of LREE. Harzburgites, pyroxenites and relatively large bodies of dunites with OI-Spl formed at this stage. At these conditions, clinopyroxene accumulate all LREE and Zr.

The main feature of clinopyroxene from the three stages is an inheritance of chondritic ratios between Y and HREE amount, testifying to the preservation of geochemical background of protoplanetary material at all stages of the formation of ultramafic mantle complexes. PGMs were not observed in the fertile harzburites and lherzolites. Actually, in harzburgites, PGMs occur only in association with spinel octahedral individuals and are unobserved with xenomorphic spinel.

The negative octahedral inclusions up to a few tens of microns have been ascertained in OI-Spl and chromite segregations in a form of “metallic octahedra”. These inclusions are represented by various mineral aggregates – native elements, intermetallic compounds and sulfides of Fe, Ni, Cu, Ru, Os, Ir, Pt, Rh and seldom Pd. The octahedral shape of the aggregates with initially different symmetry indicates these inclusions are a negative copy of octahedral interstices in OI-Spl. “Metallic octahedra” are the result of skeletal crystal growth of OI-Spl from the fluid saturated with ore components in the interstitial space of the silicate matrix. The specific of “metallic octahedra” are the direct evidence of immediate fractionation of platinum-group elements (PGEs) from the supercritical fluid in the ore cluster.

Two structural petrographic complexes form supersubduction massifs with complicated structure: (i) dunite-harzburgite Mg-rich mantle complex with lenses and schlieren of orthopyroxenites and (ii) taxitic cumulative complex of Fe-rich ultramafic rocks, formed by layered harzburgite, dunite, orthopyroxenite and websterite with schlieren of plagioclase lherzolite, olivine gabbro-norite and gabbro-pegmatite. The prevalent form of PGMs in mantle complexes are the solid solutions and sulfides of Ru, Os, Ir, isoferroplatinum in cumulative complexes and multicomponent solid solutions of Pt, Ir, Rh, Os and Ru in veined orthopyroxenites. Clinopyroxene from the mantle complexes are characterized by wide concentration range of Zr and Ti along the narrow Mg# (Mg/Mg+Fe) without any correlation that result from interaction of mantle peridotites with mafic melt and/or fluid. Clinopyroxene from cumulative complex and veined pyroxenite shows the Zr, Ti vs. Mg# co-variation; such a dependence indicates the melt crystallization differentiation. Hence rock formation of the cumulative complex and viend pyroxenite has an igneous genesis. Ti–LREE and LREE–HREE co-variation plots for clinopyroxene in association with amphibole specify these minerals as a marker of ore-forming fluid systems (since amphibole contains $H_2O$ component), therefore it suggests that the primary source of mineral assemblage of veined orthopyroxenite from mantle and cumulative complexes is the same. The nature of this source is within the partially depleted peridotite, which is a producer of mantle and cumulative ophiolites. Common point for clinopyroxene from ultramafic cumulate complex is a permanent Y vs. REE ratio and between Yb–Er–Dy–Gd–Eu–Sm within REE. LREE are depleted with respect to this group of elements as well. Such ratios between mentioned above elements indicate the chondrite nature of REE, and some of them are unreceptive to the partial melting of primary mantle during the formation of mantle and cumulative complexes.

The $Fe^{3+}/\Sigma Fe$ values in spinel obtained by Mössbauer spectroscopy widely range: from 0.06 to 0.36 (average 0.17) in mantle complex and from 0.14 to 0.31 (average 0.20) in cumulative complex. Temperatures based on equilibrated assemblages range from 600 to 1060°C. Calculated values of oxygen fugacity ($fO_2$) for studied samples subdivide into three main groups. The first group with xenomorphic spinel from mantle complex, $fO_2$ values between FMQ and WM oxygen buffers (these samples are the result of the mantle partial melting). Second are the low-temperature OI-Spl samples with a wide range of $fO_2$ from about MH buffer to the most oxidized samples with Cr-rich spinel (fluid interaction on mantle complex). Third, high-temperature OI-Spl samples from mantle complex including veined pyroxenites together with secondary spinel and chromite (igneous cumulates) with $fO_2$ values along FMQ buffer.

Thus, PGEs in depleted mantle reservoir are dispersed as in chondrite material. In a setting of “local, secondary” interaction with mantle fluid component these substance were modified with the appearance of veined pyroxenites and cumulative complexes plus the formation of different associations of PGMs and chromite ores.

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# CURRENT PLATINUM POTENTIAL OF URAL–ALASKAN INTRUSIONS AND THEIR RESULTANT PLACERS

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**ABSTRACT**. There is a general lack of understanding of Ural-Alaskan intrusions and the importance of the platinum placers that develop from them, among exploration companies outside of Russia. This paper aims to highlight the global exploration opportunities that result from this. Using successful operations in Russia as examples, it is demonstrated that there are many opportunities for similar discoveries around the world. The potential for platinum bedrock and laterite deposits is also discussed.

Ural-Alaskan (UA) type zoned intrusions seem to be particularly associated with the Pacific Rim, near the boundary between oceanic and continental plates, where they are known to occur in Alaska, British Colombia, the Russian Far East, Philippines, Papua New Guinea, New Caledonia, Eastern Australia and New Zealand. Elsewhere UA intrusions are also known to occur in the Urals, Siberia, Ethiopia, Egypt and Colombia.

The key economic importance of UA intrusions is the existence of the metallic platinum (mainly isoferroplatinum) associated generally with pods and schlieren of chromite and located within a dunite core. Being very dense and resistant to erosion, platinum can form rich placers as the intrusion erodes. The most productive economic deposits of alluvial platinum in the world are associated with UA complexes.

Placer platinum deposits have been mined in Russia (Urals, eastern Siberia and Kamchatka), Alaska, Canada, Colombia and Ecuador for many years. While a number of deposits have been mined very profitably in these countries, active exploration and mining of platinum placers currently occurs only in Russia (Kondyor – about 80 t of Pt already has been mined, Galmoenan – about 55 t), and this is the only country where knowledge of this type of deposit still exists. In other parts of the world, the exploration knowledge of this type of mineral deposit has essentially been lost or never existed. Compounding this, is the current resistance to placer mining that has developed in many countries. This makes it virtually impossible to raise money for placer exploration on any stock exchange.

Exploration and development opportunities for platinum placers still exist in many parts of the world, where either UA intrusions with well-developed dunite cores have been delineated, or where isoferroplatinum grains have been found in significant amounts. In order of priority, countries with such potential would be Australia (NSW), New Zealand and Canada (British Columbia).

The Fifield UA belt in Eastern Australia extends over an area180 km long (NS) and 80 km wide. UA complexes in the Fifield region are generally pipe-like bodies with steeply dipping internal contacts. Many of the complexes are approximately circular or elliptical in plan view, although more irregularly shaped bodies also occur. The size of the intrusions varies from a few sq km up to 120 sq km (Elliot et al, 1991). The geological position, the pipe-like form of the intrusions and style of PGE mineralisation are all similar to UA complexes in Siberia, Russia (Kondyor, Inagly, etc.). On several of these intrusions, dunite has been identified, with some significant platinum grades intersected. Recorded production from one deep lead in the Fiefield area during the 1890 s was 640 kg of alluvial platinum. This is insignificant compared with what could be expected to have accumulated from the erosion of several UA intrusions.

Almost no attention has been paid to the potential for platinum placers in New Zealand, despite the fact that UA intrusions are known to exist there. One such intrusion, Greenhills, has a well-developed dunite core. The presence of platinum and chromite clusters has also been established by some researchers (Spandler et al., 2000). There are also references to Pt-Fe alloys with secondary sperrylite in beach placers that were mined for alluvial gold at Orepuki (Challis, 1989). Recorded production of platinum was about 60 kg. It is possible that a UA intrusion exists in the Orepuki region but has not so far been recognised.

A major reason for the lack of success in these countries is the fact that for exploration of mafic/ultramafic complexes in general and for platinum in particular, the exploration methods appropriate for layered intrusions have invariably been used. As a result, attention has been focussed on the wrong part of the intrusion, and the idea of exploring for associated platinum placers has almost never been considered. For example, modern platinum exploration in the Fiefield region has, and continues to target only bedrock platinum.

There are numerous occurrences of mafic/ultramafic systems in New Zealand, including obvious signs that suggest the presence of UA massifs, but no one has actually referred to them as such. This suggests that in NZ also, those exploring for platinum had a lack of understanding of such intrusive systems and the rich placer deposits they can produce.

Given the relative ease and low cost of exploring placer deposits, the low capital and operating costs of a mining operation, the high profit margin of most placer operations and the fact that non-forested land can often be left in better condition post-mining, than its pre-mining stating state, this reluctance to become involved in platinum placer exploration and mining is surprising.

There is also the potential for economically mineable platinum deposits to exist within the bedrock of UA intrusions, particularly in the Kondyor and Galmoenan intrusions in the Russian Far East (Nazimova et al., 2011). Such deposits are likely to comprise aggregates of many mineralised clusters, occurring with sufficient density and grade to be viable. Using appropriate exploration and sampling techniques in such settings would be critical to success. A very positive feature of such intrusions is that the platinum can be recovered by simple gravity separation.

In additional to the traditional placers and the potential for bedrock deposits, a new type of platinum deposit appears to have been discovered from the lateritic weathering of several UA intrusions. For example, recent exploration of the Owendale intrusion in eastern Australia has led to delineation of mineral resources of 520,000 oz of platinum and 9,100 tonnes of scandium metal (Platina Resources Ltd, public report). Similar potential exist in all tropical countries with deep chemical weathering profiles.

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# Pt-Fe ALLOYS AS INDEX MINERALS FOR THE FORMATION OF PGE ORES IN MAFIC-ULTRAMAFIC ROCKS

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**ABSTRACT**. Pt-Fe alloys are characterized by a wide solubility field of trace elements and thus may be regarded as sensitive typomorphic platinum-group minerals to be used for the determination of physico-chemical conditions of the formation of Pt-bearing deposits associated with various types of mafic-ultramafic rocks.

The author presents ternary multidiagrams clearly showing the main trends of compositional variations of Pt-Fe alloys widespread in placer and bedrock deposits (Fig. 1).These trends may also be used in tracing bedrock sources for PGMs from placer deposits. On the Pt-(Ir+Os+Ru+Rh+Pd)-(Fe+Ni+Cu) diagram with a projection from the Cu-system (Fig. 1, A), PGMs from the Witwatersrand placers (Feather, 1976) show a continuous linear trend from the composition of isoferroplatinum ($Pt_3$ Fe) nearly up to the minerals of Ru-Ir-Os composition (see inset map). Similar Fe-Pt alloys with high amounts of other PGE impurities are described from the placers of the Guli massif (Malitch, 1999). However, complete solid solutions of PGE can only exist under high-temperature conditions, while at a lower temperature the solubility of other PGE in platinum doesn't normally exceed 20 mass.% in total. In this case, the primary high-temperature solid solutions exsolve to form intimate ingrowths of Pt-Fe alloys with Ru, Ir and Os minerals. In placer deposits associated with various types of Pt mineralization, most Fe-Pt alloys have a similar composition to $Pt_3Fe$ (isoferroplatinum), but some of them lie in the field of native platinum or deviate towards more highly ferruginous varieties. Pt particles with the highest Fe content fall into the field of tetraferroplatinum, Ni-rich phases form ferronikelplatinum, while Cu-minerals deviate towards tulameenite.

On the (Pt+Pd+Fe+Ni+Cu)-(Ir+Os)-(Ru+Rh) diagram with a projection from the Pd-system, Fe-Pt alloys show three main trends with regard to their trace elements distribution (Fig. 1, B). The Ir-trend is typical for minerals from chromite ores of dunites in zonal massifs of the Urals (Garuti et al., 2002; Volchenko et al., 2007), Kondyor, Inagli (Okrugin, 2011) and other deposits of the Uralian-Alaskan and Aldanian types. The second trend involves an increase in the contents of Ru and Rh impurities as observed in placer deposits in the eastern Siberian platform (Vilyuian type) with unknown bedrock sources. There is an intermediate trend between the two, involving a concurrent increase in Ir, Os, Ru and Rh as observed in minerals from chromite ores of the Krasnogorsk massif belonging to the Alpine-type ultramafic rocks (Dmitrenko et al., 1985). Minerals with low Ir, Os, Ru and Rh values show an increase in Pd content and form the third Pd-trend. In the Krasnogorsk massif, in the harzburgite-dunite-orthopyroxenite series, the role of hexagonal solid solutions of Ru-Ir-Os composition decreases while that of cubic Ir-Os-Ru-Rh-Pt alloys with high Fe, Ni, Cu and Pd increases (Dmitrenko et al., 1985). Small pyroxenite-pegmatite veins containing Pd-tulameenite and Pd-tetraferroplatinum have been identified in dunites of the Kytlym massif in the Urals (Volchenko et al., 2007). The PGM association of clinopyroxenites of the Kondyor massif additionally includes tulameenite, while Pt-Fe alloys are enriched in Rh and Pd, i.e., the chromite association of PGM is rich in refractory IPGE and the clinopyroxenite association – in Pd (Malitch, 1999).

Each of the above-mentioned trends is controlled by certain physico-chemical conditions of the formation of PGE mineralization. The most important is a geochemical specialization of the enclosing igneous rocks depending on the degree of their differentiation and the fugacity of sulphur. For example, Pt-Fe alloys from restite Alpine-type hyperbasites contain high values of infusible Os, Ir and Ru. A clearly defined iridium trend is particularly characteristic of isoferroplatinum from early magmatic chromitie ores of zonal dunite massifs of the Uralian-Alaskan and Aldanian types, and their Pd and Cu contents increase at later stages of mineralization. High Ru and Rh concentrations and low Ir values in ferroan platinum from the Vilyui placers in the eastern Sibe-

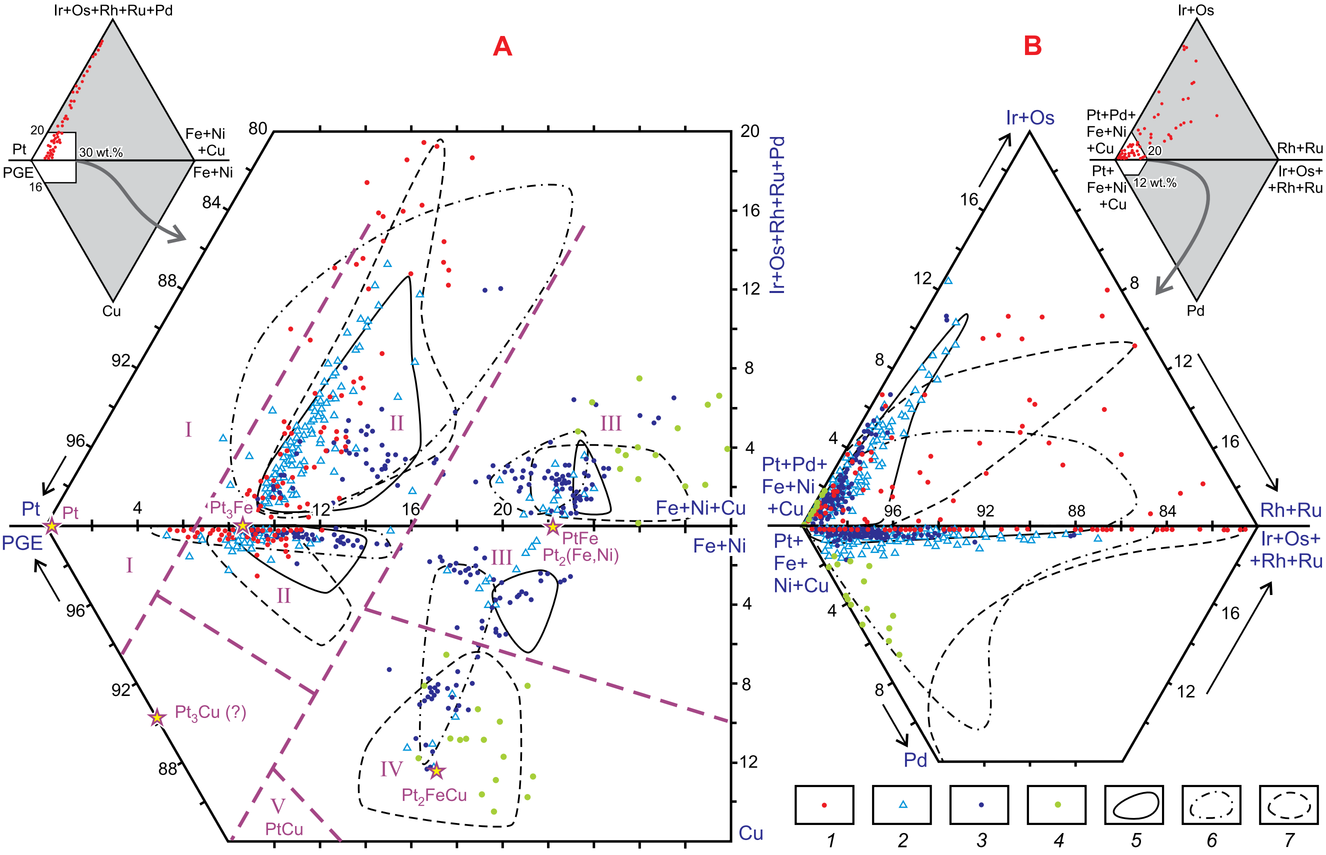

*Fig. 1.* Ternary compositional diagrams for Fe-Pt alloys. 1 – Witwatersrand placers, SAR, shown in full on inset maps, n=94, after Feather (1976); 2 – Kushva, Nizhniy Tagil and other placers, Urals, n=153 (Cabri et al., 1996); 3 – PGE-chromite ores from dunites, Urals, n=123 (Garuti et al., 2002, Volchenko et al., 2007); 4 – Cr-Ti-magnetite ores in pyroxenite-pegmatites, Urals, n=16 (Volchenko et al., 2007). Compositional fields: 5 – Kondyor placer, Aldan shield, n=204, (author's data); 6 – Vilyui r. placers, Siberian platform, n=213 (Okrugin, 2011); 7 – chromite ores of the Krasnogorsk massif, n=222 (Dmitrenko et al., 1985). Compositional fields of native Pt (I), ferroan platinum and isoferroplatinum (II), tetraferroplatinum (III), tulameenite (IV) and hongshiite (V) are separated by a thick dashed line. Stars show stoichiometric compositions of minerals

rian platform are due to S-deficiency of the primary ores, when even the most chalcophile PGE such as Ru, Rh and Pd remain in the metallic form. Low Ir and Os contents in ferroan platinum, as well as insignificant amounts of Ru-Ir-Os minerals in the placers, are indicative of the gabbroid composition of their parent magmas. By contrast, in low-sulfide and sulfide types of deposits (sulfide-chromite ores of layered intrusions – Bushveld and analogues, sulfide ores at Sudbury, Noril'sk, etc.) rare aggregates of Pt-Fe alloys occur in the form of finely dispersed phases actually free of other PGE impurities. The latter primarily form part of the basic sulfide minerals and occur as isomorphic impurities or form their own sulfide, arsenide, telluride and other intermetallic compounds.

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# SOURCE OF PLATINUM-GROUP MINERALS (PGM) FROM PYROPE-GARNET RICH PLACER DEPOSIT, BOHEMIAN MASSIF: RESULTS FROM MINERALOGICAL AND Re-Os GEOCHRONOLOGICAL STUDIES

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**ABSTRACT**. Very rare PGM were found in pyrope-rich garnet placer at Vestrev (Bohemian Massif). Mineralogical and in situ Re-Os isotopic data indicate that mantle-derived peridotites could represent source of PGM.

Very rare PGM (isoferroplatinum – PtFe) accompanied by osmium, Ir, and Ru alloys, locally with inclusions of ferroplatinum and hongshiite – PtCu) were identified in the heavy fraction of Quaternary pyrope-rich garnet placer at Vestrev (Krkonose Piedmont Basin, Bohemian Massif). The basement rocks of the Bohemian Massif represent a remnant of the Variscan orogeny spread across Western to Eastern Europe. The orogeny itself is divided into seven linear tectonic units or belts between the Rhine area in the north and the Danube region to the south (Franke, 1989; Cháb et al., 2010 and others). The pyrope-rich garnet placer deposit at Vestřev is geologicaly situated in the Lugicum, which represents a mosaic of crustal domains composed of various sized blocks (units). The Lugicum is also known as Western Sudetes (West Sudetic Belt, Zone) (Cháb et al., 2010).

Besides rare inclusions of ruthenium and osmium grains, the remaining PGM are heterogeneous. Ruthenium and Os alloys frequently contains Os exsolution lamellae, while Ir alloys contain numerous inclusions of Pt-Fe-(Ir, Rh), rare Pt-Cu inclusions and Os exsolution lamellae (Table 1). This mineralogical association is typical for various mantle settings including

Table 1

**Elemental composition of Os-Ir-Ru minerals from Vestřev** (wt.%)

| *Grain no.* | *mineral* | *Os* | *Ir* | *Ru* | *Fe* | *Total* |
|---|---|---|---|---|---|---|
| 1 | ruthenium (matrix) | 36.01 | 30.84 | 32.45 | 0.57 | 99.87 |
| 2 | iridium (matrix with Pt-Fe-(Ir,Rh) inclusions) | 37.13 | 57.83 | 2.40 | 0.63 | 97.99 |
| 2 | osmium (lamellae and a long bent inclusion) | 61.82 | 35.06 | 2.80 | 0.33 | 100.01 |
| 3 | ruthenium (matrix) | 39.48 | 30.76 | 27.20 | 0.29 | 97.73 |
| 3 | ruthenium (islet at the margin) | 43.61 | 35.32 | 20.41 | 0.42 | 99.76 |
| 3 | osmium (narrow marginal zone in corner) | 49.79 | 38.58 | 8.53 | 0.99 | 97.89 |
| 4 | ruthenium (matrix) | 40.55 | 33.70 | 23.08 | 0.15 | 97.49 |
| 5 | osmium (matrix) | 59.38 | 35.57 | 3.91 | 0.10 | 98.96 |
| 6 | osmium (matrix) | 54.49 | 43.54 | 1.27 | 0.93 | 100.22 |
| 6 | iridium (large inclusion) | 29.23 | 67.82 | 0.63 | 1.00 | 98.68 |
| 6 | iridium (thin lamella) | 21.06 | 73.31 | 0.72 | 1.46 | 96.55 |
| 7 | iridium (matrix with inclusions of Pt-Fe-(Ir,Rh) and Pt-Cu and a lamellae of osmium) | 34.06 | 59.67 | 1.92 | 0.50 | 96.14 |

ophiolites which is suggested by the chemistry of the Os-Ir-Ru minerals, showing a typical enrichment of the PGM in Ru. The irregular shape of the PGM grains, locally with preserved hexagonal and/or cubic morphology may reflect their durable nature and a short distance of transport. Despite numerous mineralogical studies of heavy mineral assemblages, no PGM were reported from other pyrope-rich garnet placer deposits in the Bohemian Massif.

In situ Re-Os isotopic data on the Os-rich phases, obtained by laser ablation MC-ICPMS, show heterogeneous Os isotopic compositions ($^{187}$Os/$^{188}$Os=0.12082-0.12505, average=0.12276) and negative γOs, indicating a subchondritic mantle source of PGE which is consistent with a close association between the PGM from Vestrev and mantle-derived rocks. The Os model ages from ~0.4 to ~1.0 Ga most likely evidence that source parental melts were extracted from distinct mantle domains that have experienced different histories of melt-depletion leading to $^{187}$Os/$^{188}$Os heterogeneity.

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# MAIN CHARACTERISTICS OF «METALLIC PLATINUM» TYPE OF ORE FROM VARIOUS RUSSIAN DEPOSITS

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**ABSTRACT**. Metallic platinum ore is an economic type of platinum mineralisation, associated with Ural-Alaskan intrusions. Despite minor production (about 300 kg) of platinum from this type of ore (Urals, end of the IXX – the early XX century), this is the first modern study of the applied mineralogy and beneficiation characteristics of these ores from various Russian deposits.

In Russia during last decade, close attention has been given to bedrock platinum mineralisation within Ural-Alaskan type zoned intrusions. Detailed and extensive exploration work was conducted between 1997 and 2008 on the Galmoenan intrusion by KoryakGeolDobytcha CJSC. Similar work is currently being carried out on the Kondyor massif by Artel Starateley “Amur” (Russian Platinum CJSC). Also, Polymetal PLC has recently received a license for exploring the potential for bed-rock deposits on the Svetloborsky massif on Urals.

Bedrock platinum mineralisation from Ural-Alaskan zoned intrusion has already been known for more than 150 years, since platinum was mined from the schlieren and veinlets of chromite on the Nizhny Tagil massif. The quantity of platinum mined from this bed rock was incredibly low compared with what has been mined from placers (300 kg against 300 tonnes). Nevertheless, exploration provided on the Galmoenan intrusion, showed that this type of bedrock deposit has significant economic potential (Nazimova et al., 2011).

Numerous earlier investigations by number of researchers on the Nizhny Tagil (Urals), Galmoenan (Kamchatka) and Kondyor (Russian Far East) deposits showed that the platinum mineralisation from these intrusions is genetically similar. An applied mineralogy and beneficiation study of the Galmoenan platinum mineralisation, led to a new understanding of the mineralogical and metallurgical characteristics of this type of ore – “metallic platinum ore” (Petrov et al., 2010; Nazimova et al., 2011). A primary economic assessment of the entire process showed that a deposit with the same platinum grade and the same metallurgical properties as the sample that was tested could be economically mined and processed through a commercial-scale plant, based on the pilot plant that was used (Bogdanovich et al., 2010).

Similar applied mineralogy and beneficiation work was carried out on the Kondyor deposit in 2012-2013. Seven mineralogical samples weighing 6-9 kg each and two one-tonne bulk samples were used for this investigation. The technical part of the study was provided in the Mekhanobr Engineering facility (St. Petersburg) by A.V. Bogdanovich.

In spite of the fact that the Kondyor intrusion is located in a different geodynamic situation and has more complicated geological composition (compared with Galmoenan and the Urals), we refer it’s platinum mineralisation to the same economic type of ore – “metallic platinum ore”.

The platinum mineralisation of the Galmoenan, Urals and Kondyor intrusions show similar characteristics of ore composition and final indexes of beneficiation (Table 1). The technological features for mine development and the main components that would be required for processing plants are also very similar. Significantly, the investigations generated similar economic parameters for each of these intrusions, indicating that if the deposits were of sufficient size, all of them could be economically mined.

Table 1

**The characteristics of the three known deposits, which contain metallic platinum ore**

| *Massif* | *Nizhny Tagil* | *Galmoenan* | *Kondyor* |
|---|---|---|---|
| Geodynamic position | Island arc system | | Activated platform |
| Shape of intrusion | Zoned, elongated | | Zoned, concentric |
| Rock petrography | Dunite, clinopyroxenite | | Dunite, clinopyroxenite,+alkaline rocks |
| Host rocks | Dunite (course- and medium grained) | | |
| Ore-associated rocks | Schlieren, veinlets, breccia, and disseminated clumps of chromitite | | |
| Ore bodies | Linear and volumetric zones of chromite accumulation, in association with course-grained dunite; strike – 500-1200m, thickness 20-150m | | Volumetric zones and tabular bodies; 300-800 m x 100-300 m. |
| PGE composition of ore | PGE distribution is achondritic with Pt and Ir peaks | | |
| Pt content in ore, g/t* | 0.8-1 | 1-1.5 | 2-3 |
| Mineral composition of ore | Chrome spinel (mainly chromite), olivine, serpentine, PGM | | |
| Main PGM | Isoferroplatinum, metallic Iridium and Osmium and their alloys, Laurite, Irarsite, Sperrylite. | | |
| | +Tetraferroplatinum, Tulameenite, Erlichmanite, Hollingworthite, Pt–Fe–Cu and Fe-Ni alloys | | +Cooperite, Konderite, Cuprorhodsite, Malanite |
| Type of ore concentration | Three stages of gravitational concentration with consequent removal of the tailings with grading waste (0.1 g/t) | | |
| Concentrates | Rich wash pan concentrate with Pt grade more than 40% | | |
| Ore recovery | 80-82 % | 83-88 % | 88-93 % |
| Minimum weight of representative sample | about 300 kg | 250 kg | 500 kg |
| Cut-off grade used | 0.2 g/t | | |
| Economic cut-off | about 0.5 g/t | 0.6 g/t | 0.8 g/t |

* – the author's evaluation of the average grade.

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# APPLIED PGE MINERALOGY AND ORE BENEFICIATION OF THE KONDYOR DEPOSIT (KHABAROVSK REGION, RUSSIA)

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**ABSTRACT**. This is the first publication regarding the applied mineralogy and beneficiation characteristics of the PGE mineralization for the Kondyor bedrock deposit. The data obtained are based on two bulk one-ton samples (both from chrome-bearing dunite, one of which contains kosvite dykes), five mineralogical samples from different varieties of dunite, and two – from kosvite.

The Kondyor massif is located in the Russian Far East about 1100 km north of the city of Khabarovsk. Forming a circular, chimney-like structure about 8 km in diameter, the massif has a well-developed dunite core 5.5 km in diameter, surrounded by a clinopyroxenite rim up to 700 m thick. Numerous dykes of kosvite have intruded both the dunite and pyroxenite. Also, a large intrusive body of kosvite has been encountered in the west part of the massif below 300 m depth.

Porphyritic and pegmatoid dunites are the main concentrators for chromespinelide and platinum mineralisation. As is the case elsewhere in the Ural-Alaskan type (UA) intrusions (e.g., Galmoenan, Nizhny Tagil), the distribution of the platinum mineralisation is highly irregular. More than 300 spot-anomalies of PGE were identified.

The average grade of Pt in dunite with accessory chrome-spinel is 0.1-0.4 ppm Pt with the maximum up to 3-4 ppm. The Pt grade in dunite with segregations of chromespinelide is much higher – up to 550 ppm in some schlieren. The lengths of such schlieren are 5-1000 cm, the width – 50-80 cm. The variation in the platinum content (using the standard sampling procedure) within samples can reach 340%.

Laboratory testing of the Pt distribution from a bulk sample of ore has shown that subsamples weighing 1 kg have 85% variability; subsamples weighing 10 kg have 55%, and subsamples weighing 100 kg have 25%. In this way, it was calculated that the minimum sample weight required to produce reliable and reproducible results from the mineralized zones with highly irregular PGE distribution, is not less than 500 kg.

The dunite consists mainly of olivine ($Fo_{91}$, Ni – 0.1%) and magnesium serpentine (Mg 2.6-2.9 formula index), sometimes diopsite and pargasite-edenite are also present in minor quantities. Chromespinelide is the main ore mineral. It is a compound of an intermediate variety of chromite and magno-chromite (Mg and $Fe^{2+}$0.5 formula index), and can be altered to chrome-magnetite and magnetite. Sulphides are secondary ore minerals, they are represented by pentlandite, pyrrhotine, heazlewoodite, and rarely by chalcopyrite, pyrite, bornite, lollingite and native copper.

During the electronic microscope study (using the MLA method in casual specimen's cross-section) 7838 mineral grains were analysed and 32 minerals were identified, of which 13 minerals are PGM. As a result, the total quantity of PGM in the concentrate amounts to 97.4 mass.%. The main PGM in the concentrate are Fe-Pt alloys (96.9 mass.%), close to isoferroplatinum ($Pt_3Fe$) by their chemical composition. The significant proportions of PGM were erlichmanite – $OsS_2$ (0.4%), cooperite – PtS (0.2%), irarsite IrAsS (0.2%) and malanite – $Cu(Pt,Ir,Rh)_2S_4$ (0.1%). Sperrylite, konderite, cuprorhodsite, laurite, hollingworthite, platarsite, Hg- and Hg-Cu-bearing native gold are present in less than 0.02%. Also several individual grains of unnamed PGM were identified: $Pt_3(Cu,Rh,Ir,Os)_9S_9$, $(Ni,Fe,Rh,Cu,Ir,Pt)_{0.97}S_{1.02}$, $(Pd,Rh,Ni,Pt)_5(As_{1.6}Pb_{0.4})_2$, $(Fe,Cu)(Ni,Rh,Pt)_2S_4$, $Pt_3Cu_2Sn$.

Usually PGM occur as clustered aggregates (up to 20 mm) of Pt-Fe alloys, cementing the chromite grains. The Pt grade in such aggregates varies from several % in large aggregates, and up to 25-42% in 4-8 mm aggregates. The average density of Pt-bearing aggregates is 5.56 g/m$^3$, that is 20-25% more than for aggregates of a pure chromite.

After crushing of the ore, the coarsest platinum grains have very complicated shapes, typical for malleable minerals; some of them are still observed in the coarse fractions (more than 1-2 mm) together with chromespinelide in the form of aggregates. But as a rule, the morphology of PGM in the less than 2.5 mm fraction changes towards the simplification: if in the fraction -0.5+0.3 mm the PGM grains are represented as fragments of interstitial cement, then the fraction less than 100 μm already consists of crystals (cubes).

The average grain-size of platinum grains is 130 μm. The coarse grains predominate in the ore: the proportion of platinum in the grains more than 0.42 mm – 44%, more than 0.2 mm (200 μm) – 68%, 100-30 μm – 17%, less than 30 μm – 4%. The maximum estimated size of PGM is 15 mm with the mass about 40 g. Despite the presence of large quantities of small inclusions of PGM in the ore (50%, <0.05 mm), the bulk of the metal content (70%) is composed of grains >0.4 mm. The size-grade distribution curve of the particles is characterized by distinct bimodal distribution: peaks represent the 150-300 μm and 1 mm size fractions. Two 5 mm size nuggets and several PGM-chromite aggregates were found in the laboratory samples. There is the possibility of finding larger nuggets, but the probability tends toward zero.

A test charge of a gravitational concentrate (4.23 g), containing about 73% of Pt-Fe alloys was used to investigate the magnetic characteristics. The residual magnetic susceptibility of the PGM and chromespinelide was shown to be identical; the maximums of magnetic susceptibility of platinum alloys matching the maximums for chromespinelides.

Aside from dunite, two samples of metasomatic clinopyroxenite (with phlogopite -titanomagnetite-diopsite compound) were investigated. The sample with titanomagnetite mineralisation contains 0.18 ppm Pt and 0.07 ppm Pd, the one with phlogopite-vermiculite turned out to be richer – 1.12 ppm Pt and 0.61 ppm Pd. The main platinum mineralisation here is represented by sulphides (cooperite, braggite, irarsite, mertieite), but not Pt-Fe alloys as in the case of mineralised dunites.

All studied ores from the Kondyor deposit are dressed very well using the gravitational method of concentration. Concentrates with a high level of platinum recovery were obtained in the majority of the tested samples. Besides a platinum concentrate, chromite can also be recovered as a byproduct.

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# PLACER PGM IN THE SHETLAND OPHIOLITE COMPLEX DERIVED FROM THE ANOMALOUSLY ENRICHED CLIFF PODIFORM CHROMITITE

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**ABSTRACT**. The highly anomalous PGE concentrations in the podiform chromitite at the Cliff locality in the Shetland ophiolite complex have been documented extensively. The focus of this study is the new discovery of placer PGM in the small stream that drains from this Cliff locality. The placer PGM have average sizes of 40 x 60 µm. The largest grain of sperrylite is up to 110 µm in diameter. The assemblage is dominated by Pt-arsenides (65%) and Pd-antimonides (17%) with less abundant grains belonging to the irarsite-hollingworthite solid solution series (10%) and minor Pt-Pd-Cu- and Pt-Fe-alloys, Pd-sulfides and laurite. Four grains of gold have also been located with the PGM. The placer PGM are more Pt-rich with less Pd-bearing PGM than in the source rocks. The sperrylite and hollingworthite-irarsite grains are often euhedral whereas the Pd-antimonides are commonly subhedral and may be etched. In this cold climate with high rainfall the PGM appear to have been derived directly from erosion of the PGE-rich rocks and there is little evidence of in situ growth of any newly formed PGM.

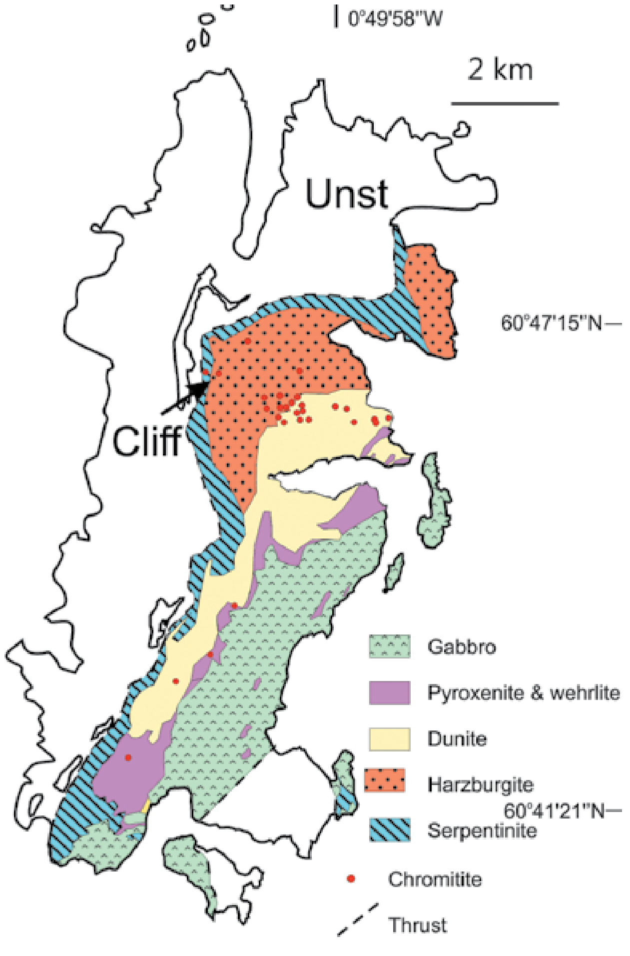

*Fig. 1.* The Shetland ophiolite showing the position of the PGE-rich locality at Cliff

## INTRODUCTION

All six PGE form PGM in chromite-rich dunites at Cliff. At this locality several *en echelon* podiform chromitites surrounded by dunite occur in mantle harzburgite belonging to the Shetland ophiolite complex. This ophiolite is located on the island of Unst, the most northerly island in the British Isles (Prichard et al., 1986; Prichard & Tarkian, 1988) (Fig. 1). The PGM in the rock assemblage consist of sperrylite ($PtAs_2$), Pd-antimonides, members of the irarsite-hollingworthite solid solution series (IrAsS-RhAsS), Pt-Pd-Au-Cu alloys, laurite ($RuS_2$), native Os and potarite (PdHg) with PGM diameters up to 30 µm. A small stream 0.5m wide drains the ponds in the disused chromitite quarries at Cliff and discharges into the Loch of Cliff 400 m to the west of Cliff. Panned samples were collected from this stream at two sites; the first within 5-20 m of the Cliff quarries and a second site in meanders 20-50 m downstream of the quarries. Panned size fractions below 150 µm were examined for precious metals using a Cambridge Instruments (ZEISS NTS) S360 scanning electron microscope (SEM), with an Oxford Instruments INCA energy plus energy dispersive x-ray analyser (EDX). Qualitative analyses were obtained of the grain surfaces.

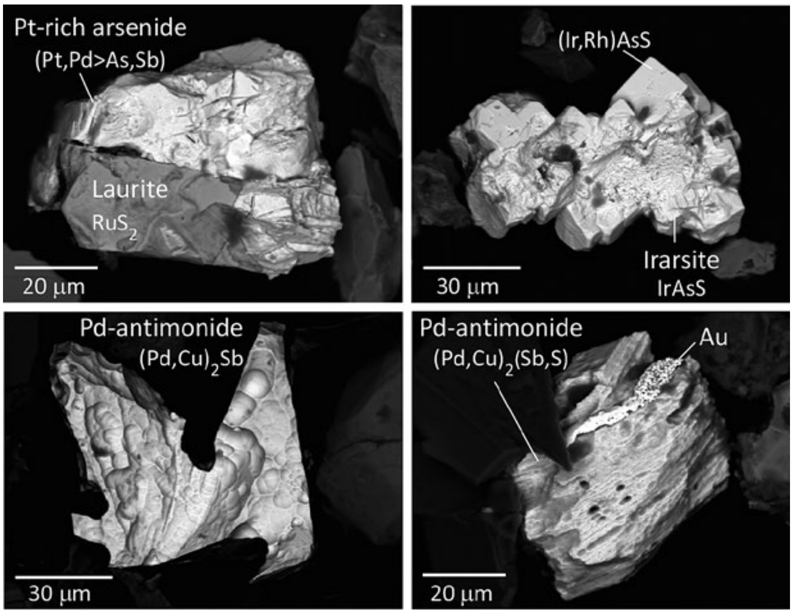

*Fig. 2.* Placer platinum-group minerals

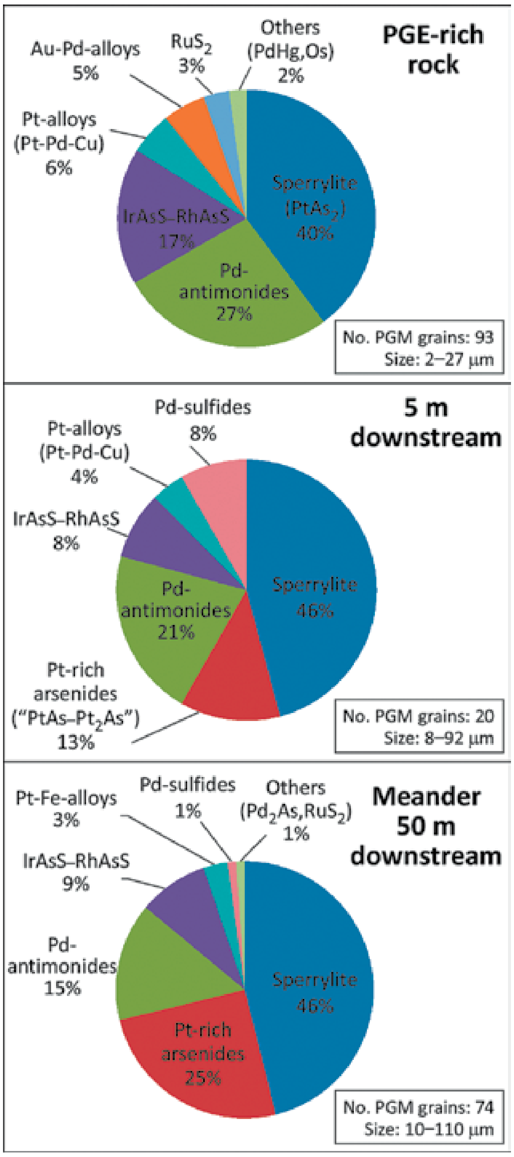

*Fig. 3.* Variation in the PGM assemblage in the rock and downstream

## RESULTS

A total of 94 PGM have been identified as well as 4 grains of gold. Most grains are single minerals but a few are composite consisting of sperrylite with Pd-antimonide, laurite, or irarsite, and composite grains of Pd-antimonide with gold or Pt-alloy. Sperrylite is commonly euhedral forming single cubes, octahedrons or aggregates of cubes but it can also be subhedral, polished and it is often cracked. Pt-arsenides with more Pt than sperrylite are more abundant downstream and these have an irregular etched appearance. Pd-antimonides are subhedral and may show a lamellar structure on their surfaces or they may show etching in the form of concave faces or irregular surfaces. They include stibiopalladinite ($Pd_{5+x}Sb_{2-x}$) and naldrettite $(Pd,Cu)_2Sb$. Irarsite and hollingworthite are subhedral but in one case a cluster of cubes of irarsite are coated with Rh on their surfaces. Pd-sulfides occur as subhedral broken particles varying from $Pd_{16}S_7$ (vasilite) to PdS (braggite). Gold is present either as round smooth grains or as irregular grains but also spectacularly as porous grains with a delicate structure. In one case a porous grain of gold is observed growing on a Pd-antimonide. The gold is Ag-poor and close to 100% pure (Fig. 2).

## DISCUSSION AND CONCLUSIONS

Examination of the PGM assemblages in the PGE-rich rocks compared with those in the stream shows a similar assemblage in both rock and stream suggesting that the PGM have weathered from the rock and their short transport distances have allowed them to preserve their composition and often euhedral shapes. There are signs of disintegration of PGM as they travel downstream. Pd-antimonides weather and have irregular forms and Pt-arsenides become more abundant and Pt-rich (Fig. 3). Cu is partially lost from the PGE alloys.

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# GEODYNAMIC CONDITIONS OF ORIGIN OF THE PLATINUM–BEARING BELT OF THE URALS

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**ABSTRACT**. The Platinum-Bearing Belt (PBB) of the Urals is a giant chain of big massifs represented at more than 90% by primarily magmatic mafic-ultramafic rocks, comprising two main discrete complexes: the earlier, layered, composed of dunite-clinopyroxenite-gabbro (DCG) rocks and the later, mostly of gabbro-norite (GN) composition. It is supposed that the first complex originated in the Vendian time, within an oceanic lithosphere of the Paleo-Asian ocean, under the influence of a vast superplume, and the second – in the Silurian, in a supra-subductional zone of the Tagil island arc.

The Platinum-Bearing Belt (PBB) is a long chain of complex intrusive and protrusive massifs situated in the Tagil zone of the Urals, composed of dunites, wehrlites, clinopyroxenites, amphibolites, olivine gabbro, gabbto-norites and granitoids. Basic rocks are predominant. Two main complexes (under different names) are established in the PBB (Efimov, 1984; Fershtater, 2013). The first, the older, has a dunite-clinopyroxenite-gabbro (tilaite) composition (DCG complex). The second (the younger and more uniform), predominately gabbro-norite (GN-complex), is represented mostly by big bodies of gabbro with relics of primary ophitic two-pyroxene gabbro-norites. These complexes make more than 90% of all PBB massifs.

The structure of the PBB massifs was studied in detail by Efimov (1984) who was the first to map and describe here high-temperature plastic deformations. He thought that metamorphic transformations completely equilibrated a mineral composition of the DCG complex, and no relics of their primary magmatic structures were not left. The subsequent studies (Savelyeva et al., 1999) have shown that some relics of primary magmatic textures are still preserved. The petrostructural analysis indicates a plastic diapiric uplift of these complexes in high-temperature conditions (Shmelev & Filippova, 2009).

Until recently, there was a disagreement concerning the nature of a dunite component of the DCG complex: restite (Maegov, 2008), or magmatic (Fershtater, 2013). As an initial melt of the complex, a composition comparable to tilaite, was suggested. Recently, a study of melt inclusions in early chromspinel grains of the Nizhni Tagil massif have shown that all rocks of the DCG complex are the product of differentiation of a subalkaline picrobasalt magma (Simonov et al., 2013). A digital modelling has shown that the early chromspinelides of the massif were crystallized in the temperature interval of 1345 to 1310°C. The olivines were formed under still higher temperatures of 1430 − 1360°C.

Nowadays the most popular idea concerning the origin of the PBB massifs is their formation as a whole in the Silurian, in a suprasubductional geodynamic regime of the Tagil island arc (Ivanov & Shmelev, 1996; Fershtater, 2013). However the general features of DCG complex are not characteristic for a suprasubduction zone. Moreover, the results of Sm−Nd dating of the complex also conflict with this hypothesis. A series of papers was published in the last decade by Ronkin, Maegov, Efimov, Popov, Belyatski, Petrov and others, showing that the complex has a Late Vendian age. The age of an olivine-anorthite gabbro of Kumba massif is 561±28 Ma. The Sm-Nd isotopic study of DCG complex of Denezhkin Kamen gave an isochron in the interval of 552-543 Ma. The analysis of 14 samples of clynopyroxene-bearing metadunites, wehrlites, olivine clinopyroxenites, tylayites, taken at Konzhakovsky Kamen massif gave a Sm-Nd errochron of 551±32 Ma. The analysis of whole-rock compositions of olivine, bi-pyroxene and amphibole metagabbro of Khorasiur massif gave a 565±50 Ma Sm-Nd evolution diagram.

Mineral fractions and whole-rock composition of olivine gabbro from Kytlym and Knyaspa massifs provided a Sm-Nd isochrone 550±25 Ma and errochron 542±25 Ma. An errochron 570±84 Ma was obtained from plagioclase, pyroxene, olivine and whole rock samples of olivine gabbro of Yalping-Nyor massif Fershtater (2013) suggested that the Vendian Sm-Nd ages of the DCG complex were formed because a part of Sm and Nd was imported from a hypothetical Pre-Paleozoic basement of the Tagil zone. But it still does not mean that the older age could be imported. On the other hand, it must be taken into account that there are also some Late Ordovician-Early Silurian dates of DCG formation, coinciding with the ages of the GN complex. Probably we have here a metamorphic resetting of Sm-Nd mineral systems – the phenomenon which is thoroughly discussed in many recent papers.

As for the GN complex, the idea of its suprasubductional nature is justified fairly well. The concentrations of the most of petrogenic and incompatible elements permit to speak about their similarity to island arc tholeiites (Ivanov & Shmelev, 1996). The predominant Late Ordovician-Silurian (410-460 Ma) U-Pb (zircon) isotopic ages of the gabbro (Bosch et al., 2006) and the same age of predominately island-arc host rocks speak in favour of this point of view.

Thus, the formation of the DCG and GN complexes are two independent, very different geodynamic-ruled processes, divided by a great spell of time, and only the second one has distinct signs of a genetic connection with a subduction. As for the first one, it can be connected with a mantle melting under an influence of a superplume, primarily situated at a significant (thousands km) distance from the Vendian orogen of Timanides. It could explain a resemblance of DCG complexes with some platform intrusions. Paleomagnetic data (Petrov & Svyazhina, 2006) do not conflict with the idea that the Tagil arc was formed primarily on a Vendian oceanic lithosphere of the Paleo-Asiatic Ocean.

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# THE PGM-BEARING VOLCANIC ANKARAMITE (URALS, RUSSIA): BRIDGING ANKARAMITE PARENTAL MAGMAS AND THE URAL-ALASKAN-TYPE INTRUSIONS

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**ABSTRACT**. We assume ankaramite as a parental melt for the Ural-Alaskan-type dunite-clinopyroxenite-gabbro intrusions. Olivine-clinopyroxene cotectic fractionation in ankaramite provides a formation of dunite, clinopyroxenite and gabbro at the latest stage of differentiation. The first finding of liquidus PGM inclusions in chromite phenocrysts from the Uralian ankaramite is supportive of this model.

Several problems related to the origin of the Ural-Alaskan mafic-ultramafic complexes are still debated. These include:

1) geodynamic position;

2) concentrically-zoned structure comprising dunite cores and clinopyroxenite rims;

3) high-magnesian composition;

4) age and genetic relationships between ultramafic rocks and gabbros;

5) chromite-PGE and Ti-magnetite mineralisation in dunites and clinopyroxenites, respectively.

The composition of the parental magma represents a key question in addressing the vast amounts of clinopyroxene, lack of orthopyroxene and plagioclase and forsteritic compositions of olivine in these complexes. The reconstruction of parental melt compositions should take into account that the total volumes of clinopyroxenites significantly exceed those of dunites, implying unusually high, for mantle-derived melts, abundances of CaO, and by inference $CaO/Al_2O_3 > 1$. The only example of such high-Ca melt is represented by ankaramites (Barsdell & Berry, 1990; Medard et al., 2006; Schmidt et al., 2004) that have been considered as a parental magma for the dunite-clinopyroxenite complexes in the south-east Alaska (Irvine, 1973; Krause et al., 2007; Thakurta et al., 2008). Additional support to the idea of the ankaramite being a parental magma to the Ural-Alaskan mafic-ultramafic complexes is provided by the magmatic-plutonic association in the Urals (Krause et al., 2007). The differentiation trends of both ankaramites and mafic intrusions are controlled by the same olivine-Cr-spinel-clinopyroxene cotectic and similar mineral compositions.

The ankaramites were first described in the tectonic melange of the Main Uralian Fault (Spadea et al., 2002). We demonstrate that the Middle Devonian Cpx-phyric volcanics are widespread in this area in the Irendyk formation. The volcanics contain phenocrysts of Cr-diopside and high-Cr spinel that are compositionally identical to those in island-arc ankaramites and the Ural-Alaskan mafic-ultramafic complexes. The most primitive Cpx-porphyritic rocks were found as fragments of dykes and lavas, intersected by typical calc-alkaline andesites, in the serpentine melange (30 km to north-west from the town of Uchaly).

The Uralian ankaramites are enriched in phenocrysts of clinopyroxene (8-10 mm, up to 4-6 cm) varying in colour and composition from apple-green Cr-diopside (Mg#=0.92-0.93, $Al_2O_3$=0.5-0.7%) to dark green augite (Mg#=0.80-0.75, $Al_2O_3$=2.5-3.0%). Another type of phenocrysts is represented by totally pseudomorphed euhedral grains that can be tentatively identified as olivine, although original orthopyroxene cannot be excluded. Octahedral grains of Cr-spinel (Mg#=0.59-0.6, $Cr_2O_3$=60-64%, Cr/(Cr+Al)=0.89-0.91) are present as microphenocrysts, up to 2-3 mm in size and as small inclusions in Cr-diopside. The Cr-spinel contains rare inclusions of olivine ($Fo_{90}$) and Cr-diopside (Mg#=0.92-0.93) and abundant melt inclusions, comprised of clinopyroxene, orthopyroxene, amphibole and felsic glass. The groundmass is dominated by zoned clinopyroxene crystals (50-100 μm).

The bulk composition of ankaramites is characterised by high Mg# (0.80) and CaO (16-17%) and moderate enrichment in light rare-earth elements $La_N/Yb_N$=3-4, whereas the contents

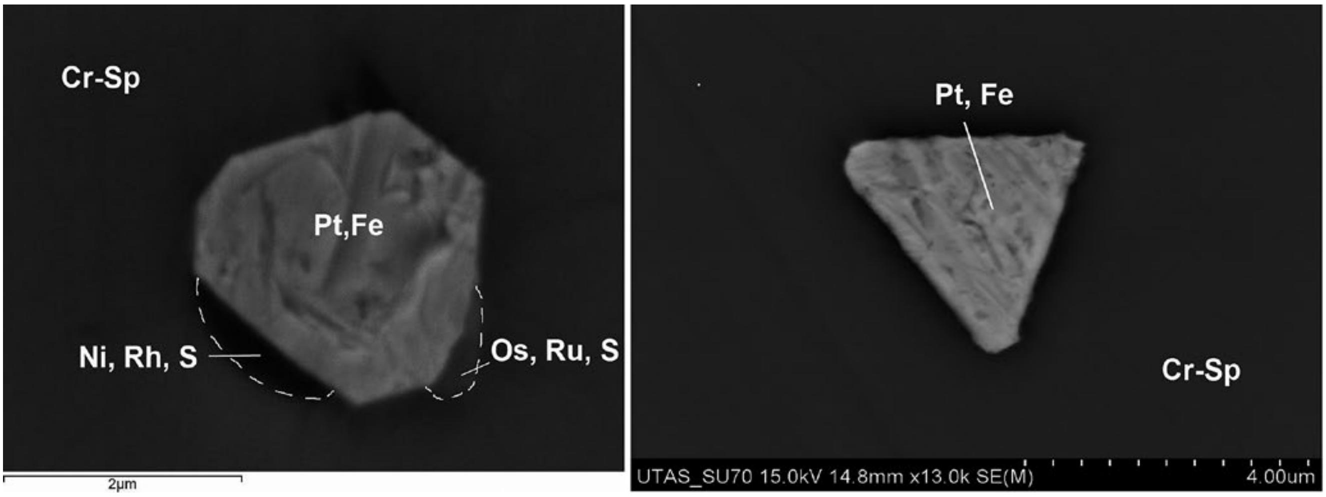

*Fig. 1.* BSE images of PGM-inclusions in chromian-spinel phenocrysts from the Uralian ankaramite

of $Al_2O_3$, $TiO_2$ and alkali elements are very low (Table 1). The groundmass and homogenised melt inclusions are compositionally similar to the bulk rocks, thus re-enforcing the affinity to the ankaramite type of melts (Table 1).

The Cr-spinel microphenocrysts contain the platinum-group minerals (PGM), typically 1-3 µm in size, represented by Fe-Pt alloys intergrown with the sulphides of Os, Ru, Rh, Cu, Ni (Fig. 1). The composition of PGM corresponds to those in the Cr-spinel from the island-arc picrite from Ambae, Vanuatu (Park et al., 2012); on the other hand, it is typical of PGM in dunites and chromitites of the Ural-Alaskan complexes. We infer that the ankaramite magma, capable of generating large volumes of olivine-clinopyroxene cumulates, is oxidised enough to be saturated in Fe-Pt alloys. These alloys may directly crystallize from the magma and be entrapped in liquidus Cr-spinel.

Table 1

**Bulk composition of ankaramite (WR), groundmass, homogenized melt inclusion and chromite phenocryst**

| *Sample Pe1466* | *WR* | *Ground-mass* | *Melt inclusion* | *Cr-spinel* |
|---|---|---|---|---|
| $SiO_2$ | 47.44 | 47.89 | 46.50 | |
| $TiO_2$ | 0.17 | | 0.16 | 0.15 |
| $Al_2O_3$ | 6.89 | 10.69 | 7.12 | 4.93 |
| Cr2O3 | 0.20 | | 1.61 | 63.54 |
| FeO | 8.84 | 9.39 | 13.75 | 18.75 |
| MnO | 0.21 | | 0.28 | 0.10 |
| MgO | 18.48 | 16.26 | 18.88 | 11.60 |
| CaO | 17.53 | 15.77 | 10.49 | |
| $Na_2O$ | 0.10 | | 0.84 | |
| $K_2O$ | 0.01 | | 0.34 | |
| P2O5 | 0.12 | | 0.08 | |
| Total | 100.00 | 100.00 | 100.00 | 99.07 |
| Mg# | 0.79 | 0.76 | 0.71 | 0.53 |

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# PLATINUM-BEARING BELT OF THE URALS: TECTONIC SETTINGS, ROCK COMPLEXES AND STRUCTURE

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**ABSTRACT**. The structural and petrological investigations of mafic-ultramafic massifs in the Ural Platinum-bearing belt reflect a very complex and long history of their formation. They are a result of combination of different magmatic processes, high-temperature plastic deformation, re-crystallization and metamorphism accompanying diapiric emplacement of the massifs.

The Platinum-bearing belt (PB) of the Urals is presented by extended (about 1000 km) submeridional chain massifs, composed mainly of mafic-ultramafic complexes of the Ural-Alaskan type studied by specialists in various fields for more than a century (Efimov et al., 1993; Ivanov, 1997 and others). The PB tectonic setting is quite definite – it is close to the border (base) of the Tagil paleo-island arc megazone within a broad band of metamorphosed mafic rocks. To the west, along the Main fault zone (thrust), traced by ultramafic bodies of the Salatim belt, they are underlain by different schists of the Urals paleocontinental region.

The PB surrounding rocks influenced by a strong metamorphism were transformed into hornfels and amphibolites (kytlymites). Among them are preserved relict fragments (blocks) of basalts and parallel dolerite dykes and also low-strontium gabbro and pyroxenites related to the upper section of the Paleozoic ophiolite association. Hornfels and amphibolites chemically correspond to basaltoides differing from N-MORB basalts by depletion in titanium and heavy REE; in general the country rocks are comparable with suprasubduction forearc ophiolites (Shmelev, 2005). In recent years there evidence of the existence of surrounding rocks with more ancient (Vendian) age has been obtained. The PB massifs also exert dynamothermal effects to andesibasalts of the Tagil megazone with the formation of two-pyroxene (amphibole) hornfels.

In the PB massifs are distinguished by several rock complexes: dunite-clinopyroxenite (I), gabbro-clinopyroxenite (II), gabbro-norite (III) and diorite-plagiogranite (IV). The Belt rock formation occurred in a wide age range – from the Late Ordovician to Devonian. However, it is assumed that dunite and olivine gabbro may have a Precambrian age. Among the features inherent to PB formations it is important to note the following ones:

(1) early complexes (I, II) have concentrically zonal or concentric structure that is the result of magmatic fractionation and layering fixed by regular changes in the composition of rocks and minerals; (2) gabbro-norite complex (III) showing signs of orthomagmatic origin and active relationship with the rocks of the early complexes. In the marginal parts of the bodies differentiation of gabbro-norites produces two-pyroxene diorites; (3) between the rocks of complexes II and III there are both intrusive and reaction relationships with the emergence of bytownite-anorthite and olivine gabbro-norites; (4) during high temperature hydration under the influence of late magmatic aqueous fluids hornblende basites formed instead of gabbro-norites and olivine gabbro; (5) gabbroids of PB complexes show structural and mineralogical discreteness, which is the result of rock crystallization at different levels of depth, (6) granitoids, finishing the formation of PB gabbros are presented by two genetic types, that had been crystallized under various conditions which determined their geochemical (low and high-strontium) specificity .

Analysis of the structure (at the macro and micro level) of ultramafic and gabbroic PB massifs allows connect it to the processes of magmatic (static and dynamic) crystallization and subsequent high-temperature plastic deformation and recrystallization (Shmelev, 1994, Shmelev & Filippova, 2010).

For the most representative Nizhny Tagil ultramafic massif the following picture is been established. At the stage of submagmatic flow during dynamic differentiation of the rising of magnesian melt layered structure formed, banding and mineral foliations forming subconcentric megastructure of the ultramafic body. Indicators of this process are adcumulative protogranular structures of dunites and pyroxenites with relicts of tiling microstructure of euhedral grains (protokrysts), as well as distinct [100] crystallographic orientations of olivine controlled by elements of conical megastructure. At the stage of plastic flow with the preservation of stress orientation, ultramafic rocks have undergone zonal metamorphism with the emergence of porphiroclastic and mosaic rock microstructures as well as mineral foliation and lineation of subconformal early elements. The flow process accompanied ultramafic rock diapiric intrusion into the surrounding rocks, which under the influence of metamorphism have been transformed into hornfels and amphibolites.

In gabbroic massifs (Khorasyur, Chistop etc.) a more complicated mechanism of evolution has been established. However, they also recorded the stages of magmatic and plastic flow with formation of subconcentric structures in the gabbro-clinopyroxenite and gabbro-norite complexes. Deformation structural elements here also coincide with early magmatic banding, indicating a diapiric mechanism of intrusion with a gradual change of magmatic flow into plastic.

In general, the spatial coexistence of different (layered and intrusive) rock complexes composing the PB, signs of crystallization at different depths, subconcentric structure pattern of ultramafic and mafic rocks reflecting their participation in magmatic and plastic flow, as well as metamorphism of the surrounding rocks, indicate the PB belongs to a special class of formations – long living diapir-plutons. Their appearance was caused by the subduction processes in the Urals.

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# Re-Os ISOTOPE STUDIES OF THE DUKE ISLAND ULTRAMAFIC COMPLEX, SOUTHEASTERN ALASKA

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**ABSTRACT**. Both Re-Os and S isotopic values of sulfide mineralized olivine clinopyroxenites from the Duke Island Complex are indicative of major addition of S, Re, and Os from country rocks. Oxygen isotope ratios indicate that bulk contamination was less than 4% and that selective addition of Re, Os and S may have occurred via a fluid. In contrast to the sulfide-rich olivine clinopyroxenites, the low-sulfide dunites are characterized by low $g_{Os}$ values consistent with low degrees of crustal contamination.

The Duke Island Ultramafic Complex (DIUC) is considered to be a Ural-Alaskan intrusive sequence located in Southeast Alaska. The Complex is one of the few Ural-Alaskan intrusions that contain a significant mass of Ni-Cu-PGE mineralization. Recent studies by Thakurta et al. (2008) have shown that the bulk of sulfide mineralization was related to the attainment of sulfide liquid saturation after considerable crystallization of olivine, at the time when clinopyroxene was becoming a liquidus mineral. However, dunite bodies in the DIUC show two contrasting features. One type of dunite contains primitive ($>Fo_{90}$) olivine with predictable Ni contents of 2000 to 3000 ppm. Another type of petrographically indistinguishable dunite is characterized by primitive olivine ($>Fo_{90}$) with anomalously low Ni contents of less than 900 ppm. Li et al. (2013) have shown that the dunites at Duke Island contain small amounts of cumulus sulfide. A possible interpretation is that the low-Ni dunite formed in a chamber where an early sulfide saturation event occurred. The low-Ni dunites tend not to show a comparable depletion in either Cu or PGEs, and for this reason, early separation of large amounts of sulfide liquid is considered unlikely.

In order to further evaluate the petrogenetic relationship between dunites, sulfide-bearing olivine clinopyroxenites, and hornblende-bearing clinopyroxenites, and to better constrain the importance of country rock contamination in the formation of DIUC sulfide mineralization, we initiated a study of Re-Os isotopic characteristics of dunites, as well as sulfide mineralized rock types. In addition, sulfur isotope values of dunites and sulfidic/graphitic metasedimentary country rocks have been determined. The data are utilized to determine the extent of country rock contamination recorded by the dunite units and the sulfide-rich olivine clinopyroxenites and hornblende-bearing clinopyroxenites.

Os isotope values of mineralized olivine clinopyroxenites and low-sulfide dunites of the Duke Island complex are distinctly different. The sulfide-rich olivine clinopyroxenites have Os isotopic compositions indicative of *major* crustal contamination with radiogenic crustal material. The $g_{Os}$ values of olivine clinopyroxenites range from 149 -2046 at 110 Ma. These data are consistent with S and C isotopic data that suggest that multiple pulses of variably contaminated and sulfide-saturated magmas were emplaced as part of the Duke Island Complex. Thakurta et al. (2008) determined the sulfur isotope values of mineralized olivine clinopyroxenites span a range of -14.98‰ to +7.53‰. Contrastingly, Os isotope values of the low sulfide dunites in the DIUC suggest *small* amounts of crustal contamination, with $g_{Os}$ values ranging from 1.0 – 15.7 at 110 Ma. Sulfur isotope values of the dunites range from -6.41‰ to +6.59‰, with sulfur concentrations from 405 to 1691 ppm.

The Os isotopic values result from interaction with Re- and Os-rich carbonaceous pelites, and are consistent with oxygen isotopic evidence that indicates low degrees of bulk rock contamination

(< ~4%) of the magmas. Alternatively, contamination may have involved a S- and Os- bearing volatile phase which strongly perturbed S and Os isotope ratios of the magmas, but not O isotope ratios. Os isotope ratios are strongly suggestive of interaction with sulfidic and carbonaceous black shales of Triassic age. Sulfidic, graphitic metasediments proximal to the Duke Island Complex are candidates for potential contaminants, and have $g_{Os}$ values ranging from 1015-1998 at 110 Ma, with sulfur isotopic values of -1.42‰ to -16.13‰.

The sulfide-rich olivine clinopyroxenites of the DIC show strong isotopic evidence for the introduction of crustally derived Os and S. The contamination process was responsible for the saturation of the magmas in sulfide liquid and occurred after considerable olivine fractionation when clinopyroxene was becoming a liquidus mineral. The contamination which drove the formation of the sulfide mineralization in the olivine clinopyroxenites occurred after major amounts of olivine crystallization (on the order of 20%). This is also consistent with the relatively low Ni contents of the sulfide mineralization in the olivine clinopyroxenites. The crystallization of olivine prior to the addition of major amounts of country rock S led to Ni sequestration, whereas Cu concentration increased as a result of incompatible element enrichment during fractional crystallization. The result of the process is the high Cu/Ni ratios of the sulfide mineralized olivine clinopyroxenites, which are similar to Cu/Ni ratios found in mineralization associated with evolved flood basalt-related systems such as that of the Duluth Complex.

The Os isotope values of the dunites are indicative of considerably less country rock contamination compared to the mineralized olivine clinopyroxenites. Petrologic data reported by Thakurta et al. (2008) indicate that the magma which produced the olivine clinopyroxenites was a derivative magma, produced as a result of fractionation of olivine. The dunites on Duke Island crosscut the olivine clinopyroxenites and hence it is not possible to directly link them to the fractionation process. The Os isotopic data indicate that the magma that produced of the dunites underwent only slight crustal contamination. We speculate that at the time the parental magma of the dunites was emplaced, the country rocks had been devolatilized and bulk contamination by the now higher grade metamorphic rocks did not occur.

Dunites that crosscut the olivine clinopyroxenites of the Duke Island Complex are characterized by low, near chondritic $^{187}Os/^{188}Os$ values. The presence of relatively uncontaminated dunite indicates that mafic magma production in the arc setting was protracted, and that magmas utilized distinct pathways in the conduit system, some of which were not favorable for extensive interaction with country rocks.

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# PLATINUM ENRICHMENT IN ALASKAN TYPE INTRUSIONS AS A RESULT OF METALS RECYCLING IN SUBDUCTION ZONES AND Pt AFFINITY TO Pt-Fe ALLOYS

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**ABSTRACT**. The PGE and Re-Os isotopic studies on ultramafic cumulates from Nizhny Tagil massif in Urals indicate significant variations in Pt/Pd ratio, increasing toward the chromite-PGE-bearing mineralization zone. The overall primitive-mantle normalized PGE pattern is very similar to that established for subarc mantle peridotites, which are characterized by positive slope and high Pt/Pd ratio; and distinct from that of typical peridotites and cumulates from Urals ophiolite massifs. Such a similarity may be explained by the derivation of magma parental for Nizhny Tagil cumulates from subarc mantle, which underwent several melt extraction events. Systematic increase in Pt/Pd ratio in cumulates toward the chromite mineralized zone suggests that Pt-Pd fractionation may be related to the retention of Pt in chromitites as Pt-Fe alloys, with Pd mainly staying in the melt.

The zoned mafic-ultramafic Urals-Alaskan-type complexes of the Platinum Belt in the Urals are generally interpreted as cumulates crystallised in a magma chamber from the melt derived from depleted mantle in a supra-subduction environment (Ivanov et al., 1997). One of the striking features of subduction-related Alaskan-type complexes is a well-pronounced positive Pt anomaly which clearly distinguishes arc-related ultramafic rocks from ophiolite complexes (cumulate series) and other tectonic environments (Garuti et al., 1997). This Pt anomaly in subduction-related rocks was interpreted as a distinctive feature of the parent arc magma having its source in a subarc mantle wedge. In this work, we have studied the Re-Os isotope systematics in ultramafic cumulates from Alaskan-type Nizhny Tagil massif, in addition to previous PGE and mineralogical studies (Augé et al., 2005) in order to identify the role of subduction-related fluid in genesis of this peridotites. We analysed 7 samples (6 dunites and one pyroxenite) from the Nizhny Tagil massif. The latter belongs to the 1000 km long submeridional Platinum belt and composed of a dunite core bounded by a narrow rim of clinopyroxenite, wehrlite, and plagioclase-bearing olivine-clinopyroxenite.

The Pt/Pd ratio in chromitites from Nizhny Tagil is reaching extremely high ratio of 271, which is about 100 time above chondritic values and much higher than that in chromitite from Urals ophiolites. The Pt/Pd ratios in ore-barren dunites ($Cr_2O_3$ < 0.5wt.%) vary greatly, increasing toward the mineralised zone from subchondritic values of 0.3 up to 13, with one value reaching 89 at 50 cm beneath the mineralized zone. The pyroxenites exhibit high Pt/Pd ratios close to 10. These values are distinctly different from that in peridotites from typical peridotites and ultramafic cumulates from Urals ophiolite complexes having Pt/Pd ratio close to primitive mantle values (1.9). Such enrichment in Pt is also a characteristic feature of subarc mantle, were the Pt/Pd ratios vary from 0.3 to 14.5 with one value up to 115, averaging 4.2 for Kamchatka mantle xenoliths (Kepezhinskas & Defant, 2001) and 9.9 for harzburgite xenoliths in Papua New Guinea (McInnes et al., 1999). This range is similar to that observed for Nizhny Tagil peridotites. Moreover, overall primitive mantle-normalised PGE pattern for Nizhny Tagil ore-barren dunites shows a slight positive slope with a degree of fractionation increasing upwards and matches very well with that of subarc xenoliths (Fig. 1A) and differs considerably from 'flat' mantle-normalized pattern of ophiolite-type peridotites.

The Re and Os concentrations in Nizhny Tagil dunites are ranging from 0.04 to 0.66 ppb (up to 3.4 ppb occasionally) and 0.21 up to 1.3 ppb respectively. The variation of Re/Os ratios for cumulate dunites and pyroxenites from Nizhny Tagil massif is extremely large (from 0.07 up to 18.8) matching these from subarc mantle xenoliths (McInnes et al., 1999). The pronounced negative correlation exists between Re/Os and Pt/Pd ratios (Fig. 1B) for both datasets, with Nizhny Tagil peridotites having about two orders of magnitude higher Re/Os ratios. This correlation for subarc mantle may be explained by the presence of 'vein melt' with higher Re/Os ratios

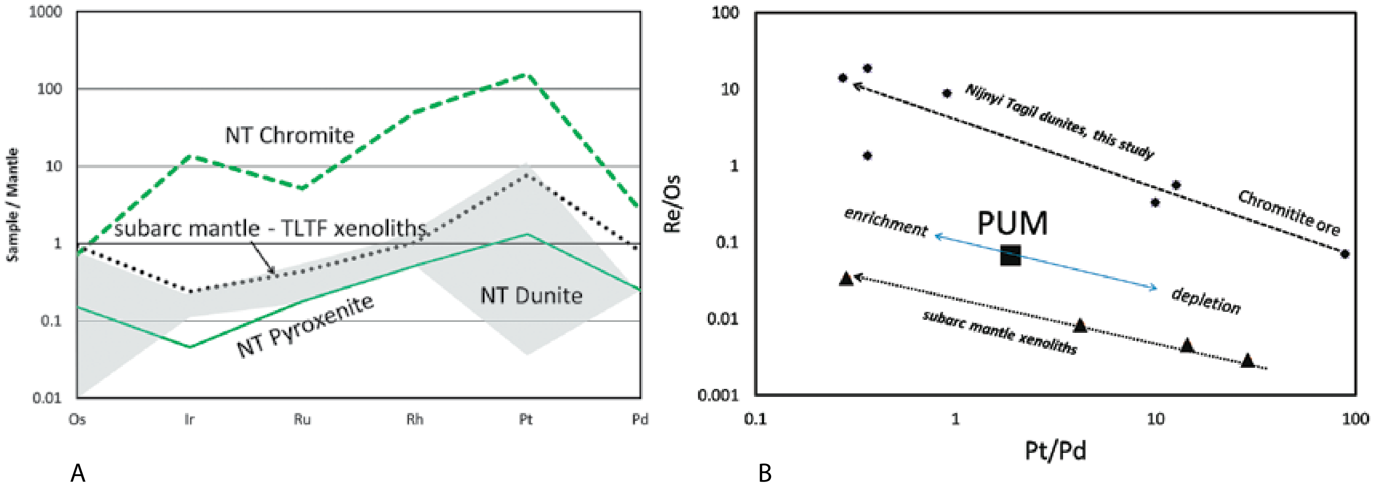

*Fig. 1.* A) primitive mantle normalized PGE pattern in Nizhny Tagil ore-barren dunites, pyroxenite and chromite compared with average from Papua New Guinea subarc mantle xenoliths (McInnes et. al., 1999). B) Pt/Pd versus Re/Os ratios for ultramafic cumulates from Nizhny Tagil massif (filled circles) and mantle xenoliths from Papua New Guinea subarc mantle (filled triangles, McInnes et al., 1999). PUM is also shown

within depleted low Re protolith. The $^{187}Os/^{188}Os$ ratio of whole-rock peridotites from Nizhny Tagil massif varies from 0.1160 up to 0.1332 averaging 0.1247. These values are close to $^{187}Os/^{188}Os$ ratio of chromites of 0.1245 (Hattori & Hart, 1991) and rutheniridiosmine (0.12425).

The Pt-enriched signature of zoned ultramafic-mafic Alaskan-type massifs was previously explained by the melt extraction from sulfide-poor, Pt-enriched arc mantle source within arc roots in Palaeozoic subduction terranes (Kepezhinskas & Defant, 2001). These workers propose a model involving multiple melt extraction events from a subarc mantle source, leaving refractory Pt alloys in the residual mantle. Remelting of this depleted, Pt-enriched mantle beneath the arc owing to hydrous flux from dehydrating subducted lithosphere can potentially generate small volumes of Pt-rich basaltic liquids that will fractionate in upper crustal reservoirs to form an entire range of Alaskan-type intrusive rocks. Good correlation between PGE patterns from Nizhny Tagil peridotites with that of subarc mantle in Papua New Guinea (McInnes et al., 1999) seems to confirm this assumption. However, the involvement of subduction-related fluid will increase the $^{187}Os/^{188}Os$ ratios of subarc mantle and melting products. Only one sample in our study has the $^{187}Os/^{188}Os$ ratio of 0.1332, which can be ascribed to the involvement of more radiogenic subduction-related fluids, characteristic for subarc mantle. The systematic increase in Pt/Pd ratio in ore-barren dunites toward the mineralized zone and pronounced negative correlation with Re/Os ratios suggests that the fractionation of Pt relative to Pd may be dependent on some other processes as well. The increase in Re/ Os ratio suggests the increasing melt fractionation, because Re is more incompatible compare to Os. The Pt and Pd fractionation coefficients are almost identical, so the increase in Pt/Pd ratio toward the mineralized zone with maximum values within chromitites may suggest the retention of Pt within the ferroplatinum alloys (Augé et al., 2005). Palladium has no such a strong affinity to form the Pd-bearing minerals and retained in the melt.

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# ORIGIN OF URAL-ALASKAN – TYPE COMPLEXES BY PERIODIC ASCENTS OF MAGMATIC PULSES FROM THE MANTLE SOURCE

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**ABSTRACT**. Although the Ural-Alaskan type complexes are routinely characterized by concentric zoning of ultramafic and mafic rock units, the mechanism of origin of concentric zoning has remained controversial. Among the Ural-Alaskan type complexes in southeastern Alaska, concentric zonal patterns have developed to various degrees, although in most instances such as the Duke Island Complex and the Union Bay complex, these have been distorted by subsequent events of structural deformation. Clear evidence of intrusive contact between individual units of the ultramafic cumulate rocks suggests episodic magmatic influx through vertical conduit systems from the mantle source. The dunite which occurs at the center of the complex is usually the youngest and frequently contains xenoliths of clinopyroxene-rich wall rocks. The commonly observed occurrence of high concentrations of Pt and Pd in the dunite unit is consistent with an origin from a magma derived from a refractory mantle source, which has already produced large volumes of magmas responsible for the crystallization of older members of the complex.

Ural-Alaskan type complexes have been traditionally identified to be ultramafic to mafic igneous intrusions characterized by the occurrence of concentric lithological zones from dunite in the core with progressively more silicious rocks such as wehrlite, clinopyroxenite towards the periphery. These intrusions are usually located along the trends of major areas of tectonic convergence such as the Ural Mountain Belt in Russia and southeastern Alaska. Many of these intrusions have also been found to be associated with placer deposits enriched in platinum group elements (PGE), and until recently these have been regarded to be mostly sulfide-depleted systems. For instance, several such complexes located along the Ural Mountains in Russia, such as Nizhny Tagil and Kachkanar have been prolific producers of platinum group elements (PGE). The chromite-rich, sulfide-poor dunite cores of these complexes are believed to be the source rocks of these placer deposits (Augé et al., 2005).

Similarly, southeastern Alaska hosts about thirty mafic-ultramafic complexes along its entire 560 Km long northwest-southeast extension. Most of these complexes show zoning of ultramafic rocks such as dunite, wehrlite and clinopyroxenite, and the concentric lithological relationship is developed in various degrees. The Blashke Island Complex, shows a near perfect concentric relationship; Duke Island and Union Bay complexes show structurally distorted concentric patterns; others such as Annette Island and Salt Chuck complexes hardly show any such relationship. Taylor (1967) described these intrusions in southeastern Alaska, highlighting their occurrence along a trend of tectonic convergence and the overall lithological and structural similarities with the Uralian complexes. Since then, the Uralian and Alaskan group of complexes have been categorized together as members of a single group, popularly called Ural-Alaskan type complexes.

However, the mechanism of origin of concentric lithological zones in these complexes has remained controversial. The relationship between the concentric nature of these rocks and the observed enrichment in PGE concentrations in the dunite cores needs to be established. From the structural relationships between the rock units in the Duke Island Ultramafic Complex, Irvine (1974) concluded that the ultramafic rock units of the complex can be divided into two phases of magma emplacements: a younger dunite-peridotite unit intrusive into the olivine clinopyroxenite and hornblende-magnetite clinopyroxenite units. Age determinations by Saleeby (1992) revealed that, the ~110 Ma old ultramafic complex is intrusive into Ordovician-Silurian and Late Triassic gabbroic units of Duke Island. Evidence of multiple intrusion of individual ultramafic units has been reported from the Union

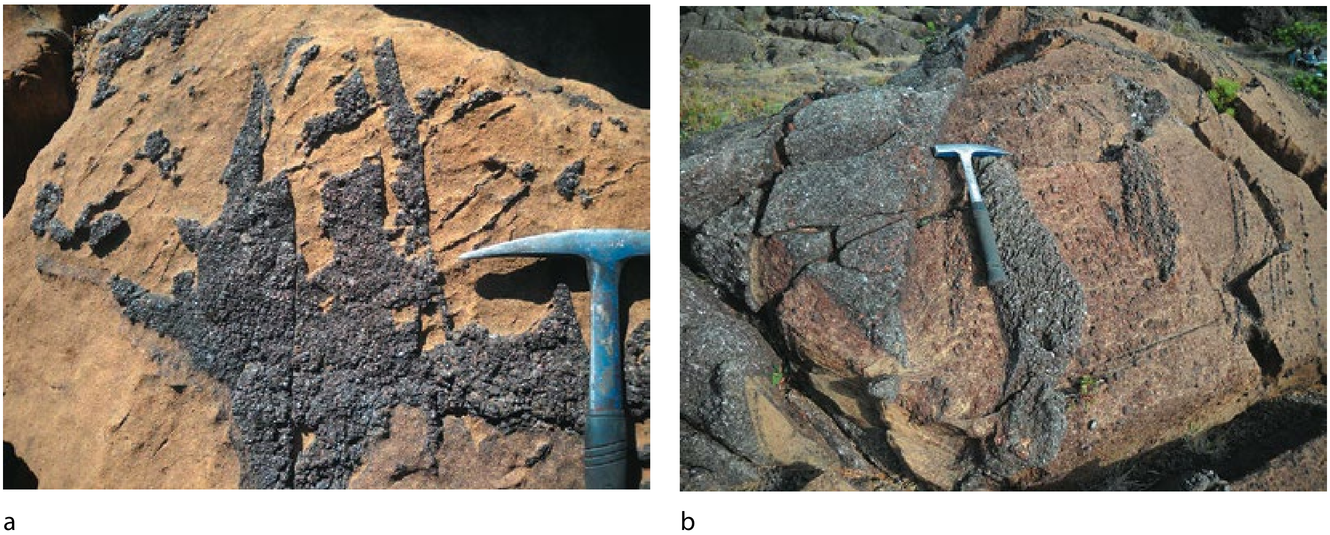
a
b

*Fig. 1.* Xenoliths of older clinopyroxenites in the dunite units at Duke Island Complex (a) and Annette Island Complex (b)

Bay Complex, although the concentric structure has been distorted by a subsequent overturned fold. The near-perfect concentric geometry of the Blashke Island Complex suggests a steeply dipping conical arrangement of the rock units suggesting multiple intrusive activities.

Widespread occurrences of clinopyroxenite and gabbro xenoliths of various sizes in the dunite and wehrlite units of Duke Island Complex (Fig. 1a) and clinopyroxenite xenoliths in the dunite unit of the Annette Island Complex (Fig. 1b) provide powerful evidence in favor of multiple intrusions. From all the observed host rock-xenolith relationships, it is clear that the dunite and wehrlite units were intrusive into older clinopyroxenite and gabbroic rocks.

Thus, it is intuitive that the concentric structures of these complexes are direct results of multiple intrusions of magmas inside wall rocks which were crystallized from pre-existing pulses. Sometimes the contact relationships between two units mark gradual transitions, as seen in the case of the olivine clinopyroxenite and hornblende-magnetite clinopyroxenite units at the Duke Island Complex. Such transitional contacts indicate magmatic differentiation within a single large pulse, but the overwhelming structure of the complex is one of multiple intrusions. In the Annette Island Complex, where only a large dunite plug is exposed, it is possible that the latest phase of magmatic activity digested the pre-existing rock units, leaving behind minor remnants as xenoliths.

The Pt and Pd rich dunite units which lie nearly at the centers of most Ural-Alaskan type complexes have thus been crystallized from magmas which were derived by late stage melting of refractory mantle sources, from where large volumes of magmas had already been extracted.

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# NEW PGE-REEF MINERALIZATION OF THE SOTKAVAARA PYROXENITE INTRUSION, ROVANIEMI, NORTHERN FINLAND

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**ABSTRACT**. New data for PGE-reef style mineralization of the Sotkavaara intrusion (Rovaniemi, northern Finland) are presented.

The Sotkavaara intrusion is located around 25 km E-SE of Rovaniemi, in the so called Kuluskaira area of the Peräpohja schist belt. The ca. 1.5 x 2.5 km sized and rounded mafic-ultramafic body was intruded into the mica schists/gneisses, quartzites and amfibolites. Country rock contains some black schist interlayers close to the intrusion (Bedrock of Finland-DigiKp, 2014), being also favourable S-source for mafic-ultramafic magma.

The central part of the intrusion consist of mainly pyroxenites. Some thin (Ø 1-5 m) serpentine altered peridotite layers/dykes occur within pyroxenite. The outer parts of the intrusion consist of gabbros and amphibolites (i.e., gabbro-amphibolite zone). The pyroxenite is a small-medium grained rock composed mostly of clinopyroxene and amphibole. Often the rock contains ca. 1 mm sized orthopyroxene ± olivine ± plagioclase spots. Diamond rillings have revealed that the pyroxentic part of the intrusion is only ca. 300 m thick in depth, surrounded by up to 100 m thick gabbro-amfibolite zone.

Pyroxenites have low $Al_2O_3$ (2-4 wt.%), moderate MgO (16-20 wt.%), $TiO_2$ (0.4-0.6 wt.%) and Cr (0.1-0.2 wt.%) contents and low sulfur (100-600 ppm) and nickel (300-500 ppm) contents. Peridotites have high MgO (ave. 37 wt.%), but low $TiO_2$ (ave. 0.15 wt.%), $Al_2O_3$ (ave. 1.1 wt.%) compare to pyroxenites. However, Cr content of serpentinites is outstandingly low (ave. 0.02 wt.%). The gabbro-amphibolite zone rocks can be classified into three groups by their composition and texture: i) Low-$TiO_2$ gabbros, ii) high-$TiO_2$ gabbros, and iii) amphibolites. The low-$TiO_2$ gabbros contain also lower iron and vanadium, but higher $SiO_2$ contents than the high-$TiO_2$ gabbro, but otherwise they are similar by their compositions. For example, their chondrite-normalized REE-patterns are identitical (flat LREE and sloping MREE to HREE), which also resemble the REE-patterns of the pyroxenites.

Visible sulfides are rare in the pyroxenites, whereas the gabbros locally contain sparse disseminated sulfides. However, one hole intercepted ca. 25 cm thick massive sulfide vein containing 2.1 wt.% Ni, 0.47 wt.% Cu, 0.26 wt.% Co and trace PGEs (79 ppb Pd). Some trace sulfides (e.g., pyrrhotite, chalcophyrite, pentlandite and pyrite) has been detected to be closely associated with an "mottled" textured pyroxenite. This texturally distinguishable rock was studied within a 3 meter interval of one diamond drill core (R6) and this section revealed to contain elevated precious metals (Au+Pd+Pt between 0.86-1.16 ppm) with very low S and base metal values (ca. 400 ppm S, 65 ppm Cu and 150 ppm Ni).

Analysis showed a up to 15 m thick PGE anomalous zone with a very sharp lower "contact" where PGEs drop from 1 ppm to some tens of ppms over one meter interval. Upwards, PGE values gradually diminish to anomalous levels (>100 ppb). So far, this reef-type PGE occurrence has been located from three drill cores (R6, R12 and R398). The best intersection (in drill core R6) contains

6 m @ 0.99 ppm Au+2PGE. At this high grade interval, the Pt-Pd ratio varies across the mineralization, with very low ratio (<0.1 - 0.5). Upwards, Pd concentration decline rapidly and Pt-Pd ratio increases to ca. 5 and moderate 2PGE values and then decrease again to values between 1 to 3, as PGE contents drop to below 150-200 ppb. Analytical data shows that the reef is marked by low whole-rock Cr. Based on SEM scanning from mineralized thin sections, Pd-phases occur within sulfides and silicates and main Pd-phases are palladoarsenite, isomertierite, kotulskite and majakite. Only platinum bearing phase is sperrylite and it occur mainly within silicates.

The only known host-rock for reef-type PGE mineralization in northern Finland is represented by the 2.44 Ga layered intrusions (e.g., Alapieti & Lahtinen, 2002; Iljina & Hanski, 2005). In these intrusions, reef type mineralizations are usually associated with border of Cr-rich and Cr-poor unit. There is no direct age data from the Sotkavaara intrusion, but age data for the country rocks indicate a maximum age of ca. 1.98 Ga (Hanski et al., 2005), representing a new potential age group for PGE deposits in the Northern part of Finland.

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# PLATINUM ALLOYS IN URAL-ALASKAN-TYPE INTRUSIONS FROM THE URALS AND THE ALDAN SHIELD

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**ABSTRACT**. Pt-Fe alloys and mineral assemblages of platinum group minerals (PGM) from massifs of the Ural-Alaskan-type, located both in mobile belts (Urals) and platforms (Aldan Shield) were investigated. Their similarities and differences have been shown. The formation conditions of magmatic alloys of all massifs (Svetly Bor, Veresovy Bor, Kondyor, Inagli) correspond to FMQ buffer and conditions slightly more reducing than FMQ. Pt-Fe alloys from Svetly Bor and Inagli massifs are enriched in Ir and alloys from Veresovy Bor and Kondyor are richer in Pd.

Assemblages of PGM in the Ural-Alaskan-type intrusions were studied in numerous samples of rocks: dunite of the Svetly Bor (Urals), chromite- rich dunite of the Veresovy Bor (Urals), dunite, chromitite and clinopyroxenite of the Kondyor and Inagli massifs (Aldan Shield). Pt-Fe alloys are predominant in all massifs: small cubic crystals are intergrown with olivine (Fig. 1b) and anhedral grains in association with chromite (Fig. 1c). PGM assemblages of the Urals show similarity, expressed in the replacement of magmatic Pt-Fe alloys by secondary tetraferroplatinum-tulameenite solid solutions as rims (Fig. 1a). Exclusivly Pt-Fe-Cu alloys were found in the Veresovy Bor massif, whereas a significant variety of mineral species in the Svetly Bor massif is known: Pt-Fe alloys in association with osmium and iridium (isoferroplatinum-osmium and isoferroplatinum iridium paragenesises), chromite, laurite, erlichmanite, sulphides-, arsenides- and sulphoarsenides of PGE, BM sulphides, secondary PGE-Fe compounds, and Pt-oxides (Tolstykh et al., 2011). PGM assemblages of the Aldan Shield differ from those of the Urals by the presence of significant amount of cooperite (Kondyor) and sperrylite grains (Inagli) among the Pt-Fe alloys as well as an abundance of PGE-spinels (malanite, cuproiridsite, cuprorhodsite) (Fig. 1c,d). Secondary tulameenite grains are found in the Kondyor massif too, and they tend to have a porous structure and were not analyzed. A magmatic parageneses (isoferroplatinum-osmium and isoferroplatinum-iridium) are very typical for samples from the Inagli massif: osmium lamellae in the matrix of Pt-Fe alloys and exolution structure between iridium and isoferroplatinum (Fig 1c,d). Most of the magmatic Pt-Fe alloys in all studied massifs

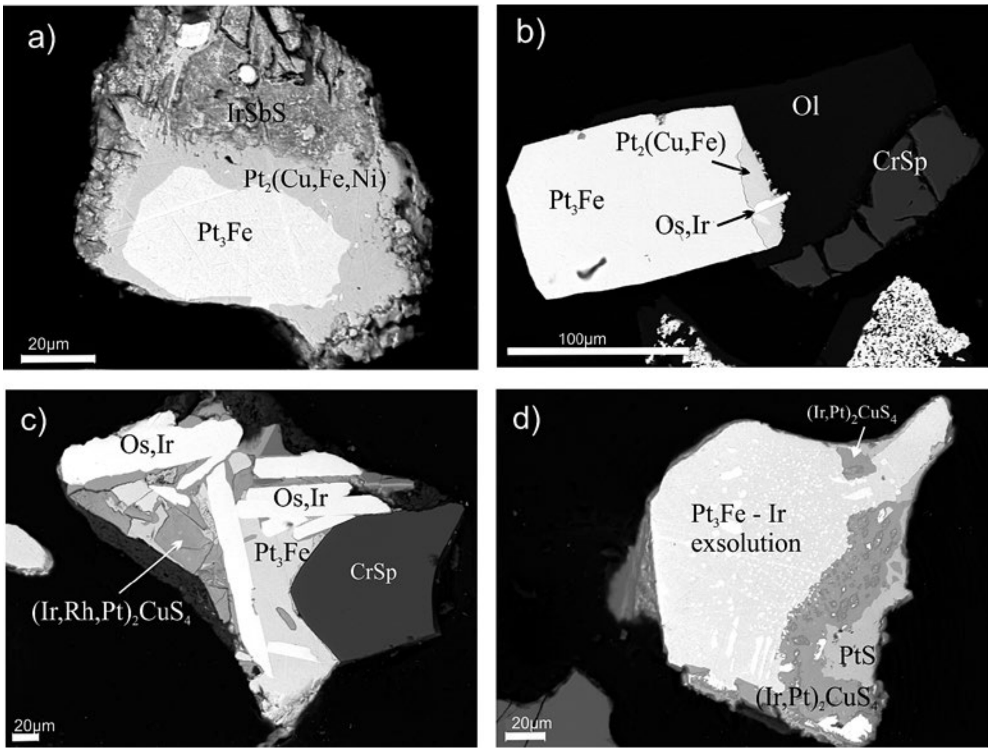

*Fig. 1*. SEM image of PGM: Svetly Bor (Urals) (a), Kondyor (b) and Inagli (Aldan Shield) (c, d)

are isoferroplatinum (Fig. 2a), in which the atomic ratio of Pt to Fe is close to 3:1. The Fe/(Fe+Pt) in magmatic Pt-Fe alloys have values in the range of 0.2-0.3 (Fig. 2b).

If the redox conditions ($fO_2$) at 1200°C (~ liquidus of basaltic melt) correspond to FMQ buffer then the ratio Fe/(Fe+Pt) of alloys crystallizing from the melt would be 0.20-0.25 (Roeder & Jamieson, 1992). Some compositions studied from both (Urals and Aldan Shield) massifs are a little richer in iron (Fig. 2b) so the conditions of their formation would be more reducing than the FMQ buffer.

Post-magmatic alloys of the Urals massifs that replace the primary Pt-Fe alloys are presented by solid solutions from tetraferroplatinum (Svetly Bor) to tulameenite (Veresovy Bor), which in turn are replaced by Fe- and Cu- rich alloys ($Cu_3Pt$, $Fe_3Pt$) (Fig. 2a). Pt-Fe alloys in most cases contain minor elements. Alloys without minor elements are typically found in intergrowths with osmium (isoferroplatinum–osmium paragenesis), which crystallize on early-magmatic stage. Ir-containing platinum alloys in association with Pt-rich iridium (isoferroplatinum-iridium paragenesis) formed later at the critical solvus temperature (~850°C). Ir is a more typical minor element in Pt-Fe alloys of all massifs. The maximum Ir concentrations are found on the Inagli alloys (up to 7 wt.%). The second most important minor element is Rh (up to 6.5 wt.% in Pt-Fe alloys of the Aldan Shield and up to 0.8 wt.% in Urals massifs). The maximum concentrations of Pd in Pt-Fe alloys (up to 3.5 wt.%) have been found in the Kondyor massif. The concentration of minor elements in Pt-Fe alloys characterizes the geochemical features of the ore-forming system. It indicates a fractionation of PGE at the magmatic source (Johan et al., 2000) and a difference in temperature of ore deposition, which decreases from Ir-rich alloys to Rh-rich and to Pd-rich alloys. The Pt-Fe alloys from the Veresovy Bor and Kondyor massifs are more fractionated (rich in Pd) than alloys from the Svetly Bor and Inagli massifs.

The mineral assemblages of PGM and range of Pt-Fe alloy composition from massifs of the Ural Alaskan-type, located both in mobile belts (Urals) and platform (Aldan Shield) are similar in main features: predominance of platinum alloys and the presence of two magmatic parageneses (early isoferroplatinum-osmium and late isoferroplatinum-iridium). Magmatic alloys of all massifs correspond to conditions of the FMQ buffer and conditions slightly more reducing than FMQ. The range of minor element in Pt-Fe alloys indicates a long thermal history for the mineral grains of all studied massifs. The association of PGM of each massif has typomorphic peculiarities which are caused by the degree of fractionation of elements in the ore-forming system. Pt-Fe alloys from the Svetly Bor and Inagli massifs are enriched in Ir while Pt-Fe alloys from the Veresovy Bor and Kondyor are richer in Pd.

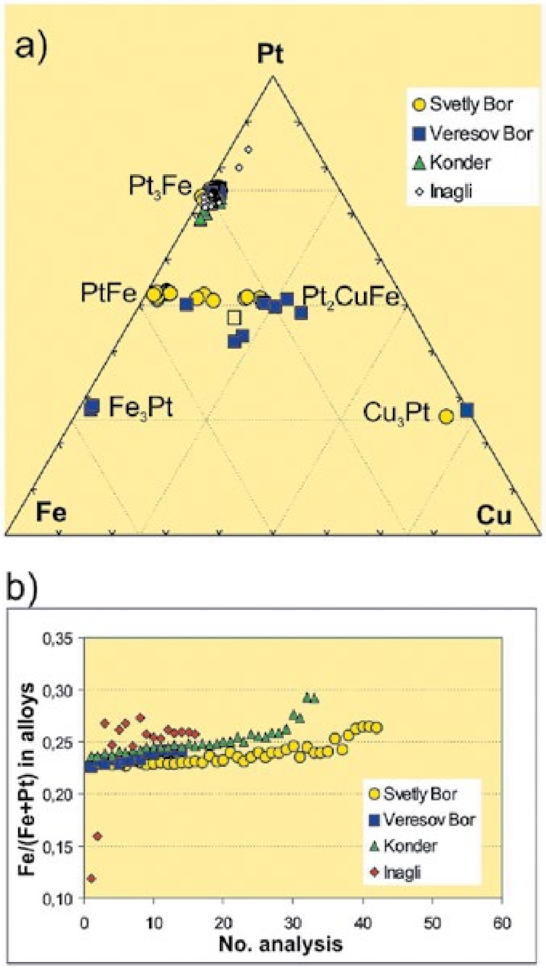

*Fig. 2.* Composition of Pt-Fe alloys from Urals (Svetly Bor, Veresovy Bor) and Aldan shield (Kondyor, Inagli) massifs: a) magmatic and post-magmatic alloys in Fe – Pt – Cu system; b) the value of Fe/Fe+Pt in magmatic alloys of all massifs

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# DATING PLATINUM MINERALIZATION BY THE NOVEL $^{190}$Pt-$^{4}$He METHOD OF ISOTOPE GEOCHRONOLOGY

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**ABSTRACT**. The retention of radiogenic helium in native metals is anomalously high. This finding allows the creation of a novel $^{190}$Pt-$^{4}$He method in isotope geochronology as the first main source of $^{4}$He accumulation in native platinum is the a-decay of the $^{190}$Pt isotope. We applied this method for dating Pt-mineralization from alkaline-ultramafic complexes (Kondyor, Inagli), dunite-clinopyroxenite complexes (Galmoenan, Fifeild) and from platinum-copper-nickel ores of the Norilsk region. Experimental data confirm that the novel $^{190}$Pt-$^{4}$He method can be successfully applied for the direct dating of minerals of platinum.

## ISOTOPE-GEOCHEMICAL BACKGROUND OF THE $^{190}$Pt-$^{4}$He METHOD

Retention of radiogenic $^{4}$He in crystals of most minerals is very low. Helium can escape easily from minerals in a course of their geological history. Thus isotope systems that are based on radiogenic helium are mainly used in the field of low temperature thermochronology. However there is a group of minerals – native metals – where the retention of radiogenic helium is anomalously high (Shukolyukov et al., 2012a). Helium, due to its very low solubility in metals tends to form atomic clusters of helium atoms, which manifest themselves as nanometer-scale bubbles. Migration of such "bubbles" in the crystal structure requires relatively high temperature close to the metal melting temperature. For this reason of special interest are native minerals of platinum. They have rather high melting temperature, implying that the retention of $^{4}$He in them is also very high. This finding allows the creation of novel $^{190}$Pt-$^{4}$He method in isotope geochronology for the direct dating of native minerals of platinum (Shukolyukov et al., 2012b).

## NUCLEAR-PHYSICAL BACKGROUND OF $^{190}$Pt-$^{4}$He METHOD

The first main source of $^{4}$He in native minerals of platinum is α-decay of $^{190}$Pt (Shukolyukov et al., 2012b) (natural abundance of $^{190}$Pt is constant – 0.01296% (Walker et al., 1997)). Thus for age determination it is only necessary to measure concentration of $^{4}$He and Pt in the sample.

$$t = \frac{1}{\lambda_{190}}((^{4})\frac{He_{Pt}}{(^{190}}Pt + 1 \quad , \qquad (1)$$

where $^{4}He_{Pt}$ – atomic concentration of platinogenic helium; $^{190}$Pt – atomic concentration of isotope of $^{190}$Pt; $\lambda_{190}$-decay constant ($1,477 \cdot 10^{-12}$ years$^{-1}$ (Walker at al., 1997)).

The strict restriction for application of the $^{190}$Pt-$^{4}$He method is the sample size. According to the Bragg-Kleeman equation (Eq. 2), the passing length for an α-particle for isoferroplatinum can be obtained as follows:

$$L - \mathbf{R}\frac{\rho_a}{\rho}\sqrt{\frac{\mathbf{A}}{\mathbf{A}_a}} \quad , \qquad (2)$$

where $\rho$ is the density of the material, $\rho_a$ is the density of the atmosphere, $R$ is the passing length of an α-particle of the same energy in atmosphere, and A and $A_a$ are mass numbers. Thus, $^{190}$Pt-$^{4}$He ages can be obtained for samples that are more than 50μm. Otherwise it will be necessary to do mathematical corrections for α-recoil effect.

## METHODOLOGY

Concentration of radiogenic helium in native minerals of platinum was measured on the mass-spectrometer MSU-G-01-M. In view of the very high melting temperature of native minerals of platinum (up to 1770°C) for release of helium in this study we have used the following approach: the weighted sample was mixed with technical copper (in ratio 1 : 3) and put into vacuum-sealed quartz tube or wrapped into tungsten foil. Dur-

Table 1

**Comparison of obtained $^{190}Pt$-$^{4}He$ ages with independent geochronological measurements**

| *Deposit* | *$^{190}Pt$-$^{4}He$* | *$^{40}Ar/^{39}Ar$* | *Rb-Sr* | *Sm-Nd* | *U-Pb* | *K-Ar* |
|---|---|---|---|---|---|---|
| Kondyor $Pt_3Fe$ | 125±6 | 120±1 | 126±1 | 131±35 | 125±2 baddeleytte | 50-160 |
| Kondyor $PtAs_2$ | 122±6 | « | « | « | « | « |
| Inagli $Pt_3Fe$ | 127±6 | - | - | - | - | 116±6;<br>141±7 |
| Galmoenan $Pt_3Fe$ | 65±3 | 71-75 | 65-84 | 75-101 | - | 65-89 |
| Fifield $Pt_3Fe$ (samples of F. Reith) | 450±23 | - | - | - | 445±6 zircon | 397±16 |
| Norilsk $PtAs_2$ (samples of S.F. Sluzhenikin) | 242±12 | - | - | - | 248±4 zircon<br>251±4 baddeleytte | - |

*Comment*. Isotope data are given by Cabri, Elliot, Kamo, Martin, Ronkin and others.

ing the heating copper reacts with the sample and reduces the melting point to approximately 1400°C (Shukolyukov et al., 2012b). Calculations considered only $^{4}He$ that released from aggregates of isoferroplatinum at temperatures higher then 1000°C. Helium that releases below this temperature is not connected with the crystal structure of isoferroplatinum. For calculation of the total content of Pt in the sample the components of isoferroplatinum (crystals and aggregates) were studied under the microscope for phase homogeneity and presence of other mineral inclusions. If found in isoferroplatinum, we took into account the distribution of micro-sized inclusions of native osmium, native iridium etc.

## SAMPLES & RESULTS

We have studied more than 25 aggregates of isoferroplatinum with weights from 0.1 to 10 mg from alkaline-ultramafic massifs; Kondyor, Inagli (Aldanian shield, Russia) and from dunite-clinopyroxenite massifs Galmoenan (Koryak highland, Russia) and Fifield (NS Wales, Australia), as well as sperrylite from platinum-copper-nickel ores of the Norilsk region and the Kondyor massif. Although sperrylite is not a native mineral of platinum the retention of $^{4}He$ in this mineral is also high due to its conductivity (Yakubovich et al., in press). Results of $^{190}Pt$-$^{4}He$ dating and comparison of them with independent geochronological data is presented in table 1.

*Acknowledgments. Authors acknowledge for funding Russian Foundation of Fundamental Research (grants 14-05-00896 and 13-05-00717).*

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# ORIGIN OF PODIFORM CHROMITITE: A NEW MODEL

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**ABSTRACT**. The new observations suggest that the formation of podiform chromitite is a multi-stage process. Massive ores form deep in the mantle under low ambient $fO_2$ from partial melts of the host peridotite. Then, as the massive chromite rises it partially reacts with host peridotite to form the nodular and disseminated chromitite ores that may develop by interaction with boninitic melts in a suprasubduction zone environment as proposed previously.

Podiform chromitites have been interpreted as the result of harzburgite/melt reaction in the upper mantle. The discovery of ultrahigh-pressure (UHP) minerals in some podiform chromitites and host peridotites raises many questions. Chromitites in the Luobusa ophiolite of Tibet range from massive to nodular to disseminated Many chromite grains in these bodies contain inclusions of forsterite and pyroxene. Forsterite inclusions have Fo numbers of 97-99. Mg# of clinoproxene inclusions are 96-98 and those of orthpyroxene 96-97. X-ray studies show that the olivine inclusions have very small unit cells and short cation-oxygen bond distances, suggesting crystallization at high pressure. However, nodular and disseminated chromites lack pyroxene inclusions and their olivine inclusions have lower Fo numbers of 94-96. In addition, Mössbauer spectroscopy shows that $Fe3+/\sum Fe=0.42$ is higher in chromite from massive ore than from the nodular and disseminated ores, which have $Fe3+/\sum Fe=0.22$. Disseminated chromites also show systematic changes in olivine and spinel composition from the dunite envelope to the massive ore, indicating melt-rock reaction. These observations suggest that the formation of podiform chromitites is a multi-stage process. Massive ores form first deep in the mantle under low ambient $fO_2$ from partial melts of the host peridotite. UHP minerals and highly magnesian olivine and pyroxene inclusions are trapped in these chromites. Then, as the massive chromite rises to the shallower in the mantle it partially reacts with their host peridotite to form the nodular and disseminated chromitite ores that may develop by interaction with boninitic melts in a suprasubduction zone environment as proposed previously.

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# PGE MINERALIZATION IN OPHIOLITES OF THE SOUTHEAST PART OF THE EASTERN SAYAN (RUSSIA)

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**ABSTRACT.** The studied PGE mineralization from the southeastern part of Eastern Sayan (SEPES) has different composition and formed under various conditions. It is associated with chromitites, carbonized ultrabasics, amphibole- and magnetite- altered basic-ultrabasic rocks.

For SEPES ophiolites are divided into Southern and Northern ophiolitic belts which stretch for more than 100 km in east-west and north-east directions. These belts frame the Gargan block – Archean micro-continent. The ophiolitic rock assemblages related to the Shigna-Shishkhid belt in the Oka zone are also defined. Ophiolites characteristics indicate different genetic types: 1) oceanic – Southern belt, >1200-1100 Ma; 2) island-arc – Northern or Dunzhugur belt, 1035-850 Ma; 3) back-arc – Shigna-Shishkhid belt, 850-800 Ma (Dobretsov, 1985; Zhmodik et al., 2006; Kuzmichev & Larionov, 2013).

Chromitites with PGE mineralization are detected among serpentine-altered dunites and harzburgites in the Southern (SOB) and Northern (NOB) Ophiolitic Belts in the forms of veins, lenses and disseminated chromite mineralization. The compositions of chromites and PGE mineralization are significantly different. Ore Cr-spinel in the NOB chromitites is represented by mid-aluminous and low-aluminous types. SOB chromitites contains only mid-aluminous Cr-spinel. Chondrite-normalized PGE patterns for the chromitites revealing two geochemical types: 1) fractionated (Os-Ir-Ru) type which predominantly consist of refractory PGE; 2) (Pt–Pd)-type in the NOB chromitites with increased concentrations of Pt and Pd. PGE minerals in the NOB chromitites are represented by: (a) high-temperature [Os-Ir-Ru] solid solutions, sulfides, sulfo-arsenides and arsenides of these metals; (b) Pt-containing high temperature assemblage – [Pt-Ir-Os-Ru] and isoferroplatinum; (c) relatively low-temperature mineralization – (Pt,Cu), (Pt,Pd,Cu), [PdHg], [$Rh_2SnCu$], [RhNiAs], [Ir,Ni,Fe], [$PtAs_2$], [$PtSb_2$]. PGE minerals in the SOB chromitites are represented by high-temperature [Os-Ir-Ru] solid solutions, sulfides, sulfo-arsenides and arsenides of these metals. Considerable amounts of Ni minerals were detected associated with PGE mineralization. The presence of these Ni minerals is an evidence of relatively low temperatures of formation for the PGE.

Carbonaceous ultramafic rocks are widespread in the SOB ophiolites (Ospa area). Our studies show that free carbon is present in the primary dunites and harzburgites (stockwork-like carbonization), also in serpentinites and talc-carbonaceous rocks (viens and vein-like bodies of the carbonaceous rocks). Carbon-bearing ultrabasic, serpentinites and talc- carbonaceous rocks (to 9.75 wt.% C) are enriched in Pt (to 1.27 ppm), Pd (to 0.11 ppm), Au (to 2.4 ppm) and Ag (to 265.2 ppm), although the distribution of these elements is irregular. In all cases the carbonaceous material is enriched with PGE. According to the data of X-ray diffraction, Raman and UR spectroscopy, and thermic analyses, free carbon from the carbonaceous ultrabasic rocks is present as graphite with a high-degree of structure ordering, graphitoid, ultra dispersed graphite, amorphous phase C. Isotopic composition of free carbon has a $\delta^{13}C$ value similar to the mantle values (-8.85 – -16.6‰ ). Precious metal minerals are present as native gold of various grade, often with Hg (to 27.22 wt.%) and Cu (to 27.85 wt.%) impurities, in the carbonaceous ultrabasites.

PGE minerals, such as native platinum and palladium ($PdPt_{0.1}$), palladium-rich platinum ($PdPt_{1.1-1.5}$), $(Pt, Pd)_3Sn$, atokite ($Pd_3Sn$), rustenburgite ($Pt_3Sn$), zvyagintsevite $(Pd, Pt)_3(Pb, Sn)$ have been detected. In addition, intermetallic compounds of Sn, Pb, Cu, Sb with Pt and Pd impurities have been found. The spatial distribution of carbonaceous substance in the rocks; forms and conditions of carbonized rock deposition; isotopic and mineralogical and geochemical peculiarities of the rocks and carbonaceous substances – all together define evidence of carbon transportation by gas-fluid streams of deep-mantle origin. Carbonaceous rocks with associated peculiarities could be considered as a fluidogenic rocks formed by decompression fluid explosions. Zircons from carbonized ultrabasic rocks were analyzed to define the age by SHRIMP method (to VSEGEI). The ages defined belong to the different rocks which were captured and carried up by the carbon-containing (CO, $CO_2$, $CH_4$) fluid streams. Carbonization of ophiolites took place in the period of 825-796 Ma and this age corresponds to the age of Shishkhid island-arc origination.

In the Oka structural-formational zone (Toustuk area) areas of intense basic-ultrabasic rock massifs amphibolization with related sulfide and magnetite mineralization were detected. The study results for amphiboles and mineral assemblages from the basic and ultra-basic rocks suggests two stages of metamorphism occurred. The characteristics of progressive metamorphic stage are: 1 – greenschist low-pressure (0.6-3.5 kbar) with ferro-magnesial and magnesial hornblende; 2 – mid-pressure (5.7-8.7 kbar) with ferro-subalcaline chermakite hornblende, chermakites and magnesio-riebeckites; 3 – high-pressure glaucophane-schists (over 7-8 kbar). Regressive metamorphicstage is represented by the winchite-barroisite-chlorite (±epidote-actinolite) and talk-tremolite-calcite mineral associations. Sulfidization and magnetitization processes are associated to the regressive stage of metamorphism. Chondrite-normalized PGE plots show enrichment of the rocks with Rh, Pd, Pt. In the amphibolized pyrite and magnetite containing rocks mineralization of Pt-Sn-Hg-Au is found. The mineralization is represented by sperrylite, low grade-Au and $Au_{2,5}Hg$-$Au_3Hg$, $Cu_4Au_{1,5}HgSn$-$Cu_3Au_2HgSn$ compounds as well as intermetallic compounds of Sn and Pb.

The obtained data suggest that PGE mineralization varies within the rocks of the Eastern Sayan ophiolitic complexes. The data also confirm the different geodynamic, mineralogical, geochemical and physical-chemical conditions of PGE formation.

*Acknowledgments. This work was supported by the IP 89, RFBR 12-05-01164; 13-05-12056; MES RF.*

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# SESSION 6

## PGE and Au through experiments

**Conveners: Alexander Borisov & Anna Vymazalova**

The session will focus on experimental studies of PGE and Au solubility in sulphides and silicate melts, PGE and Au partitioning between phases as well as PGE minerals stability and composition at T-P range from magmatic to hydrothermal conditions. Also contributions focused of phase equilibria in PGE-Au systems, and thermodynamic properties of PGE minerals and phases are welcomed.

# METAL-LIGAND ASSOCIATIONS OF THE PGE IN MAGMATIC LIQUIDS

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**ABSTRACT**. Experiments have provided important insight into solubility mechanisms of noble metals in magmatic liquids. In silicate melts, the PGE are dissolved as oxide species whose abundance increases with increasing oxygen partial pressure (Borisov & Palme, 1995, 1997, Laurenz et al., 2010). If a silicate melt is sulfur-bearing, an over-proportional fraction of the PGE are dissolved as molecular PGE-S species (Laurenz et al., 2013). Under highly reduced conditions, small amounts of PGE might be accommodated as metals (Cottrell & Walker, 2006), although the mechanisms by which neutral metal species could be dissolved in silicate melts are as yet poorly defined.

Sulfide and metal melts are more tolerant with respect to PGE speciation. In these melt compositions, the PGE can be dissolved as PGE-sulfide, as PGE-oxide, and/or as neutral PGE metal species. The relative proportions of these species are a function of the oxygen and sulfur partial pressures as well as of temperature. Minor elements as ligands may also play a role: when a sulfide melt contains As, Sb, Te, Bi, and Sn, which natural melts ususally do, a large proportion of the noble metals appears to form associations with anionic ligands of these elements (Helmy et al., 2013), in form of molecules and/or poly-atomic clusters (Tredoux et al., 1995). The PGE-ligand pairings preferred in nature can probably deduced from the compositions of discrete PGE phases, although more experiments are needed to verify that principle.

PGE-ligand associations play a major role for the PGE behavior in magmatic melts, and three examples are discussed here:

(1) If a silicate melts is sulfur-bearing, a large proportion of the $Ru^{n+}$in silicate melts is associated with the $S^{2-}$ anion and dissolved in the form of Ru-S molecules (most probably $RuS_2$) and/or $(Ru-S)_n$ polymetallic clusters. The preference of $Ru^{n+}$to bond with $S^{2-}$ over $O^{2-}$ is of the order of 100. When sulfide saturation sets in, metal-S associations present in the silicate melt are sequestered to the evolving sulfide melt.

(2) Platinum and palladium are known to be rather incompatible with monosulfide. The D (mss/sulfide melt) values range from ~ 0.1 (Pd) to 0.05 (Pt). With progressive addition of Te to sulfide systems, Pt and Pd become even more incompatible. Apparently, at magmatic temperature Pt and Pd form stable associations with Te in the form of Pt-Te and Pd-Te compounds, and in that associated form have difficulty fitting in the monosulfide lattice. The common presence in magmatic sulfide ores of discrete Pt and Pd tellurides may reflect this preference.

(3) A similar observation is made with respect to arsenic. When As is added to a Pt-bearing sulfide system, the $D_{Pt}$ (mss/sulfide melt) falls with increasing As/Pt bulk atomic ratio, from ~ 0.05 (As-free) to ~ 0.003 in sulfide systems with bulk As/Pt atomic ratios around 2. Helmy et al. (2013) investigated thin films of equilibrium monosulfides from experiments in Pt-As-bearing sulfide systems with TEM. They made visible Pt-As nano-associations in the forms of six-sided cubic $PtAs_2$ platelets and at high temperature nano-sized Pt-Fe-As melt globules, all included in equilibrium monosulfide crystals. These nanophases are observed even though the bulk sulfide systems are highly undersaturated with respect to discrete (macroscopic) $PtAs_2$ or immiscible Pt-As melts, by factors up to 100.

PGE-ligand associations at magmatic temperature have important implications for the chemical behavior of the noble metals in evolving sulfide-silicate and metal-silicate systems. When prior to sulfide saturation a large fraction of the PGE inventory of a silicate melt is associated with the $S^{2-}$ anion, sulfide unmixing alone will cause PGE enrichment in the sulfide melt. Indeed, this is observed. Sulfide globules in rapidly quenched basaltic glasses can be as enriched in PGE as magmatic sulfide ores in layered intrusions even though they have not seen large R factors. Noble metals associated with a ligand that is itself incompatible with crystalline monosulfide will behave incompatibly in evolving sulfide melts, causing very efficient enrichments of the PGE to late-stage sulfide, arsenide, and telluride melts. If nano-assciations of the PGE are as common in nature as implied by existing experiments and TEM evidence (Helmy et al., 2013, Wirth et al., 2013), caution is advised in applying partition coefficients derived in simple systems to natural, chemically more complex situations. Noble metals that occur in associated form as nanophases will partition quite differently to elements or cations. Their distribution among phases will be dominated by surface properties of the nanophases rather than by the chemical affinities of the elements.

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# NOBLE METALS IN EXPERIMENTAL COSMOCHEMISTRY

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**ABSTRACT**. We demonstrate that variations in silicate melt and/or metal phase composition and intensive parameters (T-P-$fO_2$) during core formation can considerably change the absolute values of many HSE metal/silicate partition coefficients. The existing data support models invoking the accretion of a late chondritic veneer after core formation without further metal segregation.

All PGE and Au have very high metal/silicate partition coefficients and are commonly termed highly siderophile elements (HSE).

In a series of experimental studies (see summary in Borisov & Palme, 2000) solubilities of HSE in silicate melt of anorthite-diopside eutectic composition have been determined at 1 atm total pressure and at a wide range of oxygen fugacity. Calculated metal/silicate partition coefficients, extrapolated to low $fO_2$ values relevant for terrestrial core formation (IW-2) were found to be extremely high (ca. $10^6 - 10^{15}$). This suggests that the chondritic HSE signature of the upper mantle cannot be the result of metal/silicate equilibration, at least at low pressures.

During the last decade the effect of melt composition on HSE solubilities was studied (e.g., Borisov et al., 2004; 2006; Borisov & Danyushevsky, 2011; Laurenz et al., 2010, 2013).

Here we demonstrate that variations in silicate melt and/or metal phase composition and intensive parameters (T-P-$fO_2$) during core formation can considerably change the absolute values of many HSE metal/silicate partition coefficients. However, under any realistic conditions, all partition coefficients cannot become similar. Such a similarity is mandatory to explain nearly chondritic signature of the upper mantle rocks with respect to most HSE by the model of "global mantle/core equilibrium" (e.g., Murthy, 1991). Thus the existing data still support models invoking the accretion of a late chondritic veneer after core formation without further metal segregation.

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# EXPERIMENTAL STUDY ON THE SOLUBILITY OF Te, Bi AND As IN SULFIDES AND THE EXSOLUTION OF DISTINCT METALLOID PHASES

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**ABSTRACT**. Metalloids (e.g., Te, Bi, As) are fundamental components of many platinum-group minerals (PGM). Therefore, they can effectively affect the behavior of highly siderophile elements (HSE) among sulfides during the formation of magmatic PGE deposits. An experimental study was conducted to quantify the concentration of metalloids dissolvable into sulfides prior the exsolution of metalloid phases. A mixture of Fe-Ni-Cu sulfides (doped with 50 ppm of each HSE) and metalloids (individually and mixed in a concentration of 3 wt.%) were sealed in evacuated silica tubes. Different experimental sets were melted at 1200 °C, then slowly cooled and equilibrated respectively at temperatures between 1050 °C and 600 °C. Run products consisted of monosulfide solid solution (MSS), a Cu-rich phase (quenched melt or intermediate solid solution, ISS), and metalloid-rich phases. A Te-Bi-rich liquid and a As-rich phase segregate and were found with the Cu-rich liquid (or ISS) or filling cracks within the MSS. At 900 °C, the highest metalloid content in MSS was: 4800±600 ppm, (2σ) for Te, 2500±120 ppm for As and 260±14 ppm for Bi. At other temperatures, the concentrations are not significantly different. Therefore, temperature does not have an extensive effect on the solubility.

Highly siderophile elements (HSE: Ru, Rh, Pd, Re, Os, Ir, Pt and Au) can be found in PGE deposits both in the lattice of sulfides and as platinum-group minerals (PGM), complexed with ligands such as metalloids (e.g., Te and As) or heavy metals (e.g., Bi) [e.g., merenskyite, (Pd,Pt)$(TeBi)_2$; michenerite, PdBiTe or sperrylite, $PtAs_2$; Cabri & Laflamme 1976). Even though metalloids have such an important role, little attention has been devoted to understanding their behavior during the formation of a PGE magmatic deposit. For example, the experiments conducted by Helmy et al. (2007) show that, during the crystallization of a sulfide liquid, Te segregates a liquid that is immiscible with the sulfides and sequesters most of the Pt and Pd. Helmy et al. (2010) calculated the partitioning coefficients for different metalloids between monosulfide solid solution (MSS) and Cu-rich residual phase. Moreover, Tomkins et al. (2007) reported the fluxing effect of metalloids on the melting point of sulfides. However, there seem to be no experimental data about the concentration of metalloids that can be present in sulfides before the exsolution of a metalloid liquid begins. We conducted an experimental study to fill this gap. Starting materials consisted of 70 wt. % of natural pyrrhotite, 15 wt. % natural pentlandite and 15 wt. % natural chalcopyrite. Kullerud et al. (1969) were assuming these proportions for the average sulfide composition of the Sudbury ores. Therefore, this was the proportion we chose as a starting point. Sulfides were doped with 50 ppm of each HSE, modifying the protocols of Sylvester et al. (2005) and Wohlgemut-Überwasser et al. (2007) for making PGE sulfide standards for LA-ICP-MS. Metalloids were added individually and mixed (molar ratio 1:1:1) in the concentration of 3 wt.%. Materials were sealed in evacuated silica tubes and melted at 1200 °C for four hours. Successively, temperature was slowly decreased (2 °C/h) and different sets of experiments were left equilibrating respectively at 1050 °C for 3.5 days, 900 °C (7 days), 750 °C (14 days) and 600 °C (28 days). Finally, capsules were quenched in cold water. Run products were sectioned, mounted in epoxy and manually polished. Back scattered electron images show that the run products are composed of MSS, a Cu-rich residue (either quenched liquid or ISS) and metalloid-based phases. In experiments in which metalloids had been added as a mixture, two distinct phases were observed (Fig. 1), either within the Cu-rich residue or filling cracks within MSS. The first phase is rich in As and euhedral textures indicate that it was already crystallized at 1050 °C. The second, rich in Bi and Te, was still liquid at 1050 °C, but not at 900 °C. At and below 750 °C, euhedral crystals of melonite ($NiTe_2$) were recognized in Te-bearing experiments, gersdorffite [(Ni,Fe)AsS] and sperrylite ($PtAs_2$) were detected in As-bearing experiments and Bi oxide ($Bi_2O_3$),

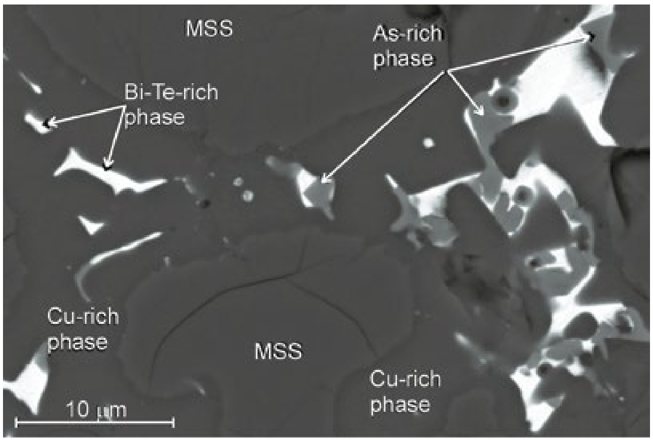

*Fig. 1.* BSE image of a final product of an experiment doped with a mixture or Te, Bi and As and run at 1050 °C. An As-rich phase (light grey) with sharp corners indicating that it was already crystallized is immerged in a Bi-Te-rich quenched liquid (white). They are both within Cu-rich quenched residual liquid (dark grey with apparent negative relief), interstitial among MSS rounded grains (dark grey, apparent positive relief)

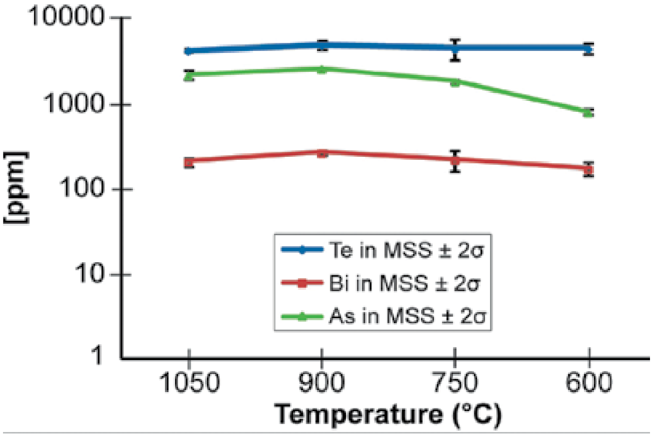

*Fig. 2.* Highest concentration of metalloids reported in MSS at different temperatures, obtained with LA-ICP-MS analysis of experiments in which metalloids had been added individually in the initial concentration of 3 wt.%

along with an undefined Bi-Pb-bearing-phase were observed in Bi-bearing experiments. Major elements (Fe, Ni, Cu and S) were analyzed with WDS in sulfides, whereas trace elements (HSE, metalloids and others) were analyzed with LA-ICP-MS. The metalloid minerals were qualitatively analyzed with EDS. The highest concentration of metalloids in MSS was measured in experiments in which metalloids had been added individually. Temperature does not have an important effect on the solubility (Fig. 2).

However, the highest concentrations of metalloids were measured in experiment run at 900 °C. Te is the most soluble in MSS (4800±600 ppm, 2σ) followed by As (2500±120 ppm) and then by Bi (260±14 ppm). At lower temperature (600 °C), only As seems to sensibly reduce its concentration in MSS, whereas no relevant changes can be observed for Te and Bi. These are the highest concentrations of metalloids beyond which the exsolution of a metalloid liquid should be expected and thus influence the partitioning of HSE.

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# BEHAVIOR OF PLATINUM METALS AT CRYSTALLIZATION OF Cu-RICH SULFIDE MELT: NATURE AND EXPERIMENTS

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**ABSTRACT**. In this work we study the joint behavior of impurities during fractional crystallization of the melt composition (mol.%): Fe 33.20, Cu 16.55, S 50.03, Pt 0.03, Pd 0.02, Au 0.02, As 0.02, Bi 0.03, Te 0.02, and Sn 0.08. Crystallized sample consisted of (I) pyrrhotite solid solution (6%) and isocubanite (77%). The composition and morphology of PGM inclusions are investigated.

Cubanite massive ore in the Norilsk deposits is the constituent of the giant zonal orebodies with a thickness up to 40-50 m. These orebodies are composed of zonal arrangements of pyrrhotite ore ($Pn+Po^h+Tr+Cp^t$), cubanite ore (PnTr, Cub, $Cp^t$) and mooihoekite ore (Pn+Cub+Mh+Hc, $Cp^t$). The lowest content of platinum metals is in pyrrhotite ore (Cu-5.6 wt. %, Pt+Pd – 12.9 g/t), whereas the Pt+Pd content increases sufficiently in cubanite ore (Cu-12.6 wt. %, Pt+Pd – 25.7 g/t) and mooihoekite ore (Cu-21.1 wt. %, Pt+Pd – 51.5 g/t) (Distler, 1994).

The present paper represents the results of the experimental study on fractional crystallization of 10-component melt with the composition (mol. %): 33.22 Fe, 16.57 Cu, 50.00 S and 0.03 each for Pt, Pd, Au, Sn, Bi, Te and As). The silica cylindrical ampoule was slowly moved from the hot zone of the furnace to the cold one with a speed of $2.3\cdot10^{-8}$ m/sec (Kosyakov & Sinyakova, 2005) to reproduce the directional crystallization. The distribution of phases and elements along the solid ingot was examined using conventional SEM, EPMA and XRD techniques. The proportion of crystalline matter ($g$) served as a coordinate of the process. The melt composition at a present time was determined by using data of element distribution and balance equations.

Pyrrhotite, which contained up to 2.7 mol. % Cu, crystallized from the melt in the beginning of the process (until $g=0.06$). A Cu excess exsolved as cubanite inclusions because of a decreasing Cu solubility at cooling of the solidified ingot. A phase with the composition $CuFe_2S_3$ crystallized in the second zone of the ingot ($0.06 \leq g \leq 0.83$) according to the bulk chemical data. This phase was partially decomposed to a cubanite-like phase with the composition $Cu_{1.1}Fe_{1.9}S_3$ and pyrrhotite inclusions at cooling. It is noteworthy that the zone II contained numerous gaseous pores up to 200 microns in size. The third zone of the ingot was composed of a mixture of mooihoekite, haycockaite and other minerals of the chalcopyrite group.

The behavior of platinum minerals during the crystallization of sulfide melts is of particular interest. The investigation of the first zone showed that the trace element content in the pyrrhotite matrix was below detection limits and there were no discrete minerals in it. The cubanite matrix from the second zone contained up to 0.15 wt. % Sn whereas the solubility of other trace elements in the cubanite lattice were below detection limits. Noble metals were present as the micron-sized grains of discrete minerals. The zone II was subdivided into two parts based on the assemblages of PGE minerals. Mineral with the composition PdBiTe – an intermediate member of the kotulskite PdTe – sobolevskite PdBi isomorphous series, sobolevskite PdBi, moncheite $(Pt,Pd)_1(Bi,Te)_{2-x}$, cooperite (Pt,Pd) S, S-rich sperrylite $Pt(As,S)_2$, lisiguangite $CuPtBiS_3$, unnamed phase with the composition $PtBiS_3$, native Au enriched in Pd and Cu were found in the zone II a ($0.06 \leq g \leq 0.16$).

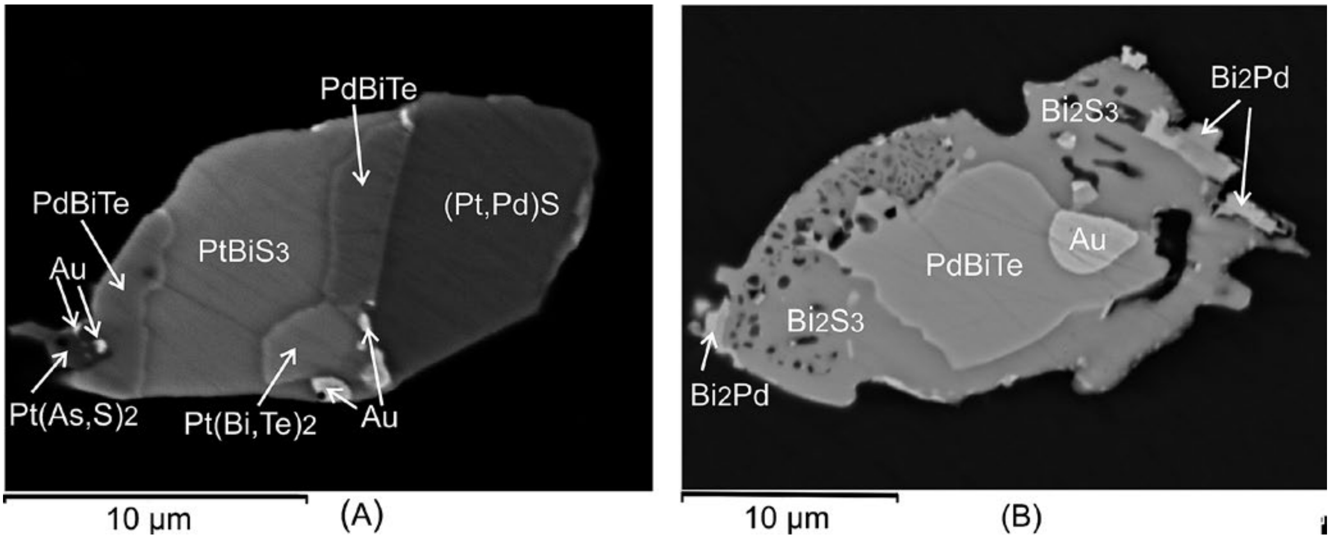

*Fig. 1.* BSE images of PGE minerals in polyphase intergrowths which are included in cubanite matrix. (A) – zone II a, $g$=0.09; (B) – zone II b, $g$=0.34

The zone II b ($0.16 \leq g \leq 0.83$) contained also froodite $Bi_2Pd$ and bismuthinite $Bi_2S_3$.

Minerals of noble metals were present as the individual grains (sperrylite $Pt(As,S)_2$ 20 x 40 microns in size, moncheite $(Pt,Pd)_1(Bi,Te)_{2-x}$ up to 5 x 10 microns in size) and two-phase intergrowths (PdBiTe+Au, $Pt(As,S)_2$+Au, $PtBiS_3$+Au, (Pt,Pd)S+$PtBiS_3$) from 1 x 2 microns to 10 x 30 microns in size. However, most inclusions had a bigger average size of 10 x 30 microns and were composed of four to seven intergrown minerals, for example:

$PtBiS_3+PdBiTe+Au+Pt(As,S)_2$,
$PdBiTe+Au+Bi_2Pd+Bi_2S_3$,
$CuPtBiS_3+PdBiTe+Au+Pt(As,S)_2+Bi_2S_3$,
$PtBiS_3+PdBiTe+Au+PtS+Bi_2S_3$,
$PtBiS_3+PdBiTe+Pt(Te,Bi)_{2-x}+Pt(As,S)_2+Au+(Pt,Pd)S$,
$PtBiS_3+PdBiTe+(Pt,Pd)(Te,Bi)_{2-x}+Pt(As,S)_2+$
$+Au+(Pt,Pd)S+Bi_2S_3$ (Fig. 1).

Platinum minerals form two types of inclusions at cubanite crystallization. The inclusions, which are not associated with gaseous pores, are located in the intergranular space or in the internal parts of the sulfide grains. The inclusions, which are associated with the gaseous pores, have the similar chemical and mineral compositions with respect to that of the inclusions unassociated with the pores. This means that the presence of the gaseous pores does not affect partitioning of the noble metal admixtures. Probably, the presence of the pores affects kinetics of nucleation and growth of admixture phases. The heterogeneity of the inclusions may be explained by a suggestion that a nucleus of the first phase appears and grows followed by crystallization of the other nuclei on its surface. A random character of the process leads to the variability of the morphology and chemical compositions of the inclusions.

The phases produced in the experiments are identical to the compositions of the most typical natural associations of PGE minerals in mineralization of the different types hosted in komatiites and layered intrusions.

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# NEW DATA ON Pd-Sn-Te PHASES

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**ABSTRACT.** The temperatures of formation and the energy characteristics of Pd-Sn-Te phases were determined using Synchronous Thermal Analysis (thermogravimetry and differential scanning calorimetry. The dependence of thermal effects temperature on varying phase composition and phase relationships is considered.

Pd-Sn-Te-As-Sb compounds are of interest for mineralogists due to complex isomorphous substitutions between Sn, As, Sb, Te etc., typical for a number of PGM (i.e. isomertieite group minerals, mertieite, vincentite and oth.). In general their composition could be presented by ternary compound with combination of "semimetals" in formula. So, the study of ternary phase of palladium with „semimetals": their compositions, associations, and temperatures of formation, needs the detailed research. In order to better understand the formation of such compounds a detail DTA study of phases in the system Pd-Sn-Te was carried out using samples with ternary Pd-Sn-Te compounds synthesized at 400 °C by Vymazalová & Drábek (2010).

Thermal characteristics of Pd-Sn-Te compounds were determined by Simultaneous Thermal Analysis (STA) [Thermogravimetric analysis, TGA; and Differential scanning calorimetry, DSC] using NETZSCH STA 449 F3 Jupiter ®). Conditions of analysis: temperature range 30 – 1050 °C; rate of heating 10.0 K°/ min; heating was carried out in the corundum crucible with a cap in Ar atmosphere. Samples were examined using a scanning electron microscope JSM 5610LV, equipped with energy dispersive spectrometer INCA Energy-450, prior to thermal analyses and consequently after the thermal test. Crystals of $Pd_{67}Sn_{11}Te_{22}$ with PdTe phase (Sample 39, Table 1) before the thermal test are shown in Fig. 1.

The phase $Pd_{67}Sn_{11}Te_{22}$ is tetragonal (Vymazalová & Drábek, 2010) corresponing to $Pd_{7-8}SnTe_2$ compound with tetragonal structure based on $Cu_3Au$ structure type (Savilov et al. 2005). Zakharova & Kuznetsov (2008) suggested that in the composition range $Pd_3Sn_{0.9}Te_{2.1}$ – $Pd_3Sn_{1.2}Te_{1.8}$ there are possibly phases of layered structure, derivates of NiAs type. That likely corresponds to Sn-rich kotulskite.

The obtained results (Table 1) allow us to determine the melting temperature and melting enthalpy of phases. Clearly expressed endothermic effects correspond to ternary phase melting: phase A ($Pd_{67}Sn_{11}Te_{22}$) ~ 590-630 °C, phase B ($Pd_{72}Sn_{16}Te_{12}$) ~ 960 °C. Along with there are several more weak effects on TG curves, that could show the phase transitions. Some variations of melting point temperatures could be caused by variation in Sn and Te contents.

*Acknowledgments. This work was supported by Fundamental Research Program n. 9, Departament of Earth Sciences of RAS.*

Table 1

**Main temperature effects and melting enthalpies (TG)**

| Samples* | *Charge composition** | Phases* | Melting point, T⁰ C | Other effects, T⁰C | Melting enthalpy, J/g |
|---|---|---|---|---|---|
| Pd11 | 5Pd+Sn+3Te | PdTe+$Pd_2(Sn,Te)$ | 689.7 | | -64.43 |
| | | | | 587.0 | -3.86 |
| Pd30 | 73Pd+16Sn+13Te | $Pd_{72}Sn_{16}Te_{12}$+$Pd_3Sn$ | 968.0 | | -11.97 |
| | | | | 614.5 | -0.838 |
| | | | | 564.1 | -4.089 |
| Pd39 | 5Pd+Sn+2Te | $Pd_{67}Sn_{11}Te_{22}$+$Pd_2(Sn,Te)$+PdTe | 592.3 | | -47.1 |
| | | | | 619.1 | -2.71 |
| Pd58 | 68Pd+15Sn+17Te | $Pd_{67}Sn_{11}Te_{22}$+$Pd_{72}Sn_{16}Te_{12}$+$Pd_2(Sn,Te)$ | 619.3 | | -21.42 |
| | | | 972.0 | | -1.227 |
| | | | | 586.3 | -2.384 |
| Pd111 | 6Pd+15Sn+17Te | $Pd_{67}Sn_{11}Te_{22}$ | 632.6 | | -11.96 |
| | | | | 588.3 | -2.223 |
| Pd135 | 67Pd+11Sn+22Te | $Pd_{67}Sn_{11}Te_{22}$ | 623 | | -12.74 |
| | | | | 652.0 | -6.492 |
| Pd137 | 72Pd+16Sn+12Te | $Pd_{72}Sn_{16}Te_{12}$+$Pd_3Sn$ | 955 | | -15.08 |
| Pd138 | 68Pd+11Sn+22Te | $Pd_{67}Sn_{11}Te_{22}$ | 620 | | -16 |

* Vymazalová & Drábek (2010)

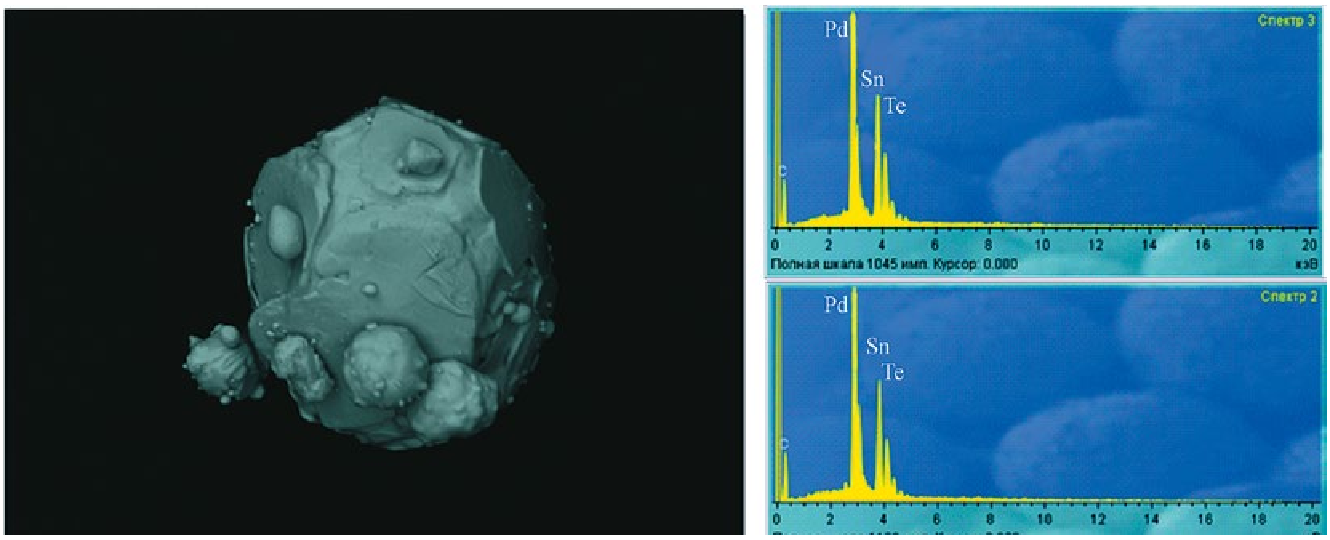

*Fig. 1.* Rounded grains and crystals of $Pd_{67}Sn_{11}Te_{22}$ (Spectra 1 and 3) are overgrowed by PdTe platelets (Spectra 2), (Run $Pd_{39}$, Table 1)

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# FRACTIONAL CRYSTALLIZATION OF THE MELT IN THE Cu-Fe-Ni-S-(Pt, Pd, Rh, Ir, Ru, Ag, Au, Te) SYSTEM IN THE REGION OF PENTLANDITE CRYSTALLIZATION

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**ABSTRACT**. The directed crystallization of the melt with composition (mol.%): Fe=18.5, Ni=19.1, Cu=16.7, S=44.1, Pt=Pd=Rh=Ir=Ru=Ag=Au=Te=0.2 was carried out and the distribution of the PGE, Ag, Au, and Te among the base sulfide minerals (BSM) and platinum group minerals (PGM) was studied.

It is generally agreed that the ore body of magmatic Ni-Cu-platinum-group element (PGE) deposits was formed by fractional crystallization of the sulfide magma. This hypothesis is consistent with their zonal structure and inhomogeneous distribution of components and impurities inside the zones. Pentlandite is one of the main PGE-bearing minerals in these ores.

The aim of this study was to establish the distribution of the PGE, Ag, Au, and Te among the base sulfide minerals (BSM) and platinum group minerals (PGM) at fractional crystallization of copper- and nickel-rich sulfide magma. The directed crystallization of the melt with composition (mol.%): Fe=18.5, Ni = 19.1, Cu=16.7, S=44.1, Pt=Pd=Rh=Ir=Ru=Ag=Au=Te=0.2 was carried out. Quartz ampoule with the melt was lowered from the hot zone of the furnace into cold one at the rate of $2.3\text{-}10^{-8}$ m/s. The cylindrical ingot with diameter of 8.2 mm and length 70 mm was divided into 12 portions which were studied by optical microscopy, SEM and EPMA. The mass fraction of the melt ($g$) was used as a coordinate of the process. The material balance equations were used to calculate the melt composition.

The sample consisted of the six zones with different chemical composition. For example, the distribution of Cu and Pd in solid and liquid is shown in Fig. 1A. There are jumpwise changes in the solid-sample composition between adjacent zones in consequence of the phase reaction with melt participation.

The sulfide assemblages is dominated by pentlandite (pn) and bornite (bn) with minor haycockite (hc), mooihoekite (mh), and monosulfide solid solution (mss) (Fig. 1 B). The majority of the BMS produced during cooling in consequence of their exsolution from the primary melt crystallized phases. The pentlandite composition is highly variable. It can be divided into two types: $(Ni,Fe)_9S_8$ – (Ni-pn) and $(Ni,Fe,Cu)_{11}S_9$ – (Cu-pn).

Precious metals behavior correlates with the chemical zoning of the sample (see Pd distribution in Fig. 1A). Impurities are concentrated in pn and mss. PGE impurities are presented in Ni-pn, but Cu-pn concentrates Pd only. The BMS matrix incorporarted includes of precious metal minerals: native Ag, $Pt_2Fe$, $RuS_2$, and alloys Au-Ag. Pd is also present as $Pd_2Te$. Both composite and solitary PGM inclusions are either located at grain boundaries (pn/bn) or within pentlandite and rarely in bornite. Distribution of PGM along the ingot corresponds to the primary zoning.

*Ruthenium, iridium.* The euhedral crystals of laurite $RuS_2$ with impurity of ~ 6 mol.% Ir, ~ 1 mol.% Pd and Rh are found in BSM of zone I (up to $g \sim 0.01$). Additionally, Ru and Ir are concentrated in Ni-pn (from 0.3 to 0.7 mol.%), mss (~ 0.4 mol.%) and $Pt_2Fe$ (Ru ~ 0.4 mol.% and Ir ~1.4 mol.%). *Rhodium.* Rh dissolves in Ni-pn (from 0.3 to 1.2 mol.%), mss (0.5 mol.%), $Pt_2Fe$ (1.4 mol.%), and in $RuS_2$.

*Platinum.* $Pt_2Fe$ forms crystal aggregates and zoned grains: $Pt_2Fe$/Au-Ag/Ag (from the center to the edge). Ru, Ir and Pd are concentrated in $Pt_2Fe$.

*Palladium.* Some amounts of Pd occur in solid solution within the BSM (Ni-pn, mss) and PGM (Au-Ag and $Pt_2Fe$). In addition, the drop-shaped inclusions of $Pd_2Te$ are found in Ni-pentlandite matrix in zone VI ($g > \sim 0.9$). A minor amount of Te (~ 0.1 mol.%) is present in solid solution within the Ni-pn, Ag and Au-Ag alloy.

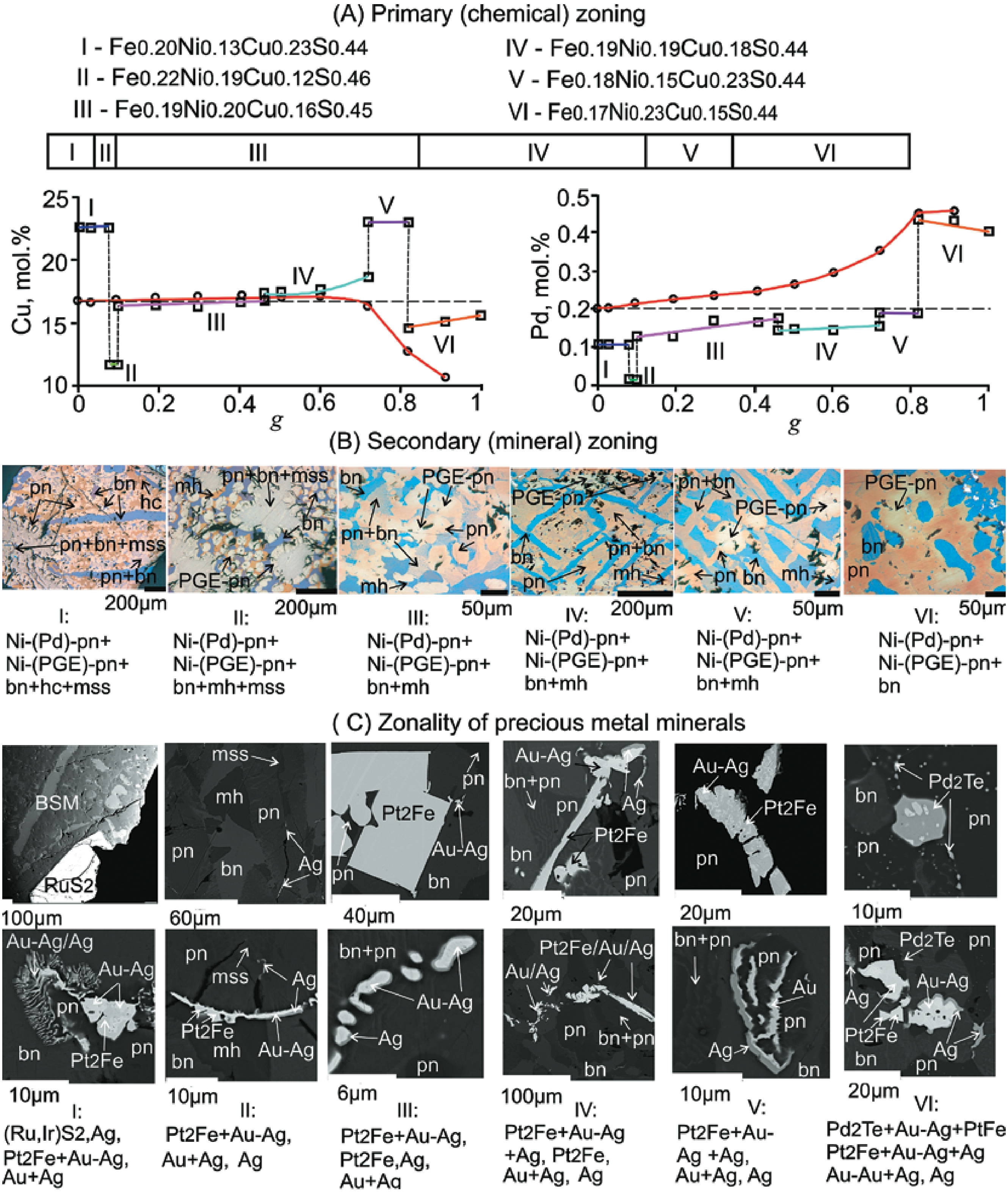

*Fig. 1.* The illustration of primary (A), secondary (B) and impurity (C) zonality of the experimental sample

*Silver.* Ag with an admixture of about 1mol.% Cu is present in solitary inclusions in the cracks of Ni-Pn and bn grains and it borders the Au-Ag and $Pt_2Fe$ grains.

*Gold.* Au dissolves up to ~ 10 mol.% Ag and other impurities (such as Cu, Pd) and associates with Ag and $Pt_2Fe$.

It should be noted that our data is generally consistent with the PGE behavior in traditional experiments and with the information on the phase composition of copper-nickel ores.

*Acknowledgments. This work was supported by the grant of RFBR 12-05-00099a and by the grant of the Branch Earth Sciences of RAS 2.*

# EXPERIMENTAL MODELING OF Ag, Au, Pd, and Pt BEHAVIOR IN HYDROTHERMAL SYSTEMS

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**ABSTRACT.** Behavior of noble metals (Ag, Au, Pd, and Pt) in hydrothermal systems, including their transport by hydrothermal fluids, and deposition with the formation of ores, is characterized using experimental data and analysis of noble metal concentrations in sulfides of some hydrothermal ore deposits. Solubility experiments demonstrate that PGE can be effectively transported by hydrothermal fluids in the form of chloride complexes, whereas the role of sulfide/hydrosulfide complexes of PGEs is limited to low-temperature (< 100 °C) sulfide-rich solutions. For deposits with Au-Te mineralization Te can contribute to transport of Au by high-temperature near-neutral to weakly acidic fluids due to the formation of Au-Te complexes, whereas at t < 400 °C calaverite ($AuTe_{2(cr)}$) controls the low-level activity of Te and Au in hydrothermal fluids. Analysis of "invisible" Au concentration in sulfides of VMS deposits shows that the distribution coefficient of Au between sulfides depends on the metamorphic grade (or temperature to which ores were heated during the formation of a deposit). The effect of temperature and sulfur fugacity on the concentration and distribution coefficients of "invisible" Au is modeled using experiments on the synthesis of Au-bearing sulfides in the Fe-S and Cu-S(±Fe) systems.

The solubility experiments have been performed using $Pd_{(cr)}$, $Pt_{(cr)}$, $PdS_{(cr)}$, and $PtS_{(cr)}$ at temperatures from 3 (for $PdS_{(cr)}$ and $PtS_{(cr)}$) to 475 °C (for pure metals) and pressures to 1 kbar.

The solubility of Pt and Pd sulfides is very low (0.01 – 0.1 ppb for Pt and 0.1 – 1 ppb for Pd at t < 100 °C, $pH_t$ from 2 to 7, and m(S) = 0.1). The solubility of $PdS_{(cr)}$ was found to decrease with increasing temperature, whereas preliminary $PtS_{(cr)}$ solubility experiments yield m(Pt) = ~ 1 ppb at 450 °C, 1 kbar and $m(H_2S) = 0.1$. The observed dependence of the solubility of Pd and Pt sulfides on pH is best described using $Pd(HS)_2$, $Pd(HS)_3^-$, and their Pt counterparts. These low concentrations of PGE hydrosulfide complexes suggest that their contribution to hydrothermal transport of these metals is insignificant and probably restricted to low temperatures. As follows from our experimental data, $PdCl_4^{2-}$, $PdCl_3^-$, and $PtCl_3^-$ are predominant complexes of these metals for geologic fluids. The concentration of these species in equilibrium with sulfides varies from a few tenths to a few ppb in near-neutral solutions and m(NaCl) = 1 at 450 °C, increases strongly towards acidic pH and higher chloride concentrations, and can reach ppm concentration level in moderately acidic solutions. A strong temperature dependence of the formation constants of Pd- and Pt-Cl complexes suggests that cooling of hydrothermal solutions, as well as their neutralization, are the most important factors that lead to the deposition of PGE.

In contrast to PGE, sulfur-bearing hydrothermal fluids can transport Ag and Au in the form of hydrosulfide complexes at $P\text{-}T\text{-}f(S_2)$ conditions typical of the formation of epithermal, VMS (volcanogenic massive sulfide), and porphyry deposits. In ores of these types of deposits, Ag and Au contents are strongly correlated with the concentrations of Se and Te. In order to evaluate the possible role of Se and Te in hydrothermal transport of Ag and Au, the solubility experiments of $Ag_2Se_{(cr)}$ (naumannite) and $AuTe_{2(cr)}$ (calaverite) in $H_2Se$- and $H_2Te$- bearing solutions have been conducted at 400 – 500 °C, P = 0.5 – 1 kbar. Based on these solubility data, the formation constants and thermodynamic functions were calculated for $AgHSe^{\circ}$, $AuHTe^{\circ}$, $Ag(HSe)_2^-$, and $Au(HTe)_2^-$. It was found that the naumannite solubility constants

$$0.5\ Ag_2Se + 0.5\ H_2Se = AgHSe^{\circ}_{(aq)}\ , \qquad (1)$$

and $$0.5\ Ag_2Se + 1.5\ H_2Se = Ag(HSe)_2^- + H^+ \qquad (2)$$

are close (at t > 150 °C) to the corresponding reaction constants in the Ag-H-S system. For example, log K(1) = -6.2 and -6.1 at 400 °C, 0.5 kbar for Se- and S- bearing systems, respectively, whereas for 200 °C, $P_{sat}$ log K(1) = -7.4 (Se) and -6.1 (S). The values of log K(2) are: -10.0 (Se) and -10.3 (S) for 400 °C, 0.5 kbar, and -9.6 (Se) and -9.3 (S) for 200 °C, $P_{sat}$. As the concentration of Se is much lower than that of S, it is reasonable to believe that Se can act only as a depositing agent for Ag. Conversely, the $Au_{(cr)}$ solubility constants with the formation of Au-HTe complexes is much higher than the equilibrium reaction constants for Au-HS species. For reactions

$$Au_{(cr)}+H_2Te_{(aq)}=AuHTe_{(aq)}+0.5\ H_{2(g)}\ , \quad (3)$$

and $$Au_{(cr)}+H_2Te_{(aq)}+HTe^{-}=Au(HTe)_2^{-}+0.5\ H_{2(g)} \quad (4)$$

the equilibrium constants are ~2 (reaction 3) to ~5 (reaction 4) log unit higher than those for analogous reactions in the Au-H-S system. This increase in the stability constants is generally in agreement with the hard-soft acid-base theory: the stability of aqueous complexes formed by a soft acid ($Au^{+}$) increases when the strength of the conjugate base decreases ($HS^{-}$-$HSe^{-}$-$HTe^{-}$). Thermodynamic calculations based upon the experimental data yield a concentration of AuHTe° ~n·10 ppb at 400 – 500 °C and $m(H_2Te) \sim 10^{-6}$. At lower temperatures calaverite crystallizes and controls the low-level activity of dissolved Te and Au at temperatures typical of the formation of epithermal Au deposits.

In order to elucidate the influence of temperature, the composition of the sulfide ores, and the fugacity of sulfur upon the concentration of "invisible" Au and its speciation, the concentration of Au in sulfides from various types of VMS deposits in the Ural region was determined using neutron activation and LA-ICPMS methods. It was found out that the concentration of Au disseminated in a host mineral matrix depends on the formation temperature of the ores. For low-temperature (weakly metamorphosed) ore deposits (t = 230 – 340 °C) the concentration of Au increases in the order: Bn ($Cu_5FeS_4$) < Cpy ($CuFeS_2$) < Sph (Zn,Fe)S < Py ($FeS_2$).

This trend in the "invisible" Au distribution coefficients is consistent with the composition of submarine hydrothermal ores. At the high-temperature (up to 600 °C) strongly metamorphosed Tarn'erskoe deposit, as well as for Cu-porphyry deposits (Kesler et al., 2002), the inverse order is observed: Py <~ Po (FeS) < Sph ~ Cpy < Bn < Cv (CuS), CC ($Cu_2S$). The observed distribution coefficients can be interpreted with the aid of laboratory synthesis experiments. Two types of experiments in the systems Fe-S and Cu-S (±Fe) were carried out: hydrothermal synthesis (400 – 475 °C), and salt-flux experiments (500 – 700 °C). The activity of Au was controlled by Au metal in both types of experiments. For pyrite ($FeS_2$), our experimental data demonstrated weak increase of Au content with increase of sulfur fugacity at 450 °C, 1 kbar (C(Au)pyrite ~ 40 – 80 ppm in the presence of Au(cr)) . At the same time, a temperature increase resulted in a drastic decrease in "invisible" Au content in pyrite, and at 700 °C C(Au) pyrite was below 100 ppb. This behavior implies the formation of submicron-sized Au particles that are disseminated within the volume of sulfide at 450 °C, but coalesce together with the formation of larger particles as the temperature increases. An opposite temperature effect was detected for Au concentration in digenite ($Cu_2$-xS): an increase in both temperature and $f(S_2)$ leads to an increase in the Au content in this mineral, which can reach n·Wt.% in sulfur-saturated system at 650 °C. Quench products of Au-bearing digenites exhibit exsolution textures with lamellae of native Au, and probably existed as a homogeneous solid solution at the experimental temperature. For covellite (CuS), an increase in temperature and $f(S_2)$ also leads to an increase in the "invisible" Au content. Au is homogeneously distributed within the mineral volume with a maximum C(Au)=0.25 Wt.%. X-ray photoelectron spectroscopy study of Au 4*f* core level indicates that no $Au_2S$-$Cu_2S$ solid solution is formed, but Au exists in the form of Au or $Au_2S$ nano-sized particles. We believe that this approach can be extended to the study of PGE speciation in sulfide minerals of magmatic and hydrothermal origin.

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# EXPERIMETAL STUDY OF SILVER-PALLADIUM SULPHIDES

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ABSTRACT. The phase equilibria in the system Ag-Pd-S were studied by the evacuated-silica glass tube method at 400 and 550°C. In the system we synthesized three new ternary phases: $Ag_2PdS$, $Ag_2Pd_3S$ and $Ag_3Pd_{13}S_4$.

The Ag-Pd-S system comprises three minerals (vysotskite, vasilite and acanthite). Five binary phases are known from the system Pd-S and one in the Ag-S system. In order to better understand the formation of minerals belonging to this system at natural conditions, predict possible new minerals and determine stable phase associations, the Ag-Pd-S ternary system has been investigated at two temperature intervals. The Ag-Pd-S system has been studied at the temperatures of 400 and 550°C. The evacuated silica glass tube technique was used for the purpose of this study. The experimental products were investigated in terms of reflected light, electron microprobe and X-ray diffraction techniques.

The binary systems have been summarized by Matkovic et al. (1976) the system Pd-S, Karakaya & Thompson (1988) the system Ag-Pd, and the system Ag-S by Sharma & Chang (1986). The experimental results proved that the thermal stability of binary phases is in agreement with the data proposed by Matkovic et al. (1976) for the Pd-S system, and Sharma & Chang (1986) for the Ag-S system. All the binary phases have been investigated in terms of solubility of the third component. Binary palladium sulphides do not dissolve Ag.

The experimental study revealed the existence of three new ternary phases in the Ag-Pd-S system, the $Ag_2PdS$, $Ag_2Pd_3S$ and $Ag_3Pd_{13}S_4$. Crystal structures of the phases were investigated. The ternary phase $Ag_2PdS$ is orthorhombic, space group *Cmcm*, $a$ = 7.9835(1) Å, b=5.9265(1) Å and c=5.7451(1) Å. The phase $Ag_2Pd_3S$ is cubic, space group $P4_132$, $a$ = 7.2389(3) Å. The crystal structure of the phase $Ag_3Pd_{13}S_4$ has not been determined yet, preliminarily investigations suggest trigonal symmetry.

The phase $Ag_2PdS$ was observed in nature in Norilsk ores by Sluzhenikin (2010), therefore it can be expected to be described as a new mineral species. New ternary phases ($Ag_2PdS$, $Ag_2Pd_3S$ and $Ag_3Pd_{13}S_4$) determined in this study can be expected to be found in nature, likely in association with palladium sulphides or other PGM.

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# SESSION 7

## New advances in the understanding of PGE mineralogy from magmatic to supergene environments

**Conveners: Tanya Evstigneeva & Federica Zaccarini**

The platinum-group elements (PGE) form specific phases, the so called platinum group minerals (PGM) or they occur in solid solution, as trace and ultra-trace elements, mainly in sulfide and oxides. With few exceptions, the PGM form minute inclusions, generally less than 50 microns in size. Thus, their identification and characterization is a difficult target. It is also not easy to determine the amount of PGE occurring in solid solution because of their low concentration. Recently, the development of advanced methodology and scientific methods allow us to better characterize the PGM as well as to detect the PGE at very low concentration at the scale of ppm or ppb using in-situ techniques. Contributions that describe the latest in analytical methods and applications to PGE mineralogical study, including LA-ICPMS, PIXE, XRD, EPMA, SEM are welcome. Abstracts discussing other techniques are also strongly encouraged.

# TRACE ELEMENT DISTRIBUTION IN PYRITE FROM THE LEVACK MINE (SUDBURY, CANADA): INSIGHT INTO THE PROCESSES AFFECTING PGE

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**ABSTRACT.** We used detailed LA-ICP-MS trace element mapping to characterize the trace element distribution in sulfide assemblages from the Levack Mine. In contrast to the zoning documented in Dare et al. (2011) and Piña et al. (2013), the trace element distribution patterns of the pyrite grains from Levack are not amenable to interpretation by a single process and likely reflect distinct stages of growth.

Trace element distribution maps of pyrrhotite-pentlandite-chalcopyrite-pyrite-magnetite assemblages from the Levack Mine (Sudbury, Canada) revealed complex trace element patterns in the distribution of Co, Se, As, Te, Bi, and PGE within pyrite. This complex zoning indicates multiple growth stages, characterized by: (a) successive Se, As, and Co zones, (b) faint rims of Te and Bi marking the edges of grains that annealed to form the euhedral pyrite grains, (c) decoupling of Ru, Rh, Os, Ir from Pt, Au, and Pd. Experimental studies have shown that pyrite can form by cooling of an immiscible sulfide liquid (if the sulfur fugacity of the system, or the S to total metal ratio, is sufficiently high) and some natural pyrite (particularly Co-rich pyrite) may be of magmatic origin. However, the complex patterns observed in the pyrite grains from the Levack Mine are difficult to reconcile with a simple origin for pyrite and likely record multiple growth stages and probably multiple processes affecting the behavior of PGE and the metalloids. Better understanding of the origin of such complex patterns in Sudbury and elsewhere may render pyrite into a useful tool to decipher ore formation processes for Cu-Ni-PGE deposits.

The complex Co zoning patterns in pyrite (py) from Sudbury ores were first documented by Craig and Solberg (1999). They described such patterns as a result of variations in Co availability during growth but did not expand on the possible origin of it. Piña et al. (2012, 2013) documented the occurrence of unusual zoning in metalloids and PGE in euhedral Co-rich pyrite in Ni-Cu sulfide assemblages of the Aguablanca deposit (Spain). Piña et al. (2013, p. 241) interpreted those py as being a “late magmatic/hydrothermal… replacement of pyrrhotite and plagioclase by pyrite”. Dare et al. (2011) also documented euhedral py enriched in IPGE in sulfide assemblages from the McCreedy East deposit (Sudbury, Canada) and interpreted those as forming via exsolution from monosulfide solid solution (MSS). This is consistent with experimental studies (e.g. Craig, 1973) showing that pyrite forms from a sulfide melt if the sulfur content is sufficiently high. However, the relative timing of py and pentlandite (pn) formation is complex (Dare et al., 2011). We used detailed LA-ICP-MS trace element mapping to characterize the trace element distribution in sulfide assemblages from the Levack Mine and also found that euhedral py also displayed complex trace element zoning patterns (Fig. 1). However, in contrast to the zoning documented in Dare et al. (2011) and Piña et al. (2013), the trace element distribution patterns of the py grains from Levack are not amenable to interpretation by a single process and likely reflect distinct stages of growth.

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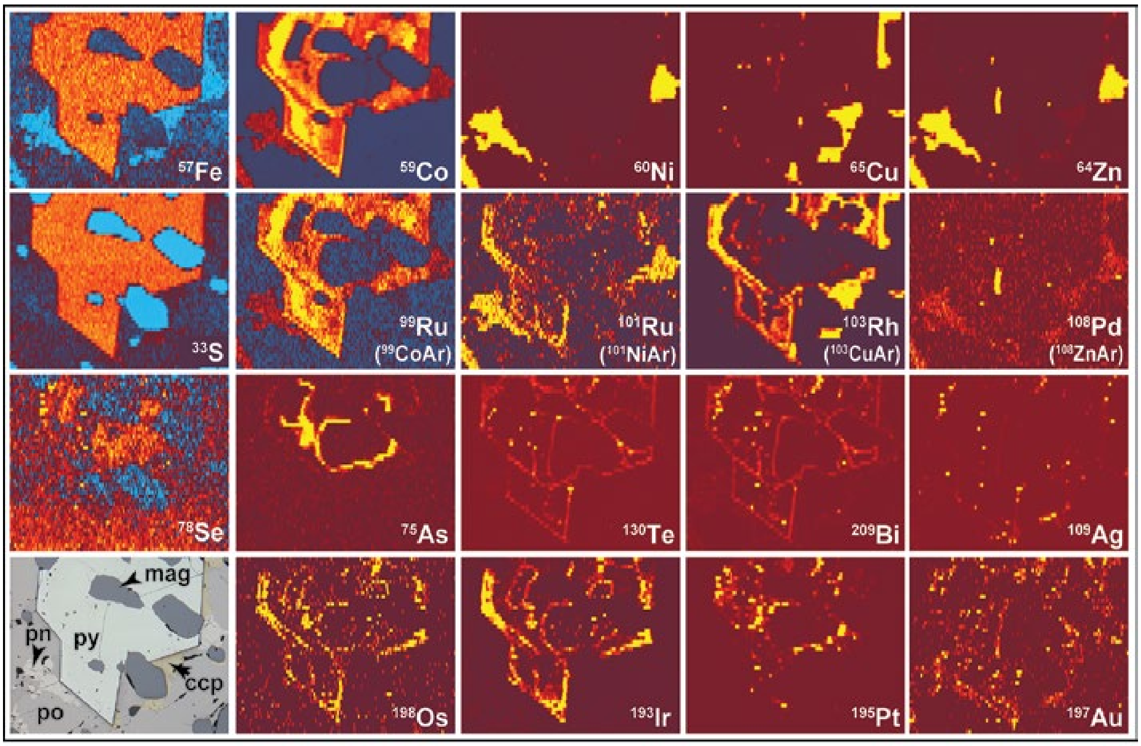

*Fig. 1.* Trace element distribution maps of a pyrrhotite-pentlandite-chalcopyrite-pyrite-magnetite assemblage from the Levack mine (Sudbury, Canada). The map is centered on the pyrite grain to show the complex trace element patterns. A reflected light image (bottom left) is provided for reference. The euhedral pyrite grain (py; lighter grey) is about 0.5 mm wide. Anhedral magnetite grains (mag; darker grey) are enclosed and also outside py. Pyrrhotite (po; intermediate gray) is the most abundant sulfide in the sample and accounts for most of the groundmass. Chalcopyrite (ccp; yellow) and pentlandite grains (pn, lighter grey than po) were also present in the mapped area. The trace element distribution maps are color coded by relative intensity (in counts per second) with yellow as the maximum counts for each isotope. The lowest counts are shown in light blue for major elements and in red to purple-red in trace element maps. For example, the orange and light blue areas in the S map correspond to py and mag, respectively. First-row transition metals and PGE are arranged relative to each other as in the periodic table. The light PGE (Ru, Rh, Pd) maps are shown under the maps of the elements that caused most interference (to track argide interferences more easily). The Ni and Cu maps clearly show the location of pn and ccp respectively. The first aspect to highlight is the complex Co zoning, which is characterized by three areas with no detectable Co that do not correspond to the location of magnetite (cf. Fe and Co maps and reference image); those rounded and anhedral areas correspond to "cores" that have higher Se content. The Se-rich cores are partially surrounded by a relatively narrow rim of high As after which the complex Co zoning starts. The most significant aspects regarding PGE distribution pertains the distribution of Ru, Rh, Os, and Ir but some aspects of isotopic interference need to be explained as well: the perfect match between the $^{59}$Co map and the $^{99}$Ru maps clearly indicate that the signal for mass 99 is dominated by $^{59}$CoAr isotopic interference. However, comparison of the $^{60}$Ni and $^{101}$Ru shows that the $^{101}$Ru distribution in py is a real signal from Ru (the same applies to the $^{103}$Rh in py). These four elements seem to be concentrated inside the py grain along specific Co zones. Osmium and Ir are not affected by any interference and show the distribution of these elements in py (which is slightly different than the distribution of Ru and Rh). Platinum does not coincide with the distribution of the Ru, Rh, Os, and Ir and seems to avoid the outer edge but it matches at least some of the As distribution. Palladium was mostly below detection (the signal shown for mass 108 likely corresponds to a $^{108}$ZnAr interference; the $^{105}$Pd map, which is affected by $^{65}$Cu-argide interference, but is not shown, validates this). Gold was the only highly siderophile element to show distribution outside pyrite; although it avoids the Se-rich core in py (and all the po) it shows no apparent preference among py, pn, and ccp but seems to be present mostly as nuggets invisible during reflected light (and SEM) petrography. Finally, the Te and Bi distribution has two components: thin, faint lines likely marking sub-grain domains and bright dots that are likely Bi-Te-PGM

# NEW DATA ON THE COMPOSITION OF SULFIDES AND TELLURIDES IN RUDNY INTRUSION (NW MONGOLIA)

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**ABSTRACT**. Previously two horizons (Lower and Upper) of sulfide globules (or droplets, inclusions) containing rich PGE mineralization in Rudny intrusion were detected. This year, we found the new zone of sulfide-bearing rocks that differ in appearance from those studied earlier. Compositions of base metal sulfide and PGE minerals were investigated. As to PGE mineralization the new zone is very similar to Lower horizon of sulfide globules since Ag-Sn minerals characteristic for the Upper horizon are absent in the new zone.

Intrusion Rudny is located in the southeastern part of Tsagaan-Shuvuut Mountains, NW Mongolia. This one, like many other small gabbroic intrusions in this area, is confined to periphery of Tuva depression. Earlier the ore zone consisting of melanocratic olivine gabbro with sulfide globules (droplets) up to 3 cm in size was described in the structure of the intrusion. Two different horizons, Upper and Lower, with different shapes of globules and PGE mineralization have been identified in this ore-bearing zone (Vishnevskiy et al., 2013). At least eight Ag- and PGE- phases have been described in polished sections. Among them there are three Sn- containing phases – paolovite – $Pd_2Sn$, taimyrite – $(Pd, Cu, Pt)_3Sn$ and stannotelluride Pt. Also there are three Ag-phases – hessite – $Ag_2Te$, sopcheite – $Ag_4Pd_3Te_4$, telargpalite – $(Pd, Ag)_3Te$. Primary PGE phase found in both horizons are minerals of moncheite – merenskyite – melonite group. They represent more than half of the investigated grains. The relatively rare Ag- and Sn-containing phases were found only in the Upper horizon (Cherdantseva & Vishnevskiy, 2013). Using SEM Tescan Mira 3 with energy dispersive spectrometer Oxford X-Max 80 about 180 grains of moncheite group minerals have been analyzed. Largest of these grains with significantly varying the ratio Ni:Pd:Pt were re-analyzed by Camebax Micro electron microprobe to compare the convergence of these two analytical methods. Conditions of microprobe analysis – the acceleration voltage 20 kV, probe current 40 nA, counting time 10 sec. for each analytical line; standards used: FeS – for Fe and S, FeNiCo – for Ni and Co, CuFeS – for Cu, $SnO_2$ – for Sn, pure Pt, Pd, Rh, Ag, Te and Bi for the respective elements. Generally the calculated deviation for both PGE and for base metals is comparable with the errors, and is not more than 3% for elements with concentration > 10 at.%, but is not more than 10% for the concentration < 10 at.%. Based on these data SEM with new series of EDS can be used not only to express mineral diagnostics, but also to general mineral composition study of PGE minerals.

Last year new area of sulfide-bearing rocks was found in the Rudny intrusion ore zone. It is represented by leucocratic trachytoid olivine gabbro with tiny spherical sulfide globules (up to 3 mm in diameter). In connection with the remote spatial position it was interesting to compare the compositions of the main sulfides and PGE minerals with data obtained previously for large sulfide globules. The structure of sulfide globules from all three types of sulfide-bearing rocks is similar. As in Norilsk deposit disseminated ores all sulfide globules are differentiated from the bottom to the top: the main sulfide – pyrrhotite occurs in the bottom, pentlandite is observed in the centre, and chalcopyrite and cubanite are dominated at the top. PGE mineralization of area with small spherical droplets is similar to that of Lower horizon, i.e. it is represented by rare homogeneous grains of moncheite group minerals. But, additionally, several small grains of gold, and very small (about 1 µm) grain of rhenium phase were diagnosted (due to the size it was not possible to analyze it correctly). Compositions

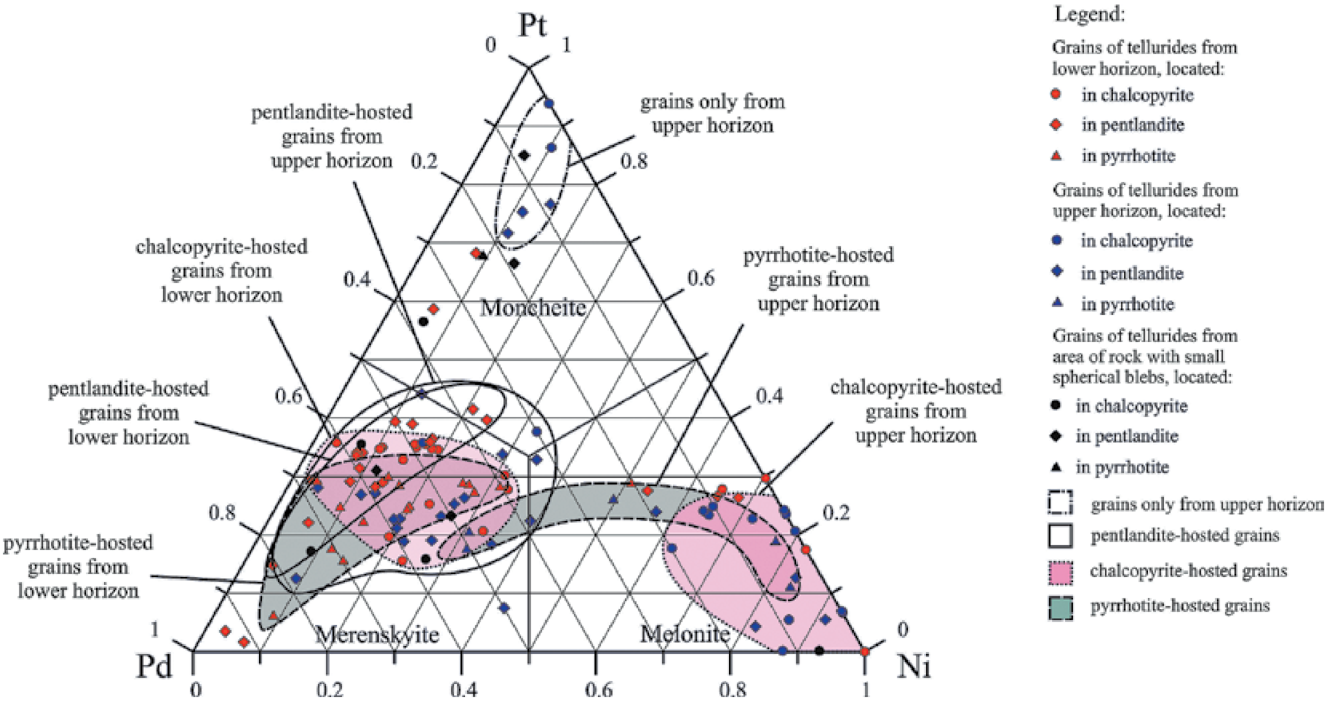

*Fig. 1.* Compositions (atomic proportions) of Pd, Pt, Ni bismuthotellurides from lower, upper horizons and from rock sector with small spherical sulfide blebs

of tellurides from all ore zones studied are plotted on the ternary diagram Ni-Pt-Pd (Fig.1) to compare with those of Upper and Lower horizons. The comparison confirmed the results obtained earlier. The chalcopyrite-hosted tellurides are located in two compositional fields: minerals from Upper horizon are nickel-rich and those from Lower horizon – are significantly richer in palladium. Compositions of tellurides included in chalcopyrite from new area with tiny sulfide globules are observed in both fields. Also some platinum-rich grains were found in pentlandite from new zone. Earlier platinum-rich phases were described only in chalcopyrite and pentlandite from Upper horizon.

Based on ICP-MS and ICP-OES analyses it was showed that regardless of the occurrence of different PGE phases, the whole-rock composition of three types of sulfide-bearing rocks (melanocratic gabbro of Upper and Lower ore horizons, leucocratic gabbro with small sulfide globules) in principle is the same. The only difference in concentration level for most metals directly depends on the content of sulfides in the rock (S content was determined by IR spectroscopy). The composition recalculation on 100 percent of sulfide (tenor) shows that our samples are characterized by relatively high Pd/Pt ratio (about 4-5) and Ni/Cu (about 1.5) ratios. These values are comparable with Pd/Pt ratio in some sulfide globules from typical Cu-Ni deposits, such as Norilsk and Sudbury.

*Acknowledgements. The study is supported by the IGCP № 592 "Continental construction in Central Asia and RFBR grants 13-05-01132, 13-05-00951 and 12-05-00435.*

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# SULFIDE-RICH PODS FROM THE LAC-DES-ILES Pd-ORE DEPOSITS, WESTERN ONTARIO, CANADA: PART 2. THE ORIGIN OF PLATINUM-GROUP ELEMENTS-BEARING PYRITES

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**ABSTRACT**. Pyrite from Lac-des-Iles sulfide-rich pods host substantial amounts of platinum-group elements (PGE). In this contribution we discuss the origin of pyrite and their PGE content.

Recent studies have shown that pyrite (Py) may be a significant host for PGE in magmatic Ni-Cu-PGE deposits (Oberthür et al., 1997; Dare et al., 2011; Djon and Barnes, 2012; Piña et al., 2012, 2013). Although common, Py is usually an accessory phase in these deposits. Consequently very little attention has been paid to processes controlling the distribution of PGE into Py which may form over a wide range of conditions (i.e. exsolution from monosulfide solid solution (MSS) to hydrothermal precipitation). The Mine Block intrusion that hosts the Lac-des-Iles Pd ore deposits also hosts occasional sulfide-rich pods which are unusual in that many of them are extensively enriched in Py. Despite the presence of significant amount of Py in most of our samples, we have interpreted the sulfide-rich pods to have formed by accumulation of MSS separating from fractionating sulfide liquids in equilibrium with surrounding silicate magma (Duran et al., 2014). In order to account for the excess of Py we suggested a model whereby formation of Py was promoted by modifications of MSS (i.e. Fe-loss during alteration). Therefore sulfide-rich pods from Lac-des-Iles provide ideal material to investigate processes that might affect MSS. Thus, to assess the role played by Py as a carrier of PGE and to consider the processes involved in its formation, we have determined by LA-ICP-MS the concentrations of PGE and chalcophile elements in pyrrhotite (Po), pentlandite (Pn) and Py from Lac-des-Iles sulfide-rich pods.

When comparing the distribution of PGE and chalcophile elements between Po and Py (Fig. 1a),

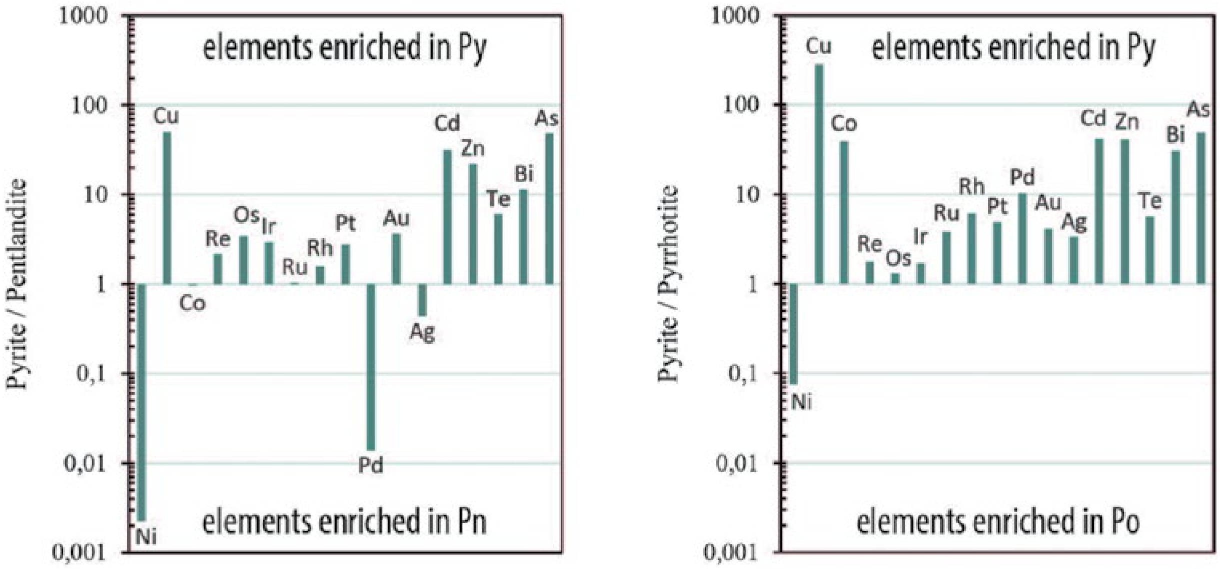

*Fig. 1.* Histograms showing the mean trace element contents in Py (n=57) vs. (a) co-existing Po (n=37); (b) co-existing Pn (n=57)

Re, IPGE (Os, Ir, Ru), Rh, Pt, Au, Ag and Te show a slight (< 1 order of magnitude) preference for Py over Po whereas Cu, Zn, Co, Pd, As, Cd, Sn, Sb, Pb and Bi show a considerable (> 1 order of magnitude) preference for Py over Po. Only Ni shows a preference for Po over Py. A similar distribution is observed between Pn and Py except that Pd and Ag are enriched in Pn instead of Py and Co is equally distributed (Fig. 1b). Considering that IPGE+Rh are immobile elements, their presence in Py could not have resulted from hydrothermal introduction and is more likely to be inherited from MSS or Po and Pn which exsolved from MSS. Furthermore Pt, Pd and Au which are the most soluble elements and which are incompatible with MSS are not significantly enriched in Py. On a primitive mantle normalized basis, Py display similar Re, Os and Ir patterns to co-existing Po (Fig. 2). Assuming that Py might replace Po, it is reasonable to argue that Py inherited Re, Os and Ir contents from Po. On the other hand Po is not a significant host for Co, Ru and Rh, and yet Py is much more enriched in these elements (Fig. 2). Therefore Co and some of Ru and Rh in Py cannot be inherited from Po. Pentlandite however hosts significant amount of Co, Ru and Rh and display similar primitive mantle normalized profiles to Py for these elements (Fig. 2). Nonetheless Py does not host significant amount of Ni and any Ni sulfides have not been observed, therefore Py could not have extensively replaced Pn. As a result we suggest that Py formed while Pn was exsolving in order to promote competition of Co, Ru and Rh between Py and Pn.

Based on the distribution of PGE and chalcophile elements among Po, Pn and Py, 2 models may be considered for the origin of Py during alteration: (1) Fe diffused out from Po while Pn was still exsolving from MSS. Therefore Py replaced Po and inherited its Re, Os and Ir contents and allowed Co, Ru and Rh to choose between Pn and Py (2) Fe diffused out from MSS prior or during Po and Pn exsolution, thus forming a S-rich MSS and allowing exsolution of important amounts of Py. At this point we do not favour a particular model but in both cases the formation of Py was likely promoted by alteration of MSS/Po during exsolution of Pn, thus providing a new host to compete for Co, IPGE and Rh.

*Acknowledgements. We are grateful to North American Palladium for funding this project via the Canada Research Chair in Magmatic Ore Deposits.*

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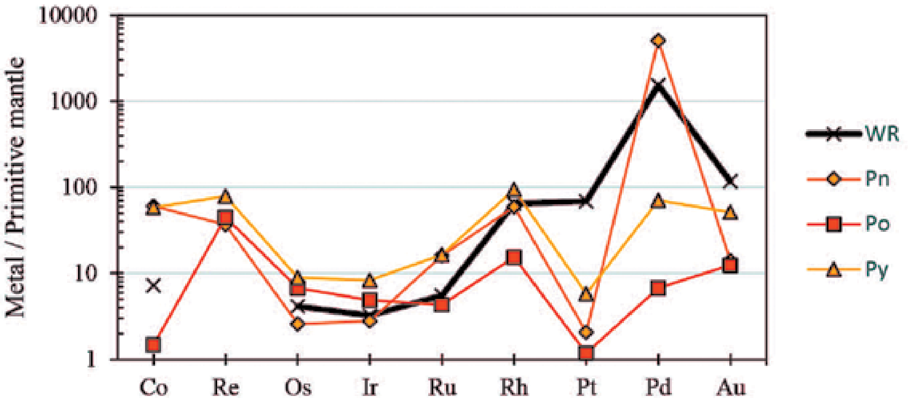

*Fig. 2.* Primitive mantle normalized metal profiles for Po, Pn and Py and whole rock (WR)

# MINERALOGICAL RESIDENCE OF PLATINUM GROUP ELEMENTS (PGE) IN THE MAGMATIC Ni-Fe-Cu SULFIDE DEPOSITS OF THE IVREA VERBANO ZONE (WESTERN ALPS, ITALY)

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**ABSTRACT**. We determined by electron microprobe the concentration of platinum group elements (PGE), Re, Te, As, Bi and the presence of specific platinum group minerals (PGM) in base metals sulfides (BMS) from Ni-Fe-Cu deposits of the Ivrea Verbano Zone, Italy. Our mineralogical observations suggest that the PGE together with other chalcogens were initially dissolved and collected by an immiscible sulfide liquid. Subsequently, they were exsolved along with Te and As to crystallize the discrete PGM described in the investigated samples. Rheniite was found only in the deposit that occurs in contact with metasediments. Therefore, it is argued that its precipitation is directly related to a contamination process from the country rocks.

The Ivrea Verbano Zone in the Western Alps of Italy represents a 120 km long and 15 km thick, section across the deep root of the Adria continental plate. It consists of a mantle plume (mainly lherzolite), and igneous mafic-ultramafic rocks (the Basic Complex) intruding a sequence of granulitic metasediments and metavolcanics (the Kinzigitic series). Magmatic Ni-Fe-Cu sulfide deposits occur in the Basic complex associated with:

1) peridotite and pyroxenite layers in fractionation *Cyclic Units* of the Basic Complex,

2) pyroxenite layers at the base of the *Main Gabbro* unit,

3) a 5 km long, layered *Ultramafic Sill* emplaced in metasediments,

4) cross-cutting *Ultramafic Pipes* characterized by alkaline geochemical signature. The deposits are believed to have formed by magmatic segregation and accumulation of an immiscible sulphide liquid which crystallized, generating a pyrrhotite-pentlandite-chalcopyrite-pyrite assemblage by on-cooling equilibration of the initial MSS±ISS.

Previous works have demonstrated that the immiscible sulphide liquid acted as a collector for the platinum-group-elements (PGE) with remarkable prevalence of Pd and Pt, carried in a suite of specific minerals (PGM). More than 250 PGM grains, varying in size from less than 15 µm (79%) up to 40 µm (21%), have been found included in the sulphide minerals. The abundance of PGM inclusions decreases from pyrrhotite (~60%), to pentlandite (~20%), chalcopyrite (~13%), and pyrite (~7%), but shows inverse correlation with the modal abundance of the sulphide host. The PGM assemblage is dominated by PGE tellurides (73%) showing variable degree of solid solution among merenskyite ($PdTe_2$), moncheite ($PtTe_2$), and melonite ($NiTe_2$). They are accompanied by other tellurides, hessite ($Ag_2Te$), altaite (PbTe), and tellurobismuthite ($Bi_2Te_3$), PGE arsenides and sulpharsenides ($PtAs_2$, sperrylite, IrAsS, irarsite) and Au-Ag alloys. A Re-S compound, having the composition of rhenite ($ReS_2$), was found in one deposit representing the first discovery of this rare mineral in the Ivrea Verbano Zone. The six PGE together with Re, As, Bi, and Te were quantitatively determined yielding the following detection limits (ppm):
Os(Lα)=81, Ir(Lα)=100, Ru(Lα)=35,
Rh(Lα)=32, Pt(Lα)=93, Pd(Lα)=30, Re(Mα)=78,
As(Lα)=194, Bi(Mα)=465, and Te(Lα)=100.

The use of the Mα-line was possible for Re, but not for Os because of the extremely weak and floating signal. As a consequence, the interference of Cu on Os could not be avoided in the analysis of chalcopyrite. A strong, unpredicted interference by Ni on Te was also observed in the analyses of pentlandite. In all the cases, Ru and Bi were systematically below detection limit, whereas 31.9% of the analyses were found to contain As, 11.5% Os, 31.7% Ir, 20.6% Rh, 27.5% Pt, 38% Pd, 11.4% Re, and 7.9% Te. The total amount of PGE is relatively higher in pentlandite (639 ppm) and pyrrhotite (606 ppm), and decreases in pyrite (519 ppm) and chalcopyrite (176 ppm). Distribution of the analyzed elements in the four sulphide minerals indicates that Os was detected only in pyrrhotite and pentlandite with maximum concentration in the deposits of the Cyclic Units). Iridium and Pt are carried in pentlandite, pyrrhotite, and pyrite, but are absent or below detection limit in chalcopyrite. The highest concentrations are found in the Main Gabbro, and the Ultramafic pipes. Palladium and Rh occur in all the sulphide minerals, however, Pd is mainly hosted by chalcopyrite of the Cyclic Units, while the highest Rh concentration is observed in pyrite of the Main Gabbro. Rhenium is particularly abundant in chalcopyrite and pyrite of the Ultramafic Pipes, and it shows a marked positive anomaly in the pyrrhotite of the Cyclic Units. Surprisingly, the lowest Re concentration is observed in pyrrhotite of the Ultramafic Sill, where the Re-sulphide was encountered. The relatively higher abundance of Pd, Re, and Te in chalcopyrite compared with the other sulphide minerals may indicate that these elements possibly concentrated in a late stage of the MSS±ISS crystallization. The lack of correlation between the abundance of PGE and Te in the analyses of the major sulphides suggests that the spot PGE anomalies are not due to the interception of PGM tellurides under surface. The PGE anomalies rather reflect the erratic occurrence of PGE and Te atomic clusters irregularly incorporated in the base metal sulphides. The bulk Pd/Ir ratio increases from the Ultramafic sill (0.38) to the Ultramafic Pipes (0.46), the Main Gabbro (0.54) and the Cyclic Units (0.57). These values are broadly consistent with relative variations of the Pd/Ir ratios of the deposits deduced from bulk PGE in the sulphide ore, except for the Main Gabbro that shows higher values. If the Pd/Ir can be assumed as a differentiation index, present data would indicate that the parental melt of the Ultramafic sill and the Ultramafic Pipes deposits were more primitive with respect to those parent to sulphide ores in the Cyclic Units. Our mineralogical observations suggest that the PGE together with other chalcogens were initially dissolved and collected by an immiscible sulfide liquid, most likely as small clusters. Subsequently, they were exsolved along with Te and As to crystallize the discrete

PGM described in the investigated samples. Rheniite was found only in the deposit that occurs in contact with metasediments. Therefore, it is argued that its precipitation is directly related to a contamination process from the country rocks.

# DIVERSITY OF PGM ASSEMBLAGES IN PGE DEPOSITS OF THE MONCHEGORSK IGNEOUS COMPLEX, RUSSIA

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**ABSTRACT**. We discuss a cause of different styles of PGE-Ni-Cu mineralization in the Monchegorsk igneous complex (MIC): a poor variety of PGM in PGE-Ni-Cu sulfide ores in the Monchepluton (including only Pt-Pd- bismuthtellurides with very scarce presence of some another PGM species) and a large variety of PGM species in low-sulfide deposits of the Vuruchuaivench, South Sopcha and Monchetundra intrusions. We suggest that PGM assemblages of low-sulfide deposits is a consequences of their derivation from residual As-, Sb-, Se-, Te-bearing sulfide melts. Primary PGM are represented by Pt- and Pd-sulfides, arsenides and bismutotellurides, and may be replaced by secondary PGM, which were formed via hydrothermal alteration of primary sulfide and silicate minerals by magmatically-derived fluids, and then by hydrotermal and supergene processes.

The early Paleoproterozoic layered intrusions of the Monchegorsk Igneous Complex – Monchetundra, South Sopcha and Vuruchuaivench, are located within the southern inner part of the Pechenga–Imandra-Varzuga rift-transform system. The MIC intruded Archean gneisses of the Kola-Belomorian series, and was overlain by volcanics and clastics of Paleoproterozoic Imandra-Varzuga Series. Some new data were obtained concerning diversity and evolution of PGM assemblages from low-sulfide PGE deposits in the Monchetundra, South Sopcha and Vuruchuaivench intrusions. We found that primary PGM experienced a wide range of isomorphic substitutions, and secondary PGM are characterized by abundance of low-sized undefined species.

The recently approved reef-type Vuruchuaivench deposit is composed of stratified taxitic quartz-bearing gabbronorite. The most common PGM are sperrylite and minerals of Pd-Te-Bi, Pd-(Ni)-As-(Sb) systems, with minor braggite, thornroosite, and some other PGM. PGM locate usually within or on the contacts of chalcopyrite with Ca-amphiboles, more rarely within other BMS. Sperrylite (Fig. 1a) and oval or bubble droplets of Pd-As (±Ni, Sb) intergrowths (Fig. 1b) apparently formed as a result of immiscibility arsenide and copper-rich sulfide melts, like it was found in experiments of Helmy et al. (2013).

The same PGM assemblages in PGE occurrences along the Monchetundra fault zone show the best example of PGM evolution in graded settings: from magmatic one through hydrothermal to supergene. Fractured sperrylite was replaced along fissures by orcelite, Pd-bearing orcelite, $Ni_6Pd_2As_3$ and late Cu-Pt-Pd alloys (Fig. 1c). Pd-As (±Ni, Sb, Te) intergrowths substituted by micrograins of undetermined PGM (Fig. 1d).

PGM association from pegmatoid pyroxenite of the South Sopcha deposit consists of minerals of Pd-Te-As, Pt-Te-Bi, Pd-Sb-As, Pd-Ni-As, Pd-Pb-(±Se) systems. Primary PGM assemblages from brecciated gabbro of the South Sopcha massif were altered by metasomatic processes to later Pd-tellurides and PGE-Co-Ni-Fe sulfarsenides.

Composition of the PGM assemblages within PGE-bearing bodies strongly varies depending on host lithology and both fluid and hydrothermal processes. Thus, primary PGM assemblage from reef-like low-grade PGE-occurrences seems to be a result of magmatic crystallization and intercumulus fluid-hydrothermal activity. Subsequent fluid-hydrothermal and tectonic processes gave rise to a multistage modification of PGM associations.

In consideration of close association between primary PGM and BMS in low-sulfide deposits of MIC, we believe to be more likely, that the source of As, Sb, and Se was a mantle melt, enriched by crustal material – by analogy with source of sulfur (Bekker et al, this volume), than hydrothermal influxes of As and Sb from overlain volcano-sedimentary rocks as previously suggested.

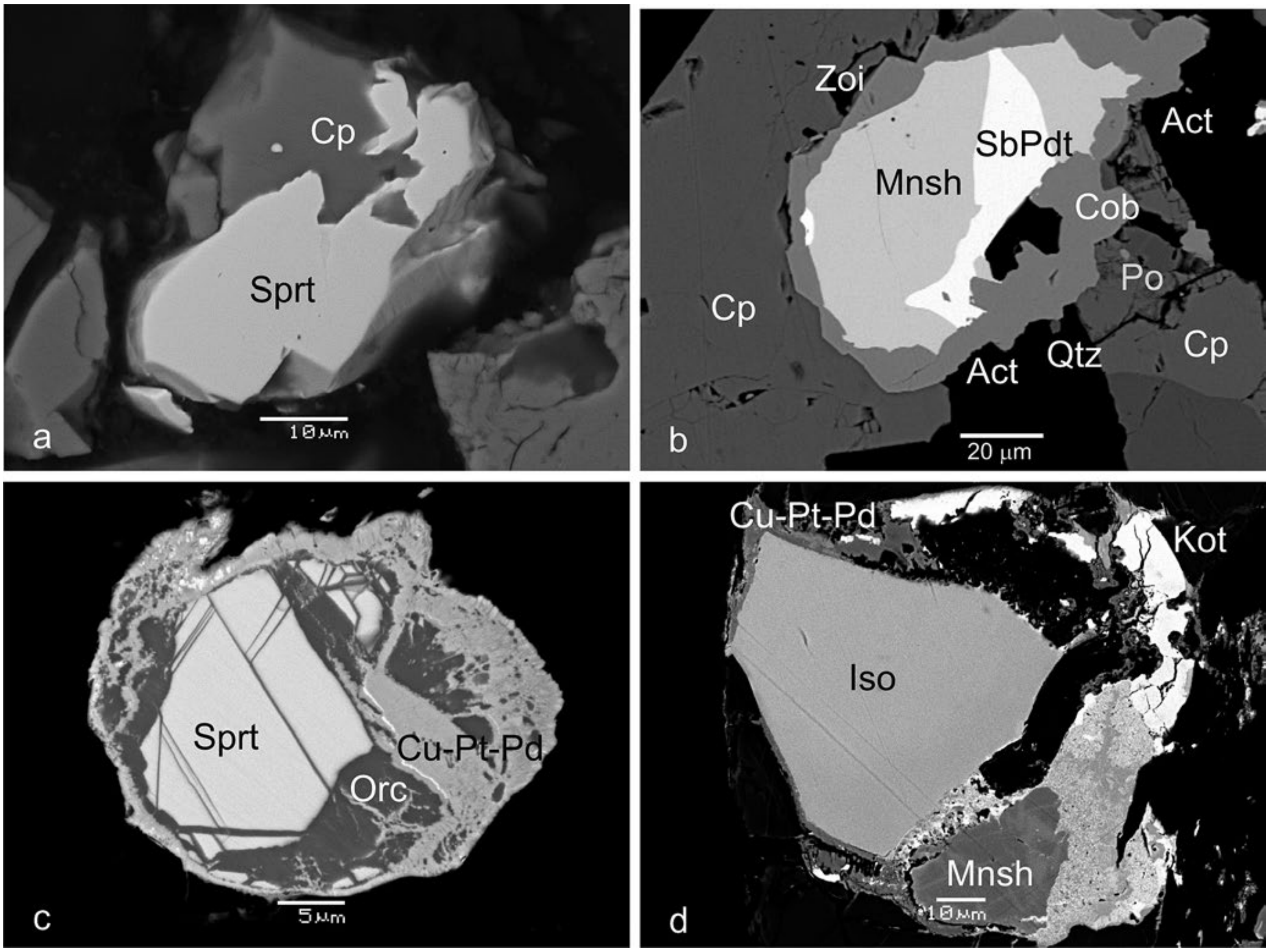

*Fig. 1.* Backscattered electron images of PGM from the Vuruchuaivench (a, b) and Monchetundra (c, d) PGE deposits of MIC: a – sperrylite (Sprt) in chalcopyrite (Cp); b – droplet-like intergrowth of menshikovite (Mnsh) and stibiopalladinite (SbPdt), replaced by Ni-cobaltite in chalcopyrite (Cp) and pyrrhotite (Po), hosted by actinolite (Act), zoizite (Zoi), and quartz (Qtz); c – fractured sperrylite, replaced by orcelite (Orc) with tiny inclusions of Pd-bearing orcelite, $Cu_3Pt$, and nielsenite (Nls); d – kotulskite (kot), isomertieite (Iso) and menshikovite, replaced by tiny intergrowths of uncertain Pd-Ni-Te-Pb-Bi minerals (Un); a – epoxy, b – d – polished sections. JSM 5600, JXA 8200

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# PLATINUM-GROUP ELEMENT DISTRIBUTION FROM PRISTINE TO NEAR-SURFACE OXIDIZED ORE IN THE PLATREEF, BUSHVELD COMPLEX

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**ABSTRACT**. Economic concentrations of platinum-group elements (PGE) in the Platreef of the Bushveld Complex are mainly restricted to sulfide ores. Near-surface oxidized Platreef ores are currently not mined due to uneconomic recovery rates. In order to investigate the behavior of PGE during weathering, three boreholes covering a sequence of oxidized and pristine Platreef ore from the Mogalakwena Mine were studied in detail. In the pristine Platreef ore, the PGE occur as discrete PGM, or within sulfide minerals. From pristine to oxidized ore, the Pt/Pd ratio increases due to the greater mobility of Pd. In the oxidized ore only relict PGM and sulfides are present. Secondary Fe-hydroxides contain up to 500 ppm Pt and Pd.

## INTRODUCTION

The Bushveld Complex of South Africa hosts the world´s largest resources of platinum-group elements (PGE). The Platreef in the northern Bushveld Complex is up to 400 m thick with sulfide contents of ca. 3% and PGE contents between 1 to 4 g/t (e.g., Vermaak 1995). Three boreholes covering a sequence from oxidized to pristine ore were studied by whole rock geochemistry, ore microscopy, scanning electron microscopy (SEM) and electron microprobe (EPMA). In the pristine ores, platinum-group minerals (PGM) are predominantly associated with base metal sulfides, either locked within or at the grain boundaries. Surface weathering in this part of the Bushveld Complex ranges down to ca. 40 m. During weathering processes sulfides are destroyed but PGE contents remain in a similar range as in the pristine ore.

## GEOCHEMICAL TRENDS FROM PRISTINE TO OXIDIZED ROCKS

In the oxidized Platreef, concentrations of Pt are grossly similar to those of the pristine ore but concentrations of Pd are lower, as evidenced by increases of the Pt/Pd ratio from 0.75 in the pristine ore to 1.15 in the oxidized ore (Fig. 1). In oxidized Platreef, the elemental gains and losses during the oxidation process show strong gains of Ba (+145) and K (+78) (formation of clay minerals?) and strong losses of S (-73), Au (-48), and Pd (-45) (destruction of sulfides and the mobilization of Au and Pd during weathering), similar to the trends observed in the Great Dyke (Evans et al 1994, Locmelis et al 2010, Oberthür et al 2013).

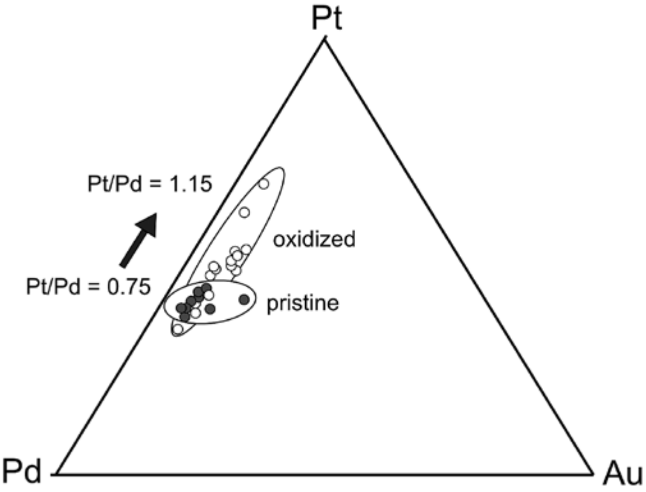

*Fig. 1*. Pt, Au and Pd contents of pristine (filled circles) and oxidized Platreef ores (empty circles)

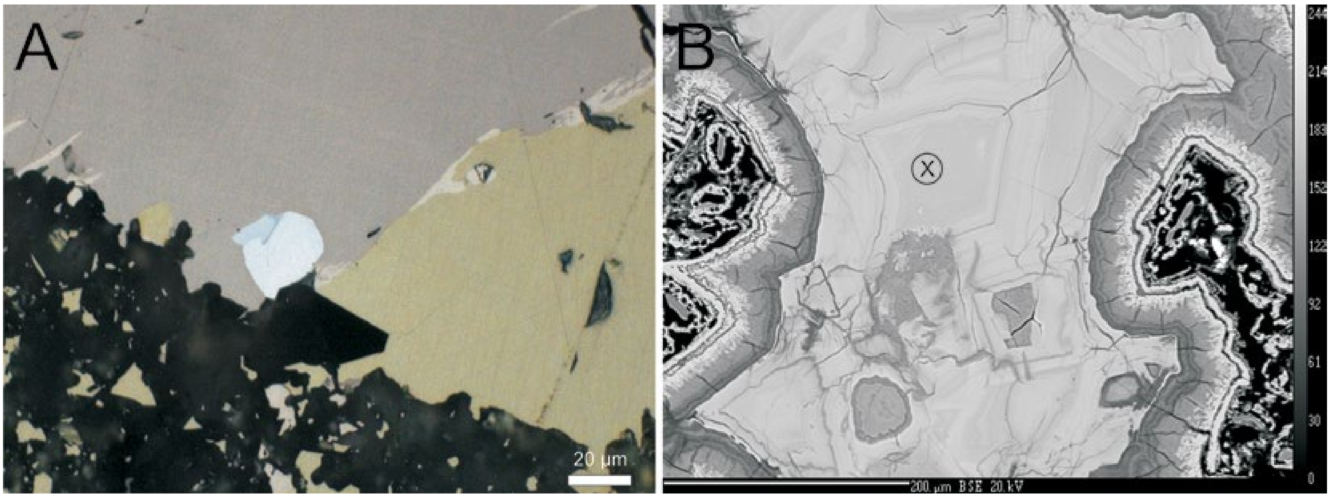

*Fig. 2.* A. Pyrrhotite, pentlandite and chalcopyrite with PGE-bismuthotelluride (white) in reflected light, in oil (AS10451). B. Iron-hydroxide with up to 400 ppm Pd (SEM backscattered electron image; AS10440)

## MINERALOGY – SULFIDES, PGM, SECONDARY PHYLLOSILICATES

In pristine ores, the main sulfides are pyrrhotite, pentlandite, chalcopyrite and pyrite. Pentlandite and chalcopyrite mainly occur around the margins of pyrrhotite. Some grains of argentopentlandite (up to 12.6 wt.% Ag) were detected. PGM (mainly (Pd,Pt)-bismuthotellurides, cooperite/braggite and sperrylite) generally occur at the margins of the sulfide grains or as micrometer sized inclusions in sulfides (Fig. 2A).

In the oxidized ores, only relict sulfides are present and major minerals are secondary Fe-hydroxides, clay minerals, chlorite, smectite and vermiculite (Fig. 2B). Ongoing work shows that these secondary Fe-hydroxides may incorporate up to 500 ppm Pt and Pd (EPMA data).

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# ISOMERTIEITE: CRYSTAL STRUCTURE REFINEMENT

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**ABSTRACT**. The crystal structure of isomertieite, $(Pd_{9.88}Cu_{1.02}Ni_{0.21}Sn_{0.07})_{\Sigma 11.18}As_{1.91}Sb_{1.9}$, from Monchetundra massif (Kola Peninsula, Russia) has been reinvestigated ($R$=0.056). Mineral is cubic, space group Fd-3m, unit cell parameters: $a$= 12.297(5), $V$=1859.3(14) Å$^3$, $Z$=8.

Crystal structure of mineral isomertieite, ideally $Pb_{11}Sb_2As_2$, was solved in 1978 (Shi N. et. al.) from powder diffraction data. The reliability factor of this determination is relatively high – 15%. In current study, a CCD-based detector mounted on an automated single-crystal diffractometer has been used to collect X-ray diffraction data, resulting in successful elucidation of the structure.

A crystal of isomertieite with approximate dimensions 0.03×0.02×0.01 mm was mounted on a Bruker «Kappa APEX DUO» diffractometer equipped with APEX II CCD detector and micro-focus X-ray tube (monochromated Mo$K_\alpha$ X-radiation). The unit cell dimensions were refined using least-squares techniques. The three-dimensional data were reduced and corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. Absorption correction was applied using the SADABS program (Sheldrick, G.M. 2004). A total of 4390 reflections were collected, of which 236 reflections were unique and 178 reflections were classed as observed ($|F_o| \geq 4\sigma_F$).

The WinGX program package was used for the determination and refinement of crystal structure (Farrugia, 1999). Structure was solved by direct methods and refined using SHELX program package (Sheldrick, G.M. 2008). Atoms Pd, Sb and As were located by direct method solutions. Refinement of these atoms positions together with isotropic displacement parameters gave R factor of 9%. Resulting model was refined to R=7%. Atomic displacement parameters were converted into anisotropic form for all atoms and were refined together with weighting scheme. Final residuals were R1=5.6% (for 178 unique reflections), wR2=10.43% and goodness-of-fit S=1.075. Final positional, displacement parameters of all atoms, and occupation factors of all structural positions are shown in table 1.

The crystal structure of isomertieite is unique, and gives a name for a new structure type. Only one another mineral – miessiite $Pd_{11}Te_2Se_2$ – have been found with the same structure type. There are tree symmetrically independent positions of Pd (c.n. 10, 9, 9), one position of As (c.n. 8), and one position of Sb (c.n. 12). Copper atoms are distributed on palladium positions in the structure (table 1).

Table 1

**Atomic coordinates and displacement parameters for isomertieite**

| *Atom* | *x/a* | *y/b* | *z/c* | *occupation* | $U_{eq}$ |
|---|---|---|---|---|---|
| *M*1 | -3/8 | 5/8 | 1/8 | Pd=0.539(2), Cu=0.461 | 0.0094(4) |
| *M*2 | -0.1554(1) | 5/8 | 1/8 | Pd=0.908(7), Cu=0.091 | 0.011(1) |
| *M*3 | 0.03557(8) | 0.71443(8) | 0.03557(8) | Pd=0.859(4), Cu=0.141 | 0.0133(4) |
| Sb | 0 | 1/2 | 0 | 1 | 0.0134(5) |
| As | -1/2 | 1/2 | 0 | 1 | 0.0114(6) |

Table 2

**Chemical composition of isomertieite**

| *Sample* | *1* | *2* | *3* | *4* | *5* | *6* | *7* |
|---|---|---|---|---|---|---|---|
| Pd | 68.43 | 70.89 | 70.67 | 70.33 | 69.89 | 70.07 | 70.34 |
| Cu | 40.42 | 4.07 | 4.05 | 4.40 | 4.68 | 4.64 | 4.06 |
| Ni | 0.55 | 0.21 | 0.27 | 1.77 | 1.63 | 0.7 | 0.62 |
| Sn | 0.58 | 0.64 | 0.58 | 0.64 | 0.58 | 0.55 | 0.59 |
| Sb | 15.63 | 15.42 | 15.61 | 15.42 | 15.66 | 15.49 | 15.32 |
| As | 9.44 | 9.49 | 9.52 | 9.29 | 9.27 | 9.74 | 9.62 |
| Total | 99.05 | 100.79 | 100.72 | 101.87 | 101.78 | 101.33 | 100.80 |

The crystal of isomertieite was analyzed with an electron microprobe (JEOL JXA-8200 microscope, IGEM RAS). PbS, AuTe, $Bi_2Se_3$, $Sb_2S_3$, $AgSbS_2$, $PtAs_2$, $MnS_2$, GaAs, CdS, HgTe, $CuFeS_2$, and pure metals were used as standards for quantitative analysis. Accelerating voltage is 20 kV, current is 20 nA, and diameter of beam is 1 μm. Results of quantitative analysis are given in table 2. The empirical formula is $(Pd_{9.88}Cu_{1.02}Ni_{0.21}Sn_{0.07})_{\Sigma 11.11}As_{1.91}Sb_{1.9}$, calculated on 15 atoms. The crystal chemical formula, resulting from the structure determination, is $(Pd_{10.05}Cu_{0.95})_{\Sigma 11}As_2Sb_2$.

*Acknowledgments. We thank Prof. S.V. Krivovichev for his assistance in this scientific research. Experimental data were collected at the Center of X-ray diffraction studies at St. Petersburg State University (XRD Center SPbSU).*

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# X-RAY COMPUTER TOMOGRAPHY OF PLATINIFEROUS STRATIFORM CHROMITITES IN THE CRITICAL ZONE OF THE BUSHVELD IGNEOUS COMPLEX, SOUTH AFRICA

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**ABSTRACT**. We have carried out X-Ray computer tomography of drill core samples of chromitite layers from the Lower and Middle Groups of the Bushveld Complex in South Africa. The tomography allows finding sulfide and platinum metal mineral grains greater than 10 microns in size inside the samples and is a great tool for mineralogical studies.

The Critical Zone of the Bushveld Complex in South Africa is defined by the presence of prominent, massive chromitite layers, which are used as stratigraphic markers and subdivided into the Lower (LG), Middle (MG) and Upper (UG) groups. Individual chromitite layers within each group are numbered sequentially from the base upwards, i.e., LG1 to 7, MG1 to 4, and UG1 and 2, plus UG3 at some locations in the eastern part of the Complex. All the chromitite layers in the Critical Zone are enriched in platinum-group elements (PGE). The PGE concentrations reach economical levels in the UG2 layer, which is currently mined and in fact constitutes the greatest PGE resource in the world. The origin of PGE concentrations in chromitite layers remains poorly understood and the problem cannot be resolved without detailed studies of PGE mineralogy. In chromitite layers, PGE mostly reside in own minerals (PGM), which are associated with aggregates of base metal (Fe-Cu-Ni) sulfides. Finding PGM is a difficult task even in the most enriched layers because the mineral grains are small (usually no more than a few tens of microns in size) and rare. A normal petrographic thin section may contain just a few PGM grains. More grains can be extracted from

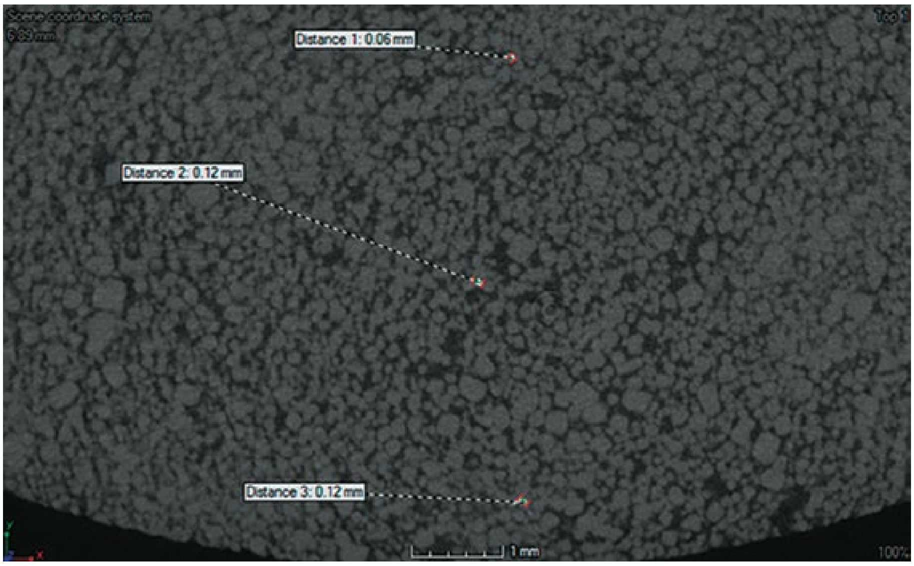

*Fig. 1.* PGM grains in the MG3 chromitite, 2D XRCT image

crushed rock samples by various mineral separation methods but textural information about spatial distribution and exact positions of the PGM grains is lost in the process. X-Ray computer tomography (XRCT) is a new and powerful tool, which allows locating PGM and base metal sulfide grains inside the rock in 3D, choosing the most interesting fragments and performing the PGM study *in situ*.

Here we present preliminary results of a pilot XRCT study of five MG chromitite samples. The study has been carried out at the Department of Mineralogy and Petrography, Perm State University using Nikon Metrology XT H 225+180 LC equipped with two X-Ray sources of 225 and 180 kV and high contrast detector 40X40 cm with 2000X2000 pixel resolution. Tomography of MG2 and MG3 samples allowed to locate numerous sulfide and PGM grains ranging in size from 30 to 120 microns. Some examples are presented in the attached 2D grayscale X-Ray image below. Exact identification of the minerals will be done by conventional microprobe methods after the grains are extracted from the rock by cutting, grinding and polishing.

# NOBLE METAL-GRAPHITE MINERALIZATION IN CARBON-BEARING METAMORPHIC ROCKS OF THE RUSSIAN FAR EAST

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**ABSTRACT**. A new noble metal – graphite mineralization has been discovered in the Riphean-Cambrian metamorphic rocks of the northern Khanka block, Primorye. High PGE and Au contents up to tens g/t at ratio Pt > Au have been detected using various modern analytical methods. Association the noble metal ores with regional graphitization, emerging in all rocks from sedimentary to magmatic, was recognized in the studied area. The variable distribution of PGE and Au in the rocks, their fine dispersion, and compositional diversity indicate that their origin is related largely to endogenic processes with the participation of deep reduced fluids. It is concluded that predominate mass of noble metals has a fluid-magmatic origin with feasible implication of exogenic and metamorphic sources.

Noble-metal (NM) mineralization is well known in carbon-bearing sedimentary and magmatic rocks commonly metamorphosed at the greenschist facies: Bushveld (South Africa), Stillwater (USA), Sudbury (Canada), Sukhoi Log (Russia) and Carlin-type deposits in USA. Carbon is considered to play a significant role in the transportation of NM by C-O-H-S-Cl-F fluids and their precipitation under the reducing influence of organic matter and graphite in host rocks.

The major economic value of such NM ores is based on C-free minerals, such as native precious metals, their alloys with base metals, sulfides, as well as arsenides, tellurides, selenides, and antimonides. Associations of PGE and Au with amorphous carbon and graphite are rarely known. Therefore, NM mineralization located in the graphite-bearing metamorphic rocks of the Bureya- Jiamusi -Khanka superterrane has been studied using different modern analytical methods (Khanchuk et al., 2009, 2010, 2013). The conjugated carbonization and dislocation belts mark zones of tectonothermal reactivation. The granulites and amphibolites form cores of narrow tightly compressed folds of latitudinal and less often northeastern orientation, enclosed in the larger dome-like structures, all cut by numerous faults. Graphite-bearing metamorphic rocks located within the core of Ruzhino diapir fold of the northern Khanka terrane are the main target of our report. The Ruzhino NM occurrence is dominated by amphibolite facies rocks including intercalation of garnet-biotite-feldspar and biotite-quartz-feldspar crystalline schists with marbles. Conformable injections of biotite and leucocratic granite-gneiss, thin dikes of K-rich gabbro-syenitic lamprophyre and metadiabase are usual. Marbles are altered into garnet-diopside-zoisite skarn at the contacts with granite-gneiss.

Almost all these rocks are graphitized with carbon content varying from 0.1 up to 32 wt%. Analyses of MN from the graphitized rocks were carried out with various methods: inductively coupled plasma mass spectrometry, atomic absorption spectrophotometry, ion mass-spectrometry, which revealed a wide scatter of NM content: Pt (0.02-62.13), Pd (0.003-5.67), Ru (0.007-0.2), Rh (0.001-0.74), Ir (0.002-0.55), Os (0.011-0.09), Au (0.02-26.0), Ag (0.56-4.41) ppm.

The NM mineralization were thoroughly studied using scanning electron microscope with energy dispersive X-ray spectrometer (SEM). Thin-prismatic crystals of isoferroplatinum (wt%): Pt=90.36, Fe=9.64 were found in graphite-sericite-quartz shales. Subprismatic microcrystals (up to 2-3 mkm) containing Pt and admixture of other elements (Pt=79.31, C=8.65, Cu=2.09, Si=1.05, O=8.93) were recorded in the graphite metasomatites. The noted admixture of oxygen, C, and Si may be result of the matrix effect of Si-C. The finding of microinclusions of Ir (7.41-21.60) with varying admixture of REE such as Y(4.75-13.26), Dy (0.79-2.86), Gd (0.49-1.67), Yb (0-1.74) and also C (14.91-68.18), F (0-0.59), Cl (0-0.16), Br (0-0.46) wt.% indicate a transfer of NM by halogen-carbonaceous fluids, responsible for inhomogeneous compositions of such grains. Dispersed Au grains have frequently microspheroid form and are characterized by the following compositional variations (at%): Au (79.3-100), Ag (0-22.02), Cu (0-2.2). The gold grains often contain graphite inclusions and carbonaceous nanofilms, suggesting their coprecipitation from the same reducing fluid. It can be assumed that NM were transported as carbonyl, halogen-carbonyl, and other carbon-bearing complexes by analogy with organoplatinum compounds described in sublimates of gaseous fluid at the Kudryavy volcano (Distler et al., 2008).

The studied graphite-ore complex displays the following features typical for deposits of NM in zones of mantle-crustal diapirism: spatial restriction to horst-anticlynal structures, a significant vertical amplitude of the graphite mineralization, occurrence of granitoids of various composition and lamprophyre dikes, high concentrations of geochemically contrasting elements, and close association of the NM with graphite.

Graphite and associated biotite from amphibolite facies rocks are characterized by $\delta^{13}C$ about 8.5-8.7 ‰, $D_{VSMOW}$ from -82.5 to -106.7‰, and $\delta^{18}O_{VSMOW=}$8.2-10.1‰, indicating that these rocks have been contributed by a C-O-H mantle-derived fluid (Mattey, 1987). The leading role of carbon and halogens along with the lack of sulfur participation in gaseous transport of metals is a distinguishing feature of ore formation in rock complexes of the Khanka terrane.

The alternative to fluid transport would be crystallization of graphite during the regional metamorphism of C-bearing terrigenic rocks of greenschist facies, usually related to the black-shale formation. Graphite-bearing rocks with the Pt>Au concentrations of mantle origin are well developed in the amphibolite facies, while typically crustal alterations and related Au>Pt concentrations are characteristic of the black shales. These two distinct processes occur close to each other in the Khanka and Byreya area defining thus polygenic character of the NM mineralization.

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# PLACER PLATINUM-GROUP MINERALS FROM SOTAJOKI RIVER, INARI, FINLAND

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**ABSTRACT**. Platinum group minerals (PGM) from the Sotajoki River, Inari, Finnish Lapland, were studied from heavy mineral samples. The PGM in Sotajoki placers suggest a Merensky Reef type PGE mineralization in a layered igneous complex with only sparse disseminated sulfide minerals. The major PGM are isoferroplatinum and sperrylite with a few Pt-Pd sulfide grains discovered. The existence of high temperature inclusions in the isoferroplatinum and the PGM paragenesis points to a magmatic origin with later hydrothermal and secondary PGM formation.

Platinum group minerals (PGM) from the Sotajoki River, Inari, Finnish Lapland, were studied from heavy mineral samples obtained from the gold miners. PGM have been discovered in the Ivalojoki River tributary (Fig. 1) since the 1875. The bedrock in the area belongs to the granulite belt of northernmost Finland. The felsic sedimentary rocks have been intruded by mafic intrusions and metamorphosed in granulite facies conditions. The zircon U-Pb age datings show an age of 1.95 Ga for the felsic granulites and 1.91 Ga for the mafic noritic layered intrusions (Tuisku & Huhma, 2006).

The PGM were analyzed in 2004-2005 at the University of Hamburg, Germany (Kojonen et al. 2005, 2006), and 2006-2013 at the GSF. The most common PGM in Sotajoki River are isoferroplatinum $Pt_3Fe$, sperrylite $PtAs_2$, cooperite PtS and braggite (Pt,Pd)S. Less common are native Os-Ir-Ru alloy, Pt, $Pt_9Pd$, hongshiite CuPt, AuPd alloy, isomertieite $Pd_{11}Sb_2As_2$, mochenite $(Pd,Pt)(Bi,Te)_2$, stillwaterite $Pd_8As_3$, rustenburgite $Pt_3Sn$, and undefined $Pd_3(Sb,As,Sn)$. Isoferroplatinum contains inclusions of laurite $(Ru,Ir,Rh,Pt)S_2$, irarsite (Ir,Os,Rh,Ru)AsS cuproiridsite $(Cu,Fe)(Ir,Rh,Pt)_2S_4$, cuprorhodsite $(Cu,Fe)(Rh,Ir,Pt)_2S_4$, osarsite (Os,Ru)AsS, erlichmanite $(Os,Ru,Ir)S_2$ and OsIrRu alloy (Fig. 2).

The PGM in Sotajoki placers suggest a Merensky Reef type PGE mineralization in a layered igneous complex with only sparse disseminated sulfide minerals. The tellurides are practically missing, a few arsenides and antimonides were found. The major PGM are isoferroplatinum and sperrylite with a few Pt-Pd sulfide grains discovered. The existence of high temperature inclusions in the isoferroplatinum and the PGM paragenesis points to a magmatic origin with later hydrothermal and secondary PGM formation.

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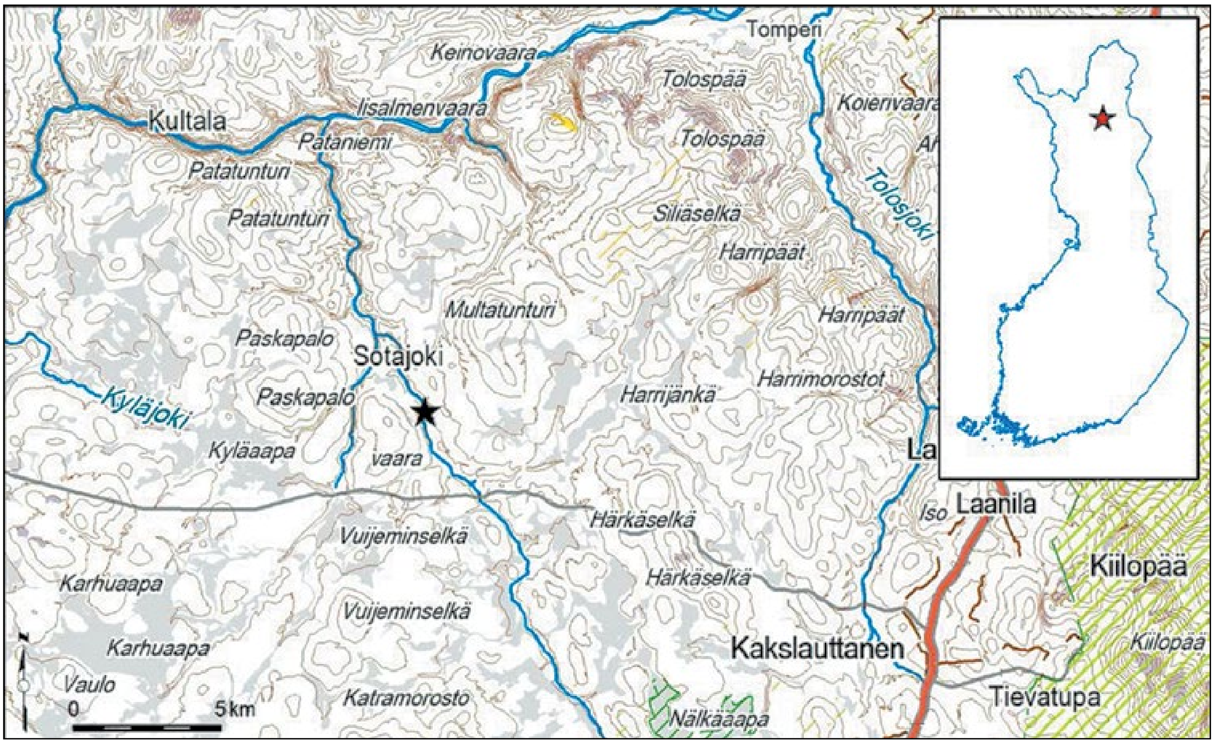

*Fig. 1*. Map of the Sotajoki River area in the Northern Finland, red star= Sotajoki River area, black star= location of the gold mine concession. Drawn by Ms. K. Keskisaari

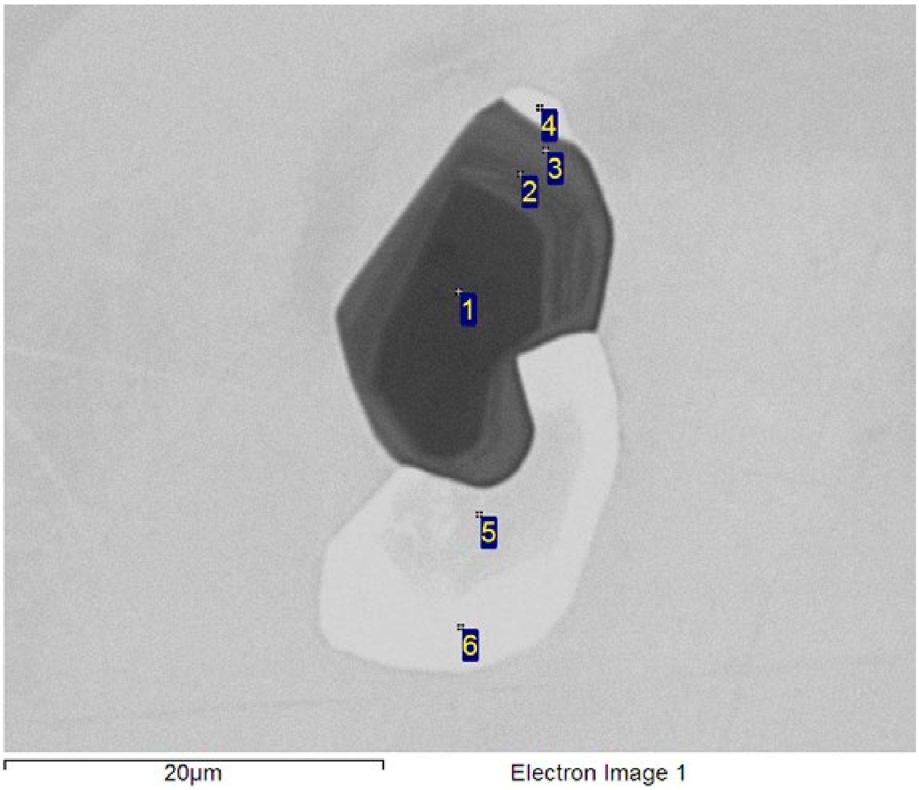

*Fig. 2*. Zoned laurite (1,2,3), IrOs (5) and OsIr (4,6) inclusions in isoferroplatinum, Sotajoki. BSE image K.Kojonen

# NON-TRADITIONAL Pt-Pd MINERALIZATION OF THE KURAMA VOLCANIC-PLUTONIC REGION (UZBEKISTAN)

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**ABSTRACT**. The distribution of Pt, Pd, Au and other elements in the samples of metasomatically altered rocks of diorite-granodiorite composition was studied.

The Kurama area is the eastern part of the Beltau-Kurama volcano-plutonic belt (Yakubchuk et al, 2005). Independent PGE deposits do not exist in this area, but high concentration of Pd in the Au-Cu deposits were noted (Pašava et al., 2011). Age of gold and Cu-porphyry mineralization is within 290-315 Ma (Ore deposits of Uzbekistan, 2001).

During prospecting on Kandyr area, bounding the Kochbulak gold ore field, the elevated Pt content (0.1-1.7 ppm) was determined in some samples (ICP MS). For check these data two samples were analyzed in the Central Laboratory of the Geological Survey of the Czech Republic. Results of these analyses confirmed the presence of Pt (1.44 ppm) and Pd (2.14 ppm). Ru, Rh, Ir, Au in the studied samples are practically absent.

Using the electron probe microanalysis (Jeol Superprobe 8800R) some phases with variable Pt-Pd, Sn, Cu and Agconcentrations were determined (Fig. 1). Moreover Au-Cu-Sn intermetallic compounds were established (Table 1). Phases seem be nonstoichiometric, but in compositions they are close to Pt-bearing paolovite $(Pd,Pt)_2Sn$ and niggliite (PtSn).

The special feature of identified mineralization is its development in the tectonic areas of metasomatically altered intrusive rocks of diorite-granodiorite composition. Traditionally, this mineralization is associated with basites and hyperbasites (Norilsk, Bushveld).

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Table 1

**Chemical composition of minerals PGE** (wt. %)

| *№ п.п.* | *№ проб* | *Pt* | *Pd* | *Au* | *Ag* | *Fe* | *Cu* | *Ni* | *Sn* | *Σ* |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | КНДТ–21–11 | 59,37 | 3,73 | – | – | 0,73 | – | – | 35,79 | 99,62 |
| 2 | КНДТ–21–10 | 35,84 | 32,52 | – | 1,56 | 0,65 | 0,44 | – | 28,49 | 99,50 |
| 3 | КНДТ–21–3 | 0,72 | 52,33 | – | 4,33 | – | 4,13 | 1,15 | 37,35 | 100,01 |
| 4 | КНДТ–21–10 | – | 0,39 | 53,80 | 0,99 | 0,38 | 5,37 | – | 39,56 | 100,49 |

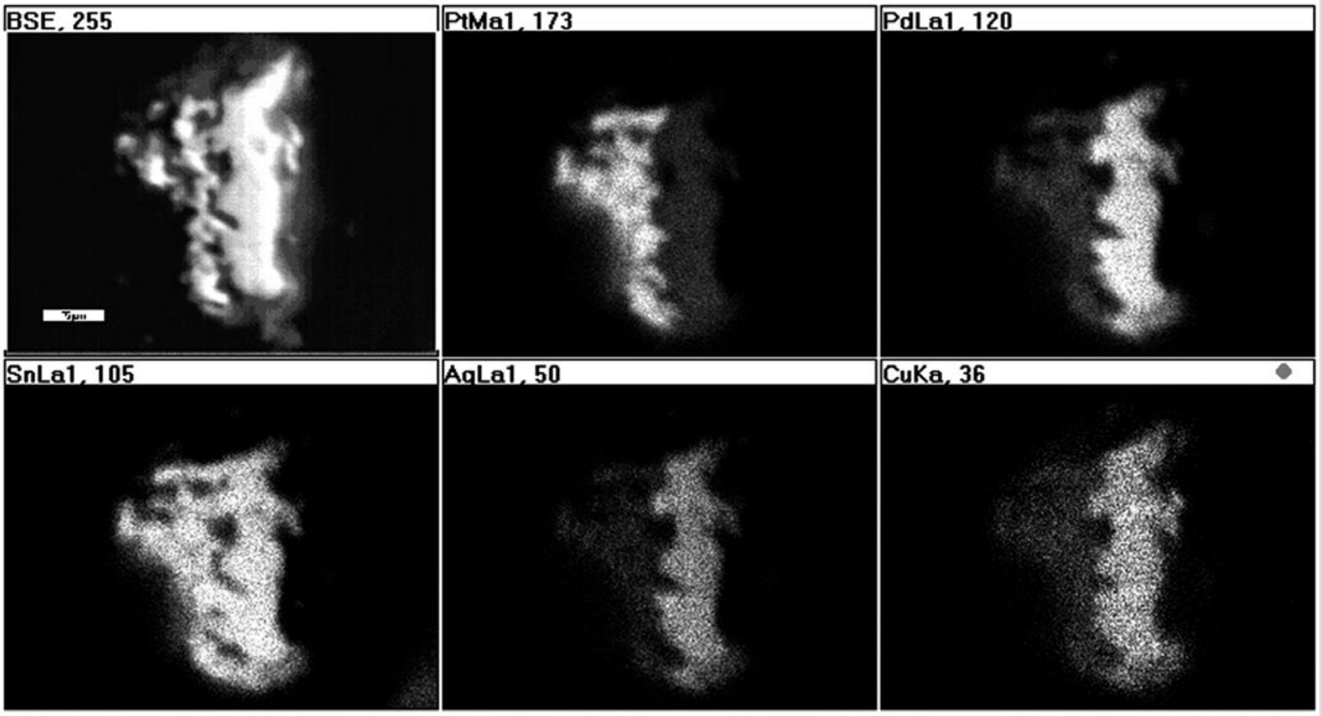

*Fig. 1*. Distribution of elements on the area PGE-minerals. BSE and X-ray image

# RE-DISTRIBUTION OF PLATINUM-GROUP ELEMENTS DURING OXIDATION OF THE MERENSKY REEF, EASTERN BUSHVELD COMPLEX

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**ABSTRACT**. In the Bushveld Complex, platinum-group elements (PGE) are mainly recovered from pristine, unweathered ores of the Merensky Reef, UG-2 and the Platreef. Oxidized PGE ores are currently not mined due to uneconomic recovery rates achieved by conventional metallurgical methods. In order to understand the behavior of PGE during weathering, five drill cores containing fresh and weathered Merensky Reef (originating from the Twickenham and Richmond properties of AngloPlatinum in the eastern Bushveld Complex), were studied by chemical analyses, reflected light and scanning electron microscopy. In the pristine ores, the platinum-group minerals (PGM) occur mainly as sulfides, arsenides and minor tellurides. They are mainly found in contact or close to base metal sulfides (BMS). In the oxidized ores, discrete, relict PGM are rare, indicating remobilization of the PGE during weathering.

## INTRODUCTION

The Merensky Reef (MR) is pursuable over several 100 kilometers in the eastern and western limb of the Bushveld Complex. The MR has an average thickness of one meter, varying from 4 cm up to 4 m. The top and bottom PGE mineralization is limited mainly to thin chromitite stringers with thicknesses of approximately one cm. These stringers are also the upper and the lower limits of the economic mineralization of the MR. Sulfides (mainly pyrrhotite, pentlandite, chalcopyrite and minor pyrite) make up ca. 3 vol.% and occur interstitially to chromite and silicate grains (Lee, 1996). In the mineralized part of the MR, PGE are associated with the sulfides (Lee, 1983). The content of PGE in the MR ranges from 5 to 7 g/t (Cawthorn et al., 2002).

## ANALYSIS

During our investigation of the pristine MR samples, a wide spectrum of PGM was detected including sulfides (laurite, cooperite-braggite) and arsenide such as sperrylite. PGM mainly occur at the grain boundary or rarely within base metals sulfides (BMS). By comparing fresh and weathered ore, a loss of As (-36%) and S (- 93%) can be seen. This is caused because of the weathering processes, which removed these elements. Pt/Pd-ratios increase from pristine to weathered ore from an average of 1.8 up to 4. This indicates a larger mobility of Pd, which is transported out of the system, whereas the Pt contents still remain high in the weathered ore. This finding is similar to the weathering of the Main Sulfide Zone of the Great Dyke in Zimbabwe (e.g. Oberthür et al., 2013).

## OUTLOOK

In continuation of our study, more investigations using ore microscopy and also a detailed analysis by electron microprobe are carried out. This is used in order to unravel whether PGE are hosted in sulfides. In the fresh ore, PGE are suspected to be hosted within BMS and as separate PGM grains. In contrast, in the oxidized samples, the PGE are presumed to be present in relict PGM and BMS and also as authigenic new minerals. The investigation aims at contributing to a better understanding of the remobilization of PGE during supergene oxidation and weathering processes.

*Acknowledgments. We thank Jacques Roberts and Robert Schouwstra (AngloPlatinum) for the* *possibility to visit and sample in the Germiston and the Driekop core yards and for valuable data and information supplied during discussions.*

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# THE APPLICATION OF XCT IN DETERMINING THE 3-D ENVIRONMENT OF IN-SITU PGM GRAINS AND ASSOCIATED MINERALS FROM THE BUSHVELD COMPLEX, SOUTH AFRICA

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**ABSTRACT**. This study assesses the validity of using high resolution X-ray computed tomography in order to observe the characteristics of PGM and associated mineralogy in their natural state as they occur within the reef samples obtained from both the western and eastern limbs of the Bushveld Complex.

Platinum group mineralisation within the Merensky and UG2 reefs, Bushveld Complex is thought to be intimately associated with sulphide and oxide phases. The relationships between the platinum group minerals (PGM) and associated mineralisation have previously been studied using conventional 2-D techniques which, in this study, have been shown to be inadequate at accurately constraining the mode of PGM occurrence. The purpose of this study was to assess the validity of using high resolution X-ray computed tomography (XCT) in order to observe the characteristics of PGM and associated mineralogy in their natural state as they occur within the reef samples obtained from both the western and eastern limbs of the Bushveld Complex. PGM grain characteristics, associations and compositions were compiled using conventional scanning electron microscopy (SEM). PGM imaged using a SEM that appeared to be included within the grain boundaries of associated minerals were imaged using XCT with different results. An intimate relationship between PGM occurrence and base metal sulphides (BMS) such as pentlandite and chalcopyrite was established with many PGM occurring on the outside boundary of host sulphides. In addition, many PGM grains were found to be of significant size (100-200 microns), many times larger than previously reported with SEM analysis. Furthermore, the ability to manipulate and view 3-D volumes representative of whole rock samples down to a voxel resolution of 15 micron enabled the user to observe small scale structures, texture variations and clearly discern the mode of PGM occurrence.

Oriented studies of core samples from different locations in the Bushveld Complex allowed for the comparison of PGM environments and the variation of these characteristics in relation to stratigraphic position in the reefs. In addition, the grain shape and interconnectivity of PGM and BMS can be used to indicate directions of fluid flow during the emplacement of mineralisation. The correlation between images and compositions obtained from SEM analysis with 3-D volumes and image slice stacks from XCT was done to authenticate the validity of the results obtained from the XCT (Figure 1). This is due to the fact that during post processing of XCT data, mineral phases are identified using properties such as mineral specific gravity values and average atomic numbers, not composition. The combination of 2-D techniques such as SEM and 3-D XCT proved to be necessary in order to accurately delineate the boundaries of different mineral phases to ensure accurate thresholding of grey-scale values obtained from the XCT. The non-destructive technique of XCT yielded important findings regarding the in-situ characteristics of PGM. However, the validity of XCT data is dependent upon a sound geological knowledge of the samples being scanned. Continued use and refinement of XCT for samples of this nature will contribute to advances in the understanding of PGM deposits throughout the world.

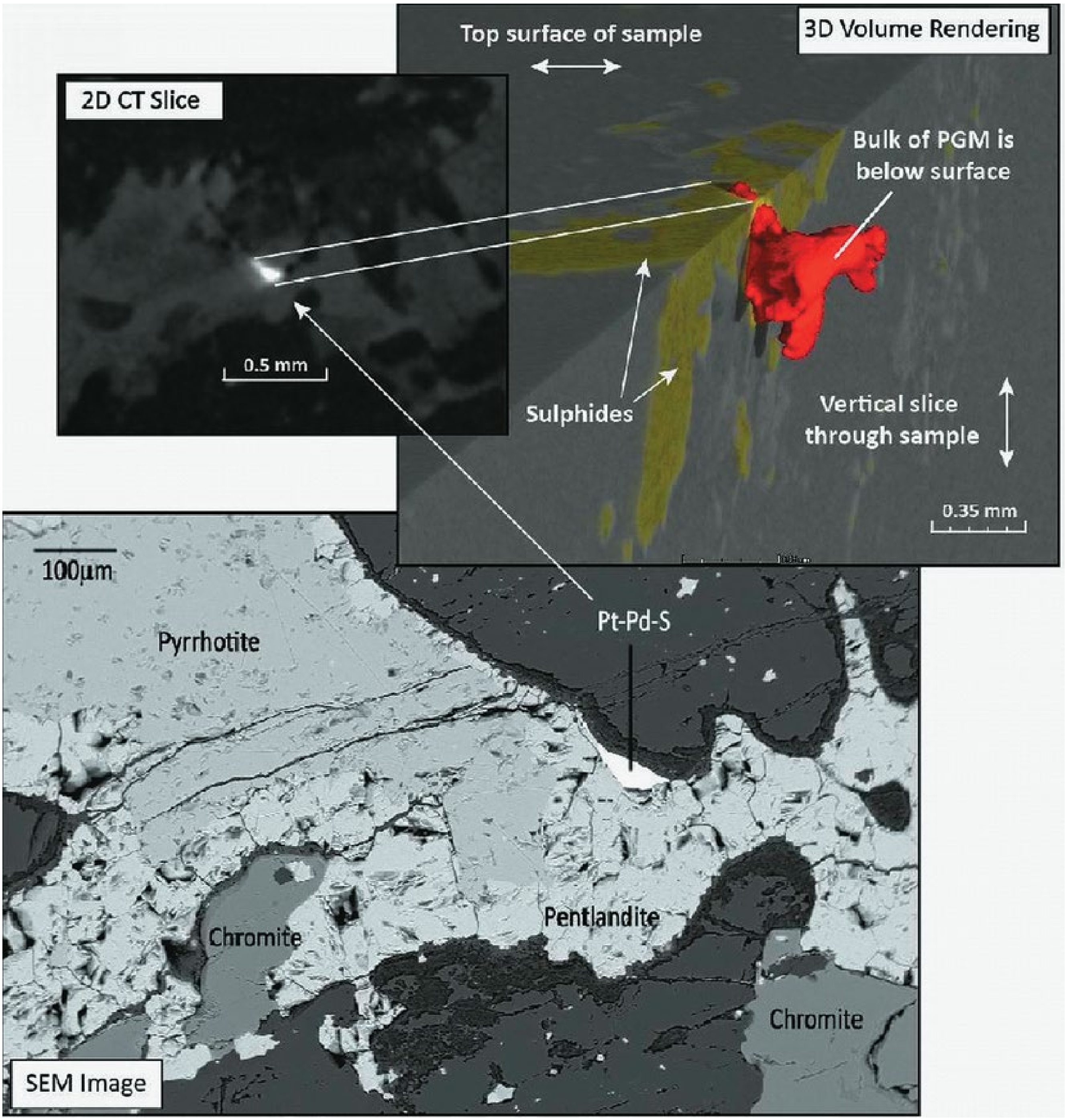

*Fig. 1.* 2-DCT slice correlated with SEM image and 3-D volume rendering of highlighted PGM (Pt-Pd-S). The CT slice and volume rendering have a resolution of 10 µm. The PGM grain is situated on the boundary of pentlandite grain. The volume of PGM has been segregated and left intact whilst the top surface has been skimmed in order to expose the PGM grain. In addition, a vertical slice through the PGM grain has been removed to view the full extent of the PGM

# CHROMIAN GLAGOLEVITE AND OTHER HIGH-Cr SILICATES IN PGM-RICH CHROMITITES IN THE URAL-ALASKAN-TYPE INTRUSIONS AS GENETIC MARKERS

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**ABSTRACT**. The mafic silicates in the PGM-rich chromitites of the Ural-Alaskan-type intrusions are enriched in chromium and alkalis. Chromian glagolevite is one of the typical Na-rich low temperature mineral in chromitite. It intergrows with chromite, PGM and other silicates, indicating a low temperature origin.

The genesis of PGM-rich chromitites in the Ural-Alaskan-type intrusions is still a debatable problem (Auge et al., 2005; Chaschukhin et al., 2002; Garuti et al., 2002; Pushkarev et al., 2005). The study of silicate minerals coexisting with chromian spinel and PGM can provide important information about their origin. Most of them are Cr-rich and occur in different textural positions and association: 1) they form single inclusions in chromite and in the PGM or intergrown with them; 2) they consist of polyphase inclusions in the same position, with a shape of negative crystals with an octahedral symmetry; 3) they form an intergranular matrix between chromite and PGM grains. The composition of the chromium-rich silicates plays an important role in the formation of the latest metasomatic veins and miarolitic holes in dunite and especially in coarse-grained dunite-pegmatite. In chromitite matrix and in the metasomatic veins they are associated with carbonate, apatite and other non-silicate minerals. The most widespread chromium-rich silicates are: forsterite, diopside, amphibole, phlogopite, glagolevite, chlorite and garnets. Such minerals as Cr-diopside, Cr-amphibole and Cr-phlogopite are also typical for the interstitial assemblage of dunite-host and they have similar compositions with those found in the chromitites.

Chromian glagolevite is one of the most important mineral in PGM-rich chromitites. It was discovered recently in the metasomatic skarns in the Kovdor alkaline-ultrabasic complex in the Kola Peninsula (Krivovichev et al., 2004). Its chromian rich varieties were described approximately at the same time in platinum-bearing chromitites of the Nizhny Tagil massif (Anikina et al., 2001). Under microscope glagolevite is similar to chlorite and shows anomalous optical properties. It contains 1.5-3.0% $Na_2O$ and a similar amount of $Cr_2O_3$ (table 1). Glagolevite forms inclusion in PGM, thin films around forsterite inclusions in chromite, it intergrows with sodium rich Cr-phlogopite and serpentine in polymineralic inclusions in chromite and in the silicate matrix of ore. Glagolevite was not found in dunite host, so it reflects a composition of the ore-forming system and relatively low temperature conditions of its evolution. High sodium alkalinity of the ore-forming system is confirmed by the high sodium content of Cr-rich amphibole and phlogopite (table 1). Even diopside from chromitites is enriched in sodium as well as LREE (Krause et al. 2007). Diopside and amphibole often grow on the surface of the PGM inclusions in chromite and have their own crystal shape. It indicates that they were formed before to be included in the chromite grains. However, their compositions reflect a relatively low temperature origin, less than 900-800°C. It is supported also by high CaO (25-26%) content in Cpx and its coexistence with phlogopite, serpentine, Ca-garnet and other minerals typical of skarn mineralization. We suppose that such geochemical features of minerals reflect their precipitation in the presence of alkaline fluids under deep subsolidus conditions.

Inclusions of forsterite in the chromite ore, 20-150 μm in size, are characterized by extremely

Table 1

**Typical compositions of silicates from the PGM-rich chromitites**

| *Mineral* | *Glagolevite* | *Serpentine* | *Olivine* | *Diopside* | *Amphibole* | *Phlogopite* |
|---|---|---|---|---|---|---|
| $SiO_2$ | 28.49 | 41.76 | 42.05 | 54.43 | 42.46 | 41.41 |
| $TiO_2$ | 0.05 | 0.00 | 0.06 | 0.09 | 0.40 | 0.20 |
| $Al_2O_3$ | 15.68 | 0.07 | 0.00 | 0.56 | 11.5 | 13.88 |
| $Cr_2O_3$ | 1.95 | 0.56 | 0.88 | 1.67 | 2.85 | 2.00 |
| $FeO^*$ | 1.75 | 3.77 | 3.09 | 1.18 | 3.81 | 1.51 |
| MnO | 0.00 | 0.01 | 0.05 | 0.00 | 0.00 | 0.00 |
| MgO | 35.67 | 39.31 | 52.94 | 16.81 | 19.18 | 26.31 |
| CaO | 0.00 | 0.04 | 0.18 | 25.84 | 12.81 | 0.01 |
| $Na_2O$ | 2.85 | 0.06 | 0.00 | 0.12 | 3.27 | 2.36 |
| $K_2O$ | 0.00 | 0.02 | 0.00 | 0.00 | 0.68 | 7.24 |
| Total | 86.48 | 85.59 | 99.23 | 100.71 | 96.98 | 94.91 |

high Cr contents, up to 1.5% of $Cr_2O_3$. They are zoned with the core enriched in Fe and depleted in Mg. From core to rim magnesium increases together with chromium and iron decreases. The amount of $Cr_2O_3$ in the rim of inclusions approaches 1-1.5%, but it is not an influence of the host chromite because the amount of iron in this zone is minimal. Forsterite from the chromitite matrix contains very low amount of chromium, close to detection limit of microprobe analyses. The preservation of the nice Mg-Fe-Cr zonation of forsterite inclusions can indicate that they were captured under low temperature when the exchange processes and Mg-Fe diffusion between olivine and chromian spinel were blocked (Lehmann, 1983).

The observation of setting, relationships and chemical features of the high-Cr silicates from the PGM-rich chromitites of the Ural-Alaskan-type complexes allow to assume their low temperature origin together with chromian spinel and PGM in the presence of alkaline fluids. Chromium-rich composition of the most mafic silicates indicates that the ore-forming system was extremely enriched in chromium, what is forbidden for true magmatic melts but permitted for hydrothermal solutions (Arai & Akizawa, 2014).

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# PLATINUM-GROUP MINERALS (PGM) FROM PLACERS – INDICATORS OF BEDROCK MINERALIZATION: MORPHOLOGY, TEXTURE (STRUCTURE), TYPES OF INCLUSIONS, COMPOSITION (A CASE STUDY IN SOUTH SIBERIA)

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**ABSTRACT**. PGM in placers can provide a lot of information concerning bed rocks and ores types as well as ores formation and alteration conditions (McClenaghan & Cabri 2011, et al.). Modern local quantitative analysis (EPMA, SEM) allows us to identify different characteristics of the minerals. The example of PGM from South Siberian placers shown that the morphology of the grains, their composition, structure and morphology as well as silicates, oxides and intermetallic compounds micro-inclusions composition and minerals alteration could be used to better understand their provenance and their lode deposits.

Preliminary investigation results revealed numerous new areas with anomalous PGM concentrations in the placers of the Siberian platform Southern part. PGM were collected from alluvial gold placers in the western part of the Altay-Sayan folded area (Altay-Sayan Folded Belt – ASFB). ABSF consist of Kuznetsk Alatau, Mountain Shoria and Salair Ridge folded structures of Caledonian and Hercynian age. PGM concentrations in the placers vary from one to tens of mg/m$^3$. Territorial prospects for alluvial and ore PGE mineralizations are not defined. PGM found in placers are of great interest since they could be used to define their parental sources. The main PGM analysis methods used are EPMA (Camebax Micro) and SEM (TESCAN) with thermal field emission (analyst: N.S.Karmanov).

The studied PGM are relatively small, ranging in size from 0.1 mm to 1 – 2 mm. They show diverse morphology: rounded to spherical, tabular, cloddy, irregular and columnar. Crystals with rounded edges of the hexagonal, cubic and octahedral habit are frequent. PGM consist of two main types: dominating (> 50%) iron-platinum alloys and poorly widespread (< 20%) osmium-iridium-rutenium ones. Both types occur together often (in 30%). Sperrylite and sulphoarsenides of PGE are sporadical minerals, their share doesn‘t exceed 5-10% of total PGM. The most grains of Pt-Fe alloys are represented isoferroplatinum and native platinum; content of Fe+Cu in the these alloys ranges from 15 to 32 at.%. Rh, Ir, Os, Ru, Pd – usual, but not constant, impurity in these alloys. Their total content usually doesn‘t exceed 20%. The Pt-Fe alloys are quite often replaced sperrylite, cooperite, erlichmanite (Fig. 1), rhodarsenide, irarsite, hongshiite and other minerals. The grains of Os-Ir-Ru alloys are represented varieties of osmium, ruthenium, and iridium with prevalence hexagonal alloys of Os(Ir) and Ru(Os), which form osmium-iridium and ruthenium trends in the Os-Ir-Ru system respectively.

Osmium occurs as a good-shaped flat faceted crystals more frequently than platinum. Slightly rounded grains in the most cases still retain the basic features of the primary endogenous forms. Smoothed and rounded up to the spherical PGM grains were formed in the endogenous conditions. The indications of non-supergene zone (absence of the mechanical abrasion) forming conditions for PGM grains are: edging with PGE sulfarsenides (Fig. 1) and edge subparallel grain microtexture (Fig. 1). Rounded up to the spherical single PGM crystals were formed during the early stages of crystallization differentiation and segregation of the melt.

The investigated PGM display different microtextures: 1-massive; 2-disseminated; 3-emulsion-liquation; 4-banded; 5-spotty. These textures reflect the conditions of PGM formation and degree of they epigenetic transformation. Also, the important examples for these kinds of textures are: 6-structure of a solid solution decay 7-gridded or loopy and metasomatic substitution. Some placers contains wide range of Pt-Fe alloys with structure of a solid solution decay; another plac-

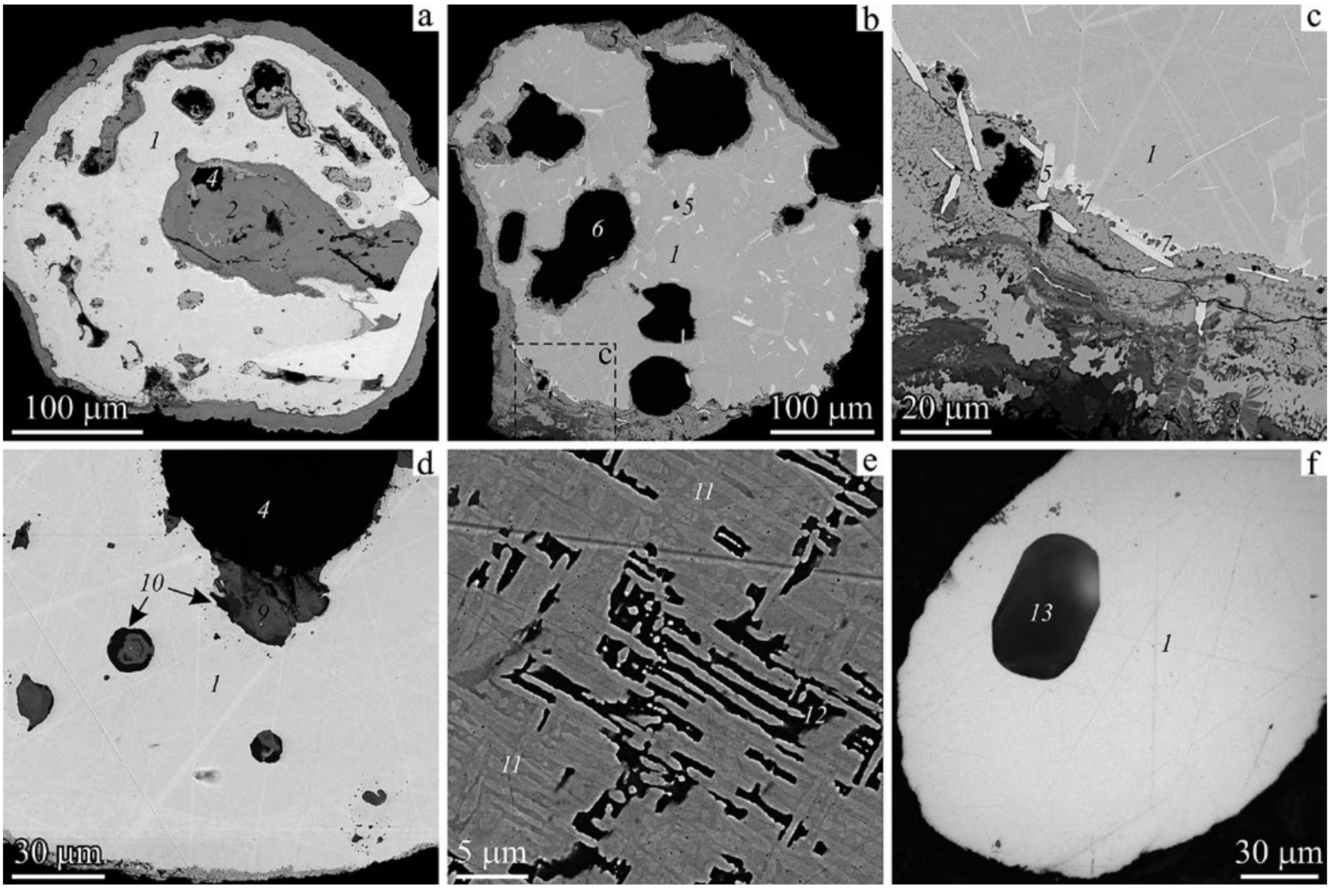

*Fig. 1.* BSE image SEM (a-e) and microphoto (f) of PGE minerals. 1 – Pt-Fe alloys with compositions similar to isoferroplatinum ($FePt_3$); 2 – sperrylite ($PtAs_2$); 3 – cooperite (PtS); 4 –amphibole group minerals; 5 – osmium ($Ru_8Ir_8Os_{84}$); 6 – Cr-Fe-spinels of variable composition ($FeO\bullet Fe_{1.2}Cr_{0.4}A_{l0.2}Ti_{0.1}O_3$-$FeO\bullet Fe_{0.9}Cr_{0.7}Al_{0.2}Ti_{0.2}O_3$); 7 – gold ($Ag_{24}Au_{76}$); 8 – erlichmanite ($OsS_2$); 9 – tiospinels of cuprorhodosite-malanite range; 10 – chalcopyrite; 11 – Pt-containing alloys mixture ($FePt_{20}Os_2Ru_{10}Ir_{55}Rh_{12}$-$Fe_{16}Cu_3Pt_{66}Pd_2Ir_5Rh_2Sb_5$); 12 – rhodium antimonide (RhSb); 13 – olivine

ers do not have them, but contains alloy particles with a massive, dense texture or with metasomatic substitution structures. It is known that the structure of solid solution decay occurs under slow cooling conditions in the solidifying melt at relatively large depths and probably within a large size melt mass. Accordingly, the absence of these structures may be an evidence of alternative formation conditions such as the formation within the basic rocks dike complexes which are widespread in the region. Metasomatic alterations of PGM are connected with the processes of serpentinization of ultramafic Pt-bearing rocks.

Part of PGM contains microscopic and submicroscopic inclusions which are very diverse in many ways: 1-the structures of solid solution decomposition; 2-hydrothermal-metasomatically transformed parental melts; 3-"relic" inclusions (silicates and oxides captured by the cooling melt); 4-emulsion-segregated inclusions. In addition, there are faceted shape inclusions: rectangular, laths, hexagonal, square, irregular smoothed „ragged" shape, oval and round (drops, balls). Mono-and poly-mineral inclusions consist of rock-forming minerals and various PGM. All these inclusions play an important role to understand the conditions of PGM formation.

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# PLATINUM MINERALIZATION OF THE GREAT DYKE, ZIMBABWE, AND THE BUSHVELD COMPLEX, SOUTH AFRICA – THE FATE OF PGM FROM SULFIDE ORES VIA THE WEATHERING CYCLE (OXIDIZED ORES) INTO PLACERS

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**ABSTRACT**. The world's prime sources of metallurgical chromite and platinum-group elements (PGE) are layered intrusions of Proterozoic and Archean age (e.g. the Bushveld Complex, South Africa; the Great Dyke, Zimbabwe; and the Stillwater Complex, USA). This contribution summarizes previous studies of our working group on pristine and oxidized platinum-group element (PGE) ores as well as related placer accumulations on the Great Dyke and the Bushveld Complex.

The Great Dyke of Zimbabwe hosts the world's second largest reserve of PGE after the Bushveld Complex in neighbouring South Africa. Economic PGE mineralization is restricted to sulfide disseminations in pyroxenites of the Main Sulfide Zone (MSZ), sited some metres below the transition of the Mafic and the Ultramafic Sequence of the Great Dyke. The geochemical and mineralogical fine structure of the MSZ is regarded to reflect primary magmatic features of consecutive batches of sulfide accumulation, concomitant scavenging of PGE, and fractionation (e.g., Oberthür et al., 2003a; 2003b; Oberthür, 2011). In the Bushveld Complex, the PGE ores are largely related to sulfide mineralization. The three major ore bodies mined are the Merensky Reef, the UG-2 chromitite, and the Platreef.

Mineralogically, in the pristine sulfide ores of both the Great Dyke and the Bushveld, most of the Pd and Rh are hosted in pentlandite (e.g., Oberthür et al., 2003a; Kuhlmann et al., 2006; Oberthür 2011; Osbahr et al., 2013; Junge et al., 2014), whereas Pt is dominantly present in the form of discrete platinum-group minerals (PGM) like sperrylite, cooperite/braggite, malanite/cuprorhodsite, and (Pt,Pd)-bismuthotellurides (Fig. 1). These findings indicate that a large proportion of the PGE, primarily concentrated in sulfide under magmatic conditions, was redistributed in the subsolidus stage and formed discrete PGM with available reaction partners. Chemical gradients and magmatic-hydrothermal fluids probably led to small-scale redistribution of PGE within the MSZ.

The behaviour of the PGE in the exogenic cycle was examined in a number of profiles of oxidized MSZ ores, and work on oxidized Merensky Reef and Platreef ores including eluvial accumulations (Fig. 2) is in progress. Geochemically, in the oxidized ores of both the Great Dyke and the Bushveld, the general metal distribution patterns of the pristine ores are grossly preserved. However, at similar Pt grades, significant proportions of Pd have been lost from the system (Locmelis et al., 2010; Oberthür et al., 2013; work in progress).

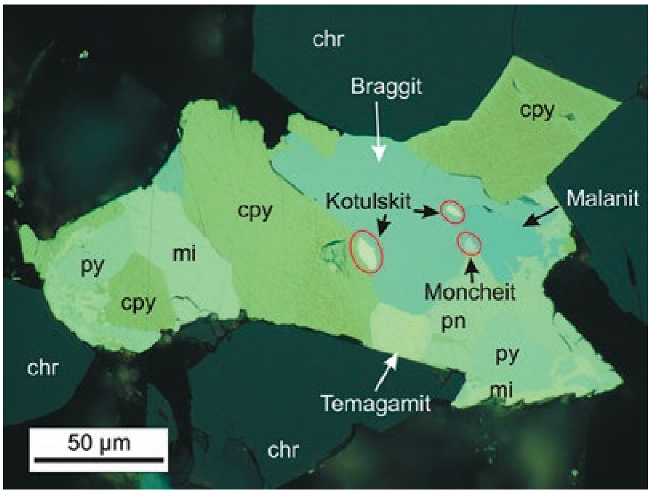

*Fig. 1.* Assemblage of sulfides (cpy, pn, mil, py) and various PGM (moncheite, braggite, malanite, kotulskite and temagamite) in the UG-2. Lebowa Mine (AS 7631), reflected light, in oil

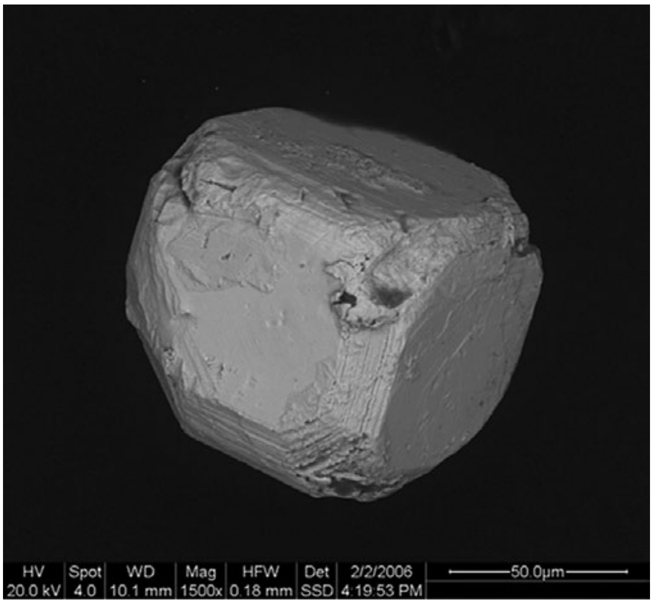

*Fig. 2.* BSE image of eluvial Pt-Fe alloy grain (4-59), Onverwacht Pipe downslope

This indicates that Pd is more mobile than Pt and is dispersed in the supergene environment. Mineralogically, in the oxidized ores of both the Great Dyke and the Bushveld, sperrylite and cooperite/braggite are stable whereas the (Pt,Pd)-bismuthotellurides, common in the pristine ores, have disintegrated, and ill-defined (Pt,Pd)-oxides or -hydroxides have formed. Furthermore, elevated contents of Pt and Pd are found in iron- and iron-manganese-oxides/hydroxides (MSZ data). The resource of ~250 Mt of oxidized MSZ (Oberthür et al., 2013) and significant resources of oxidized Platreef and Merensky Reef calls for novel exploitation methods for these ores.

The assemblages of detrital PGM found in rivers draining the Great Dyke and the Bushveld Complex indicates further mineralogical changes (Oberthür et al., 2004; 2013; Melcher et al., 2005). Sperrylite largely remains stable whereas most cooperite/braggite grains have been partly altered or completely destroyed. Grains of Pt-Fe alloy are ubiquitous in the alluvial sediments. Most likely, these grains (at least in part) may be neo-formations that either formed from pre-existing, unstable PGM, or via a solution stage under low-temperature conditions.

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# THE ROLE OF PYRITE AS CARRIER OF PLATINUM-GROUP ELEMENTS IN MAGMATIC SULFIDE DEPOSITS

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**ABSTRACT**. Recent studies have revealed that pyrite can host appreciable amounts of PGE in Ni-Cu-PGE magmatic sulfide deposits. It is the only of major sulfides hosting Pt and is, generally, the richest in Rh; it also contains Os, Ir and Ru in similar abundances to pyrrhotite and pentlandite and, in some cases, exhibits a distinct and marked PGE compositional zoning. These results highlights that pyrite must be taken into account to understand the distribution of PGE in this ore type.

In recent years, the development of microanalytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has led to better understand the distribution of platinum-group elements (PGE: Os, Ir, Ru, Rh, Pt and Pd) in Ni-Cu-(PGE) deposits by measuring the *in situ* concentrations of these elements in sulfides (i.e., pyrrhotite, pentlandite and chalcopyrite) (e.g., Dare et al 2011; Piña et al 2012; Vukmanovic et al 2014). These studies show that Os, Ir, Ru and Rh typically occur in solid solution in pyrrhotite and pentlandite, whereas Pt occurs as discrete platinum-group minerals (PGM, bismuthotellurides, tellurides, arsenides and sulfides) associated with base metal sulfides. Palladium occurs both in solid solution in pentlandite as well as discrete PGM. Despite pyrite being a relatively common phase in magmatic sulfide deposits, it has been neglected as carrier of PGE. Only few studies report PGE data in pyrite from Ni-Cu-PGE ore deposits: Oberthür et al (1997) in the Great Dyke of Zimbabwe, Dare et al (2011) in the McCreedy East deposit of Sudbury, Djon & Barnes (2012) in Lac des Iles and Piña et al (2012, 2013) in Aguablanca. These studies show that pyrite can host substantial amounts of PGE, especially Rh and, interestingly, Pt, a PGE typically absent in pyrrhotite, pentlandite and chalcopyrite.

A review of the inventory of available PGE data leads to the following conclusions:

1. Pyrite replacing pyrrhotite contains similar Os, Ir, Ru and Rh (IPGE) abundances to those of host pyrrhotite. It is thought that pyrite inherits the IPGE contents of the pyrrhotite. Similarly, pyrite replacing silicates is depleted in PGE because silicates do not host any PGE.

2. Pyrite is much richer in Pt and Rh than any of the other base metal sulfides (up to 244 ppm Pt in the Great Dyke and 113 ppm Rh in McCreedy East). Despite these high Pt contents, mass balance calculations indicate that pyrite only accounts 5 % or less of Pt due to a combination of the low modal abundance of pyrite (generally less than 5 vol. %) and the tendency of Pt to form PGM. In some cases, pyrite does account most of Rh present in the rock. There is a positive correlation between Pt and As. The ability of As to enter the pyrite and not the pyrrhotite structure may be the reason that Pt enters pyrite but not pyrrhotite.

3. Laser ablation ICP-MS maps reveal the presence of trace element zoning in pyrite from McCreedy East and Aguablanca consisting of Os-Ir-Ru-Rh-As-rich layers and PGE-depleted and Se-Co-rich layers parallel to the grain boundaries (Fig. 1a). A model of boundary layer effect during pyrite formation from pyrrhotite explains this zonation (Dare et al. 2011; Piña et al. 2013). Some pyrite from Aguablanca further shows Pt-rich bands that coincide with high Co values rather than with high IPGE values (Fig. 1b). Probably, in those cases where pyrrhotite hosts Pt-bearing phases, the fluids responsible of pyrrhotite replacement by pyrite dissolved these phases, making Pt available for incorporation into pyrite.

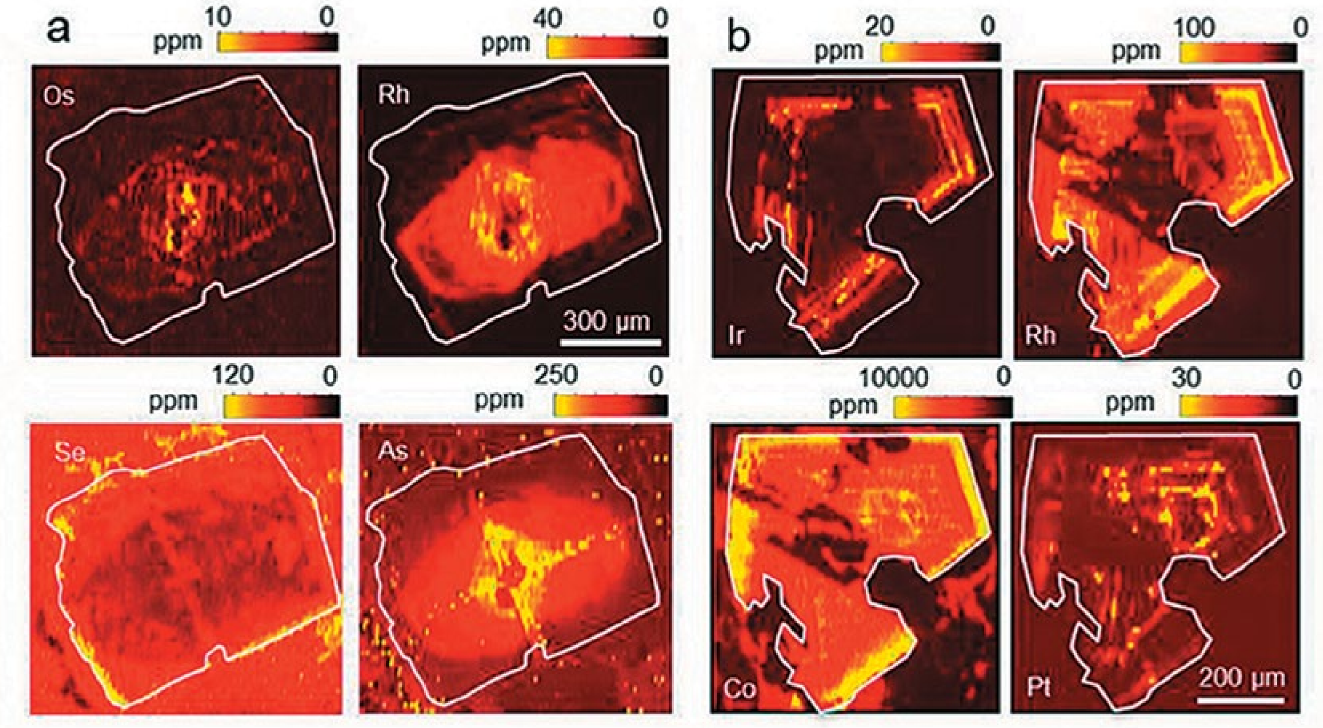

*Fig. 1.* Typical compositional Os, Rh, Se and As zoning (a) and unusual zoning with respect to Pt (b) in pyrites from the Aguablanca Ni-Cu sulfide deposit (Piña et al. 2013)

In summary, the identification of significant amounts of PGE in pyrite from a number of Ni-Cu-PGE sulfide deposits remarks the importance of pyrite to fully understand the magmatic and postmagmatic/hydrothermal evolution of PGE in magmatic sulfide systems.

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# NON-MAGMATIC ORIGIN OF PGM-RICH CHROMITITES IN THE URAL-ALASKAN-TYPE INTRUSIONS: MINERALOGICAL AND STRUCTURAL EVIDENCES

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**ABSTRACT**. The geological, mineralogical and geochemical data suggest that PGE-bearing chromitites within the Ural-Alaskan complexes have non-magmatic origin. Their formation relates to redistribution of chemical elements and recrystallization of precursor minerals in low temperature, fluid-rich environment.

Dunite-clinopyroxenite (±gabbro) complexes belonging to the Ural-Alaskan-type represent the main source of platinum placers worldwide (the Urals, Russian Far East, SE Alaska, British Columbia, Australia). The Pt-group minerals (PGM), closely associated with chromitites, occur as sparsely disseminated small (< 100 µm) grains and in net-textured cement of chromite grains together with various silicate and non-silicate minerals. The latter type is a possible source of PGM nuggets in placers. However, the origin of large accumulations of PGM in chromitites is still debated.

The ore-bearing schlieren are considered to originate due to accumulation of liquidus chromite and PGM from the melt percolating through dunite host rocks (Auge et al., 2005). On the other hand, the magmatic origin is contradicted by textural and mineralogical data (Pushkarev et al., 2005) that demonstrate: a) lack of evidence for melt percolation in dunites in and around schlieren; b) non-conformity of chromitites in relation to dunites; c) systematic change of Cr-spinel compositions in chromitite bodies towards from the center of schlieren; d) paragenetic association of chromite and PGM with low-temperature, non-magmatic minerals; e) unusually high Mg# of Cr-spinel and associated silicate minerals.

In particular, the chromite contains euhedral inclusions of extremely magnesian (Mg#>0.94)

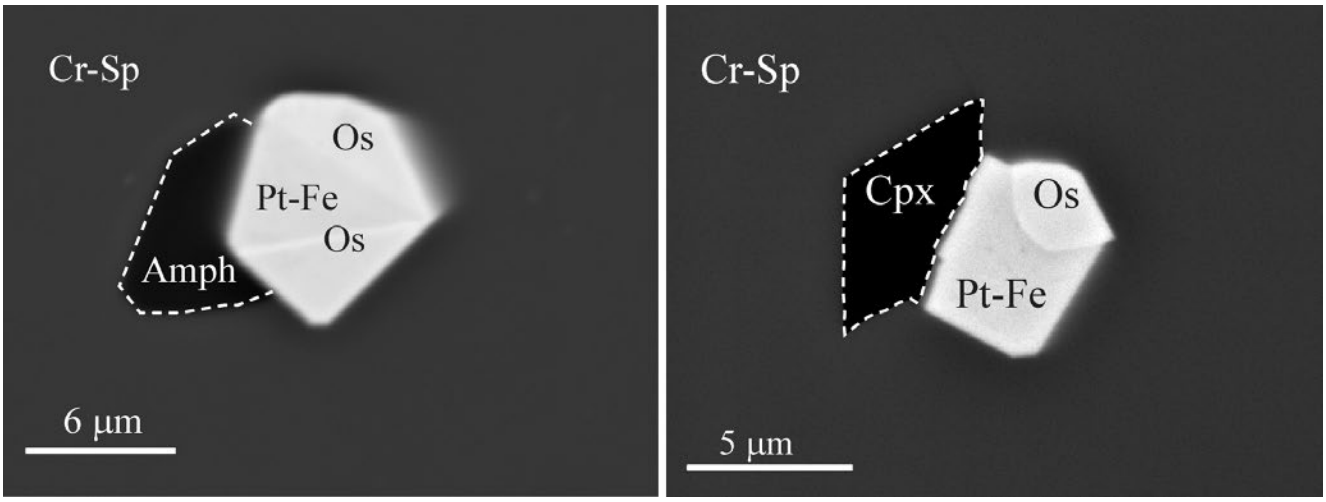

*Fig. 1*. PGM associated with euhedral amphibole (Amph) and clinopyroxene (Cpx) are included in Cr-spinel

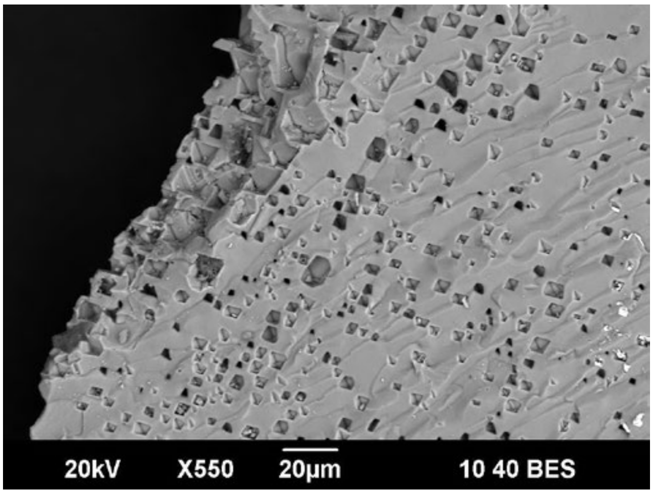

*Fig. 2.* Trails of octahedral fluid inclusions in Cr-spinel of the Kondyor massif

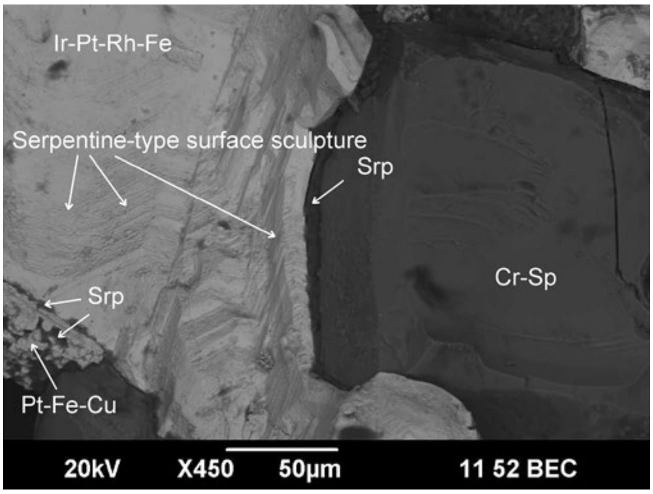

*Fig. 3.* PGM from chromitite matrix (light gray) with serpentine intergrowths and serpentine-type surface sculpture. Serpentine is dark-gray

silicates – amphibole, Cr-diopside and olivine (Fig. 1) that crystallized prior to and together with their host chromite, but such mineral and compositional paragenesis excludes magmatic origin. The chromites also associate with a skarn-like assemblage of diopside, amphibole, garnet (andradite-grossular), phlogopite, glagolevite, apatite, chlorite, serpentine etc (Arai et al., 2014).

The PGM-bearing Cr-spinel from the Kondyor massif contains numerous trails of octahedral gaseous inclusions (Fig. 2) that are randomly disturbed and bear no evidence of magmatic crystallization of the host chromite. The chromite and PGM in the most massifs contact with phlogopite, chlorite and serpentine has "imprints" of these minerals on its surface (Fig. 3). Later PGM, such as cuprous platinum, form porous aggregates and dendrites intergrown with serpentine.

All these geological, structural and compositional features of the PGM-rich chromitites allow to assume their non-magmatic origin related with the re-distribution of components and mineral nano- and micro-particles within dunite at low temperature conditions in the presence of fluid.

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# NOBLE METALS IN THE CHROMIUM ORES OF LAGORTINSKO-KERSHORSKY AREA (POLAR URALS)

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**ABSTRACT**. Two generations of laurite, copper gold, copper with a high content of platinum and microinclusions of palladium palladium-bearing PGM (e.g., sobolevskite, potarite and probably zvyagintsevite, and plyumbopalladinite), and unnamed minerals of complex composition (Pt-Ir-Rh and Pt-Pd-Rh sulphides) have been recognized.

Sulphide and platinum-group minerals (PGM), mainly Pt-Os-Ir-Ru phases, are well known in chromium ores and rocks of Voykarosyninsky massif (Anikina, 1995; Gurskaya et al., 2004). In recent years, a copper-gold-platinum-palladium occurrences characterized by different composition and the platinum ratio with palladium predominance were discovered in the northern part of the massif in chromitites associated with clinopyroxenites, located in the Lagortinsko-Kershorsky area (Kuznetsov et al., 2007; Pystin et al., 2011).

This contribution presents a mineralogical investigation based on the presence of PGM in these chromitites. The most common PGM is laurite (Fig. 1a). It generally occurs in the chromite ore and is formed (1) at early stage simultaneously with crystallization of chromite (minerals of the laurite–erlichmanite serie) and (2) at later stage characterized by the addition of antimony and arsenic, and the redistribution of osmium and iridium. The first occurrence is represented by a set of isometric inclusions in chromite up to 10 microns. Average chemical formula corresponds to the $(Ru_{0.67}Os_{0.23}Ir_{0.12})_{1.02}S_{2.00}$. The second occurrence forms angular grains in caverns and fissures in chrome spinel. It has dimensions up to 7 microns; antimony (up to 1.10 wt. %) and arsenic (up to 5.94 wt. %). Average formula corresponds to $(Ru_{0.67}Ir_{0.17}Os_{0.16})_{1.00}As_{0.08}S_{2.00}$. Also we found grains and inclusions close to erlichmanite ($OsS_2$), with Os up to 47.5 wt %. Ru-Os sulfides of the laurite-erlichmanite serie are known to be the most common minerals in the chromite-rich ores of the Voykaro-Syninsky massif (Anikina, 1995). Irarsite and iridian osmium (Fig. 1b, c) have been observed in some laurite grains. Irarsite represents angular grains confined to the areas of fracture, cavities in chromite with grain sizes up to 5 microns, and is also found in the laurite edges as a result of redistribution of Os-Ir-Ru elements. An average crystal-chemical formula of the mineral is $(Ir_{0.79}Ru_{0.09}Rh_{0.04})_{0.92}As_{0.74}S_{1.00}$. Crystal-chemical formula of iridian osmium corresponds to $Os_{0.71}Ir_{0.24}Ru_{0.05}$.

Copper with high platinum content was found in the structure of millerite decay (Fig. 1d). Copper forms an elongated grain with size of several microns. It is composed by Cu up to 38.20 and Pt up to 35.24 wt. %. In addition it includes an admixture of Sn up to 2.54 wt % (sum of the components is 76.37 wt. %). Calculated crystal-chemical formula of this phase is $(Pt_{0.90}Sn_{0.12})_{1.02}Cu_{3.00}$.

Palladium minerals have 0.2-5.0 microns in size. They form tiny inclusions in millerite. Sobolevskite (Fig.1e) and potarite have average formulas $Pd_{1.26}(Bi_{0.99}As_{0.01})_{1.00}$ and $Pd_{1.22}Hg_{1.00}$, respectively. Potarite is usually characterized by a small deficit of mercury that is likely due to a reduction during microprobe analysis. Interestingly, the potarite and sobolevskite previously were observed in Syumkeusky ultramafic massif, located to the north from Voykarosyninsky (Gurskaya & Smelova, 2003). Pd, Pb and Hg were found as main components in some submicron grains. Calculated formulas correspond to zvyagintsevite estimated average chemical composition of which has the form $Pd_{3.65}Pb_{1.00}$, $(Pd_{2.99}Hg_{0.34})_{3.33}Pb_{1.00}$ or to a lesser extent, plyumbopalladinite – $Pd_3Pb_2$.

In addition, several PGM grains are intergrown with pentlandite (Fig.1f). In most cases, their

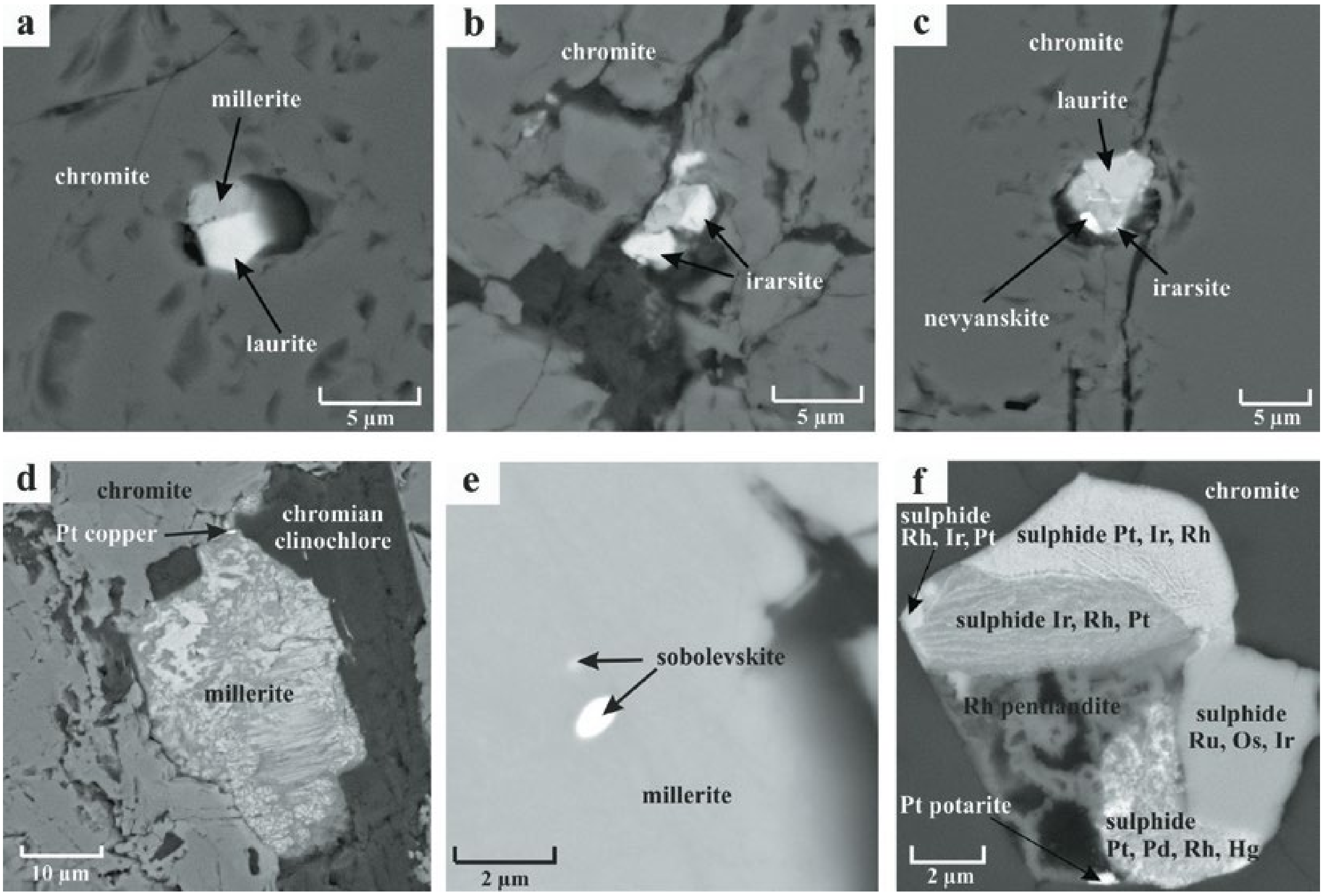

*Fig. 1.* Scanning electron-micrographs showing different PGM found in the chromitite of Lagortinsko-Kershorskaya area: a – aggregate of millerite and laurite in chromite; b – irarsite in chromite; c – Os-Ir-Ru phase in chromite; d – millerite and Pt-rich copper in contact with chromite and chromian clinohlore, e – sobolevskite in chromite; f – aggregate of unnamed Pt-Ir-Rh and Pt-Pd-Rh sulphides with Rh-rich pentlandite.

composition is controlled by the Pt-Ir-Rh system together with Fe-Ni-S or Pt-Pd-Rh together with Fe-Ni-Cu-Hg-S. In the first case (Fig.1f, top) three phases characterized by different proportion of Pt-Ir-Rh were observed. PGE contents vary in the following limits (wt%): Pt – 7.28-30.53, Ir – 17.7-20.3, Rh – 3.93-43.4, accompanied by Fe – 22.4-36.6, Ni – 3.85-20, S – 3.39-24.63. In the second case (Fig.1f, bottom) two phases associated with pentlandite contain Pt (5.28-29.21 wt.%), Pd (11.70-31.70 wt.%), Rh (up to 1.86 wt. %) and Hg (17.69-62.00 wt. %:).

As a result of research within the Lagortinsko-Kershorsky area (Polar Urals), we conclude that two generations of laurite, copper gold, copper with a high content of platinum and microinclusions of palladium (presented by sobolevskite, potarite and probably zvyagintsevite and plumbopalladinite) and unnamed minerals of complex composition (e.g., Pt-Ir-Rh and Pt-Pd-Rh sulphides) were recognized.

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# PGE, Au AND Ag IN SUPERGENE NICKEL DEPOSITS ON OPHIOLITIC COMPLEXES IN URALS

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**ABSTRACT**. PGE and noble metals content are discussed in the Buruktal, Ufaley, Serov and some other deposits associated with large ultramafic complexes of the Ophiolitic belt in the Urals. Noble metals minerals described in these deposits mainly consist of native Pt, Pd, Au and Ag. Comparison of paragenetic association of platinum group minerals in the supergene nickel deposits with primary ultramafites of the ophiolite complexes shows a significant difference between them. Newly formed supergene minerals of platinum group elements and gold are probably the most abundant phases in the supergene nickel deposits of the Urals.

Most of the supergene nickel deposits associates with ophiolite complexes occur in the tropical zone of the Earth. In Russia, there are the Serov, Ufaley, Kempirsay, Buruktal and some other deposits, formed in large ultramafic complexes of the Ophiolite belt of the Urals. Primary harzburgites of these complexes are characterized by low PGE content ($\sum PGE=33.5$ ppm) and Ru-Ir-Os specialization (Zoloyev et al., 2001, Lazarenkov & Talovina, 2001).

Geochemical peculiarities of PGE behavior in weathering processes were previously discussed using the example of the Buruktal deposit (Talovina, 2012; Lazarenkov et al., 2006; 2011). The PGE content in nickel ores of this deposit are presented at the table 1. According to table 1, the schema of PGE specialization in nickel ores of the Buruktal deposit corresponds to (Ru>Pd>Pt>Ir>Os>Rh). Maximum PGE and noble metals content were found in asbolan-goethite rocks, where the concentration of Os+Ir+Ru is higher than those of Pt+Pd.

The average PGE and Au content in nickel ores of the Ufaley deposit is shown in table 2. The maximum Pt concentration is observed in the clinochlore-goethite nickel ores (0.436 ppm) and maximum Pd content in the pecorait-chrysotile-quartz ores (0.068 ppm). In the clinochlore-goethite and pecorait-chrysotile-quartz ores Pd prevails over Pt. All types of the nickel ores contain relatively high concentrations of gold.

Data on the PGE content in nickel ores of the Elov deposit were published by Volchenko et al. (1998) and by Lazarenkov et al. (2011). Geochemical data of this deposit are given in table 3.

The total PGE content in nickel ores of the Elov deposit is about 0.077 ppm in goethite ores, 0.263 ppm in chamosite ores and 0.253 ppm in lizardite serpentinites. The total amount of noble metals is maximal in chamosite rocks – 1.213 ppm, i.e. two times higher than in lizardite serpentinites – 0.576 ppm, and it is the lowest in the goethite rocks – 0.116 ppm.

Minerals of noble metals in ores of the Buruktal, Ufaley and Elov deposits are represented, mainly, by native Pt, Pd, Au and Ag. Their relict and newly formed supergene PGM grains show irregular shape and have a size variable from 0.1 to 120 microns. Native gold occurs as smaller grain, 5-15 microns in size and rarely up to 160 microns. Their composition corresponds to fine gold $Au_{94.83}Ag_{4.87}Cu_{0.62}$ with impurities of silver (2.94-9.4 wt %) and less amounts of copper, nickel and cobalt. In nickel ores of the Buruktal deposit were found a specific phase of iodide silver with admixture of sulfur, iron, silicon and aluminium.

Comparison of paragenetic association of platinum group minerals in the supergene nickel deposits with primary ultramafites of the ophiolite complexes shows a significant difference between them. In the ultramafite bedrock Os, Ir, Ru phases, in particular sulfides, are predominant. Most of them were found in chromitites (Zoloyev et al., 2001, Lazarenkov & Talovina, 2001) and very few data are available for the presence of PGM in dunite and harzburgite (Moloshag & Smirnov,

Table 1

**The average PGE, Au and Ag content in nickel ores of the Buruktal deposit, ppm**

| *Nickel ores* | *n* | *Ru* | *Rh* | *Pd* | *Os* | *Ir* | *Pt* | $\sum$ *PGE* | *Au* | *Ag* | *NM* | $\frac{\mathrm{Os+Ir+Ru}}{\mathrm{Pt+Pd}}$ | *Pt/Pd* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Quartz-goethite | 40 | 0.033 | 0.005 | 0.033 | 0.014 | 0.014 | 0.031 | 0.130 | 0.064 | 0.065 | 0.260 | 0.88 | 0.93 |
| Asbolane-goethite | 15 | 0.060 | 0.005 | 0.037 | 0.014 | 0.018 | 0.037 | 0.170 | 0.088 | 0.100 | 0.359 | 1.16 | 1.00 |
| Nontronite | 7 | 0.002 | 0.003 | 0.029 | 0.010 | 0.020 | 0.031 | 0.095 | 0.020 | 0.060 | 0.175 | 0.51 | 1.07 |
| Lizardite serpentinites | 30 | 0.026 | 0.004 | 0.023 | 0.013 | – | 0.016 | 0.082 | 0.036 | – | 0.118 | 0.91 | 0.69 |

*Note*: n is the number of samples, «–» – was not determined, NM – sum of the noble metals.

Table 2

**The average PGE and Au content in nickel ores of the Ufaley deposit, ppm**

| *Nickel ores and rocks* | *n* | *Ru* | *Rh* | *Pd* | *Ir* | *Os* | *Pt* | *PGE* | *Au* | *ΣNM* | *Pt/Pd* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Clinochlore-goethite | 20 | 0.018 | 0.004 | 0.050 | 0.015 | – | 0.030 | 0.117 | 0.466 | 0.583 | 0.60 |
| Asbolane-goethite | 10 |  | – | 0.021 | – | – | 0.050 | 0.071 | 0.025 | 0.092 | 2.38 |
| Lizardite serpentinites | 30 | 0.004 | 0.021 | 0.016 | 0.011 | 0.006 | 0.035 | 0.093 | 0.170 | 0.263 | 2.19 |
| Pecorait-chrysotile-quartz | 5 | – | 0.020 | 0.068 | – | – | 0.040 | 0.127 | 0.095 | 0.222 | 0.59 |
| Harzburgites of substrate |  | 0.0083 | 0.0009 | 0.0061 | 0.0034 | 0.0047 | 0.0064 | 0.0298 | 0.0136 | 0.043 | 1.05 |

*Note*: n is the number of samples, «–» – was not determined, NM – sum of the noble metals.

Table 3

**The average PGE and Au content in nickel ores of the Elov deposit, ppm (Talovina, 2012)**

| *Nickel ores* | *n* | *Ru** | *Rh* | *Pd* | *Os** | *Ir** | *Pt* | *PGE* | *Au* | *ΣNM* | *Pt/Pd* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Goethite | 20 | 0.004 | 0.006 | 0.031 | 0.007 | 0.010 | 0.035 | 0.077 | 0.038 | 0.116 | 1.1 |
| Chamosite | 50 | – | – | 0.230 | – | – | 0.033 | 0.263 | 0.950 | 1.213 | 0.2 |
| Lizardite serpentinites | 20 | – | 0.013 | 0.157 | – | – | 0.083 | 0.253 | 0.323 | 0.576 | 0.5 |

*Note*: n is the number of samples, «–» – was not determined, NM – sum of the noble metals, * – after Y.A. Volchenko & Friend (1997).

1996, Lazarenkov et al., 2011). Native alloys of platinum and palladium is mostly observed in the supergene nickel ores. Obviously, newly formed supergene minerals of platinum group metals and gold are the most abundant phases in the supergene nickel deposits of the Urals.

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# PLATINUM GROUP ELEMENTS AND GOLD IN SUPERGENE NICKEL DEPOSITS IN ZONAL ULTRAMAFIC MASSIFS OF THE URALS

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**ABSTRACT**. PGE distribution in supergene nickel deposits developed on two zonal ultramafic massifs of the Urals is reported. The sum of Pt+Pd in nickel ores is higher than those of IPGE (Ru+Os+Ir) in supergene nickel deposits, and platinum dominates over palladium (Pt/Pd>1) in goethite ores of the deposits. Average PGE content in the goethite ores of the upper zone of the deposits is higher than in supergene serpentinites. Most grains of platinum group minerals in the nickel ores consist of native alloys, predominantly platinum and palladium of supergene origin.

Supergene nickel deposits on zonal ultramafic massifs in Urals namely Sakhara deposit, developed on the Sakharinsky dunite-clinopyroxenite massif, and the former Elizavet iron-cobalt-nickel deposit, developed on the Uktus zonal massif. Distribution of platinum group elements (PGE) in the Sakharinsky massif is unknown now; data on PGE content in primary dunites and clinopyroxenites of the Uktus massif is listed in Table 1 after Garuti and others (Garuti et al., 2003).

According to our data (Lazarenkov et al., 2006), bedrock of the zonal Ural-Alaskan type massifs of the Urals contain platinum alloys, especially isoferroplatinum, as the most abundant PGM.

Geochemical characteristics of PGE in nickel ores and rocks of the Sakhara deposit were discussed by us previously (Lazarenkov et al., 2006, Talovina, 2012) and are shown in the Table 2.

As shown in Table 2, iron-cobalt-nickel ores of the Elizavet deposits take platinum specialization over the dunites of the Uktus massif. The ores of the iron-oxide (goethite) zone contain up to 0.5 ppm total amount of PGE. Nickel ores of the Sakhara deposit contain mainly Pd and Pt. In the lizardite serpentinites of the lower zone of the deposit, Pd noticeably prevails over other PGE. In nontronite zone PGE show an enrichment in Pt-Pd and in the upper iron-oxide zone Pt dominates over the rest of the PGE. Gold has a maximum content in quartz-goethite ores of the upper zone of the deposit (0.050 ppm).

The PGM of the Elizavet deposits consist of native platinum and palladium (Lazarenkov & Talovina, 2001). Platinum is found in goethite ores, accompanied by mineral phases of palladium, such as Pt-Pd alloys with impurities of bismuth, antimony and tin. The grains have colloform structure and a size of 3-5 micron.

List of platinum group minerals in supergene ores of the Elizavet deposit (Lazarenkov & Talovina, 2001) is quite different from those of the Uktus massif primary rocks (Garuti et al., 2003) as well as from those reported from alluvial-eluvial sediments in the Uktus massif (Zaccarini et al., 2013).

Thus, according to our data, sum of Pt+Pd is higher than those of IPGE (Ru+Os+Ir) in supergene nickel deposits, and platinum dominates over palladium (Pt/Pd>1) in goethite ores of the deposits. Average PGE content in the goethite ores of the upper zone of the deposits is higher than in supergene serpentinites. Most grains of PGM in the nickel ores consist of fine native alloys, predominantly platinum and palladium of supergene origin.

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Table 1

**PGE and Au content in dunite and clinopyroxenites of the Uktus massif (Garuti et al. 2003), ppm**

| *Rock* | *Os* | *Ir* | *Ru* | *Rh* | *Pt* | *Pd* | *Au* | *Pt/Pd* |
|---|---|---|---|---|---|---|---|---|
| Chromitite (3) | 72.3 | 351.0 | 60.9 | 27.7 | 159.0 | 13.8 | 75.6 | 11.50 |
| Dunite (4) | 3.5 | 6.5 | 7.4 | 1.4 | 66.5 | 7.1 | 14.2 | 9.33 |
| Ol-gabbro (1) | 0.6 | 0.3 | 0.5 | 0.2 | 18 | 18 | 10 | 1.00 |
| Gabbro (1) | 4.2 | 1.4 | 3.3 | 1.2 | 50 | 48 | 6.5 | 1.04 |
| Pyroxenite (1) | 2.1 | 0.4 | 1 | 0.4 | 24 | 8.8 | 9.1 | 2.73 |

Number of grains in brackets

Table 2

**The average PGE and Au content in nickel ores of the Sakhara and Elizavet deposits, ppm**

| *Rocks* | *Ru* | *Rh* | *Pd* | *Os* | *Ir* | *Pt* | *Pt/Pd* | *Au* |
|---|---|---|---|---|---|---|---|---|
| Sakhara deposit | | | | | | | | |
| Quartz-goethite (20) | 0.080 | 0.018 | 0.075 | 0.018 | <0.01 | 0.244 | 3.3 | 0.050 |
| Nontronite (40) | 0.032 | 0.035 | 0.316 | 0.024 | <0.01 | 0.232 | 0.7 | 0.020 |
| Lizardite serpentinite(40) | 0.019 | 0.076 | 0.280 | 0.034 | <0.01 | 0.060 | 0.2 | 0.020 |
| Elizavet deposit | | | | | | | | |
| Goethite(2) | 0.068 | 0.010 | 0.031 | 0.012 | <0.01 | 0.380 | 12.2 | <0.02 |
| Nontronite (2) | 0.050 | 0.005 | 0.075 | 0.013 | <0.01 | 0.180 | 2.4 | <0.02 |
| Lizardite serpentinite (2) | 0.066 | 0.005 | 0.045 | 0.070 | <0.01 | 0.038 | 0.8 | <0.02 |
| Chrysotile serpentinite (2) | 0.018 | <0.005 | 0.008 | 0.004 | <0.01 | 0.070 | 8.7 | <0.02 |

Number of grains in brackets

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# PLATINUM-GROUP MINERALS (PGM) NUGGETS FROM THE URAL-ALASKAN TYPE COMPLEX OF UKTUS (CENTRAL URALS, RUSSIA): GENETIC ASPECTS

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**ABSTRACT**. Platinum group minerals (PGM) and copper-gold nuggets have been found in the Uktus Ural-Alaskan type complex, Central Urals (Russia). Our data suggest the existence two types of PGM nuggets: i) primary with a magmatic origin, i.e., only mechanically liberated from their source rock, and ii) secondary, i.e., reworked and probably grown in the placers.

Few tens of platinum group minerals (PGM) and copper-gold nuggets have been found in the Uktus Ural-Alaskan type complex located in the southern outskirts of Yekaterinburg, Central Urals (Russia). The investigated nuggets were collected in alluvial-eluvial deposits from 3 small valleys, with temporary water flows, cutting across the Uktus massif. The volume of the washed samples varies from 0.03 to 0.08 m$^3$. The PGM nuggets have a size variable from about 100 µm up to about 2 mm, and occur as polygonal grains or they show an irregular morphology characterized by the presence of a porous rim and zoning. On the basis of electron microprobe analyses, they mainly consist of iridium, osmium and alloys in the Pt-Fe-Cu-Ni system, accompanied by minor sulfarsenides of the irarsite-hollingworthite-platarsite series, sulfides such as laurite, cuproiridsite, kashinite and the sulfantimonide tolovkite. One alloy corresponding to the formula $Cu_3Au_2$ was analyzed and, according to x-ray data, proved to be a Cu-rich tetraauricupride. The Uktus nuggets occur as monophase crystals or they form polyphase grains, composed of different PGM. One nugget consists of a Pt-Fe alloy associated with osmium and Cu-rich tetraauricupride (Fig. 1). These minerals are in contact with quartz that contains tiny inclusions (about 2 µm in size) of hollingworthite and

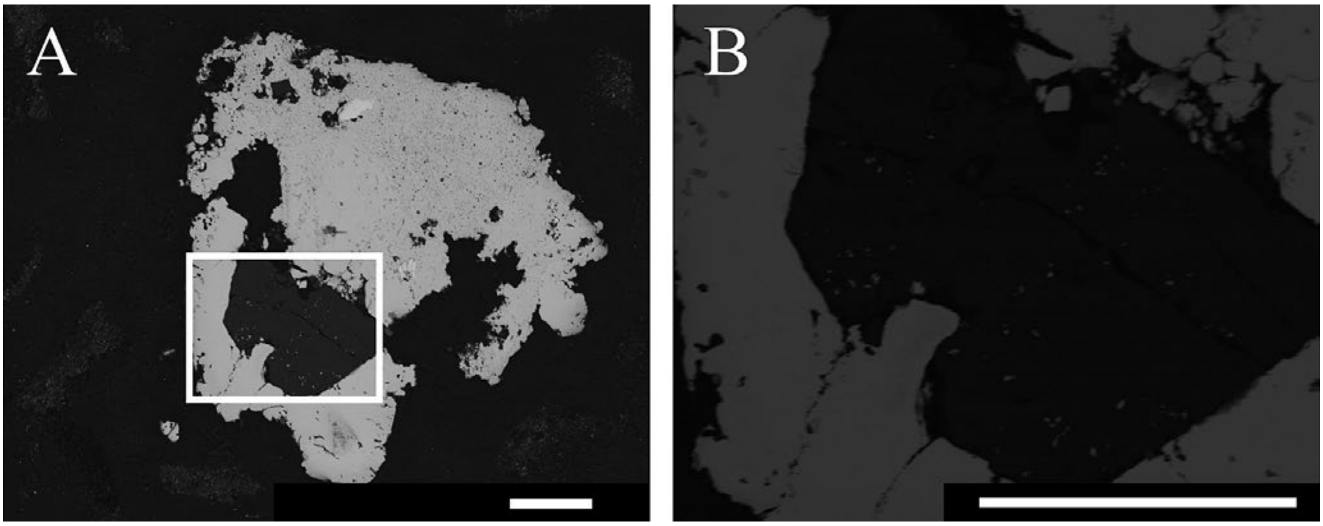

*Fig. 1.* SEM-BSE images of Uktus PGM nugget composed of (A) Pt-Fe alloy, $Cu_3Au_2$ and osmium, (B) enlargement of (A) showing an inclusion of quartz containing small spot of irarsite and hollingworthite. Scale bar is 50 µm

platarsite. The mineralogical similarity with the PGM previously reported in the Uktus chromitites indicate that these rocks represent the primary source for the discovered PGM nuggets. The faceted morphology characterizing some nuggets suggests that they were mechanically liberated from their lode deposits, and transported only for a short distance. The nuggets characterized by a rounded shape and occurring in association with quartz and Cu-rich tetraauricupride were reworked in the placer environment. We can conclude that in the Uktus placers deposits contain two types of PGM nuggets:

i) primary with a magmatic origin, i.e., only mechanically liberated from their source rock,

ii) secondary, i.e., reworked and probably grown in the placers. The discovery of a Cu-rich tetraauricupride and its crystal-structure investigation allowed to provide a better definition of phase relations in the Cu-Au system (Zaccarini et al., 2013).

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# SESSION 8

## Open Session

**Conveners: Elena Anikina & Frank Melcher**

This session intends to highlight various aspects of PGE research in geological environments that are not covered by topics of the other sessions. The session also welcomes contributions with focus on PGE and PGM related to osmium isotopes, analytical methods, mineral processing, including quality and process control, hydrometallurgical processing, refining and product developments.

# MAGMATIC AND SUPERGENE EVOLUTION OF THE UNCONVENTIONAL PIROGUES Pt MINERALIZATION IN THE NEW CALEDONIA OPHIOLITE

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**ABSTRACT**. The New Caledonia ophiolite is host to an unconventional Pt-Cr mineralization, located at the base of a magma chamber, itself presenting specific differences compared to the other cumulate sequences of the ophiolite. The primary mineralization and its magmatic environment are presented. The strong weathering having affected the mineralized zone has provoked a decoupling between the Cr and the Pt mineralization, with dissolution of the Pt minerals and their redistribution in the profile owing to heterogeneities in the porosity of the weathered profile. Moreover, weathering conditions having affected the PGM have locally provoked the formation of oxygen-bearing Pt-Fe grains according to a mechanism that will be proposed.

## GEOLOGY

The New Caledonia ophiolite, covering about 40% of the island (i.e. about 7500 km$^2$), forms a now discontinuous nappe, 1.0-3.5 km thick, emplaced during the Late Eocene. It is mainly composed of mantle harzburgite with minor dunite bodies, except in its southern part where cumulate series occur, not thicker than 700 m, dominated by ultramafic rocks. The Pirogues River sequence, one of six cumulate localities, is characterized by an unconventional Pt-Cr mineralization. The sequence consists of a massive basal dunite unit grading up into a layered orthopyroxene-dominated pyroxene-peridotite unit. The upper part of the dunite unit and the whole pyroxene-peridotite unit are cut by dykes of various rock types and thickness, and both units contain rare, small (cm-size), chromite schlieren.

The Pirogues River sequence is significantly different in terms of mineral composition from the other five sequences, having a relatively high Fe/Mg ratio in the silicates, highly Al-Cr-impoverished pyroxenes, and Fe$^{3+}$-enriched chromite that suggests derivation from a different magma, possibly with a boninitic composition related to a second-stage hydrous melting in a supra-subduction environment.

The pyroxenite dykes comprise >80% pyroxene along with olivine and rare magmatic amphiboles, and contain disseminated euhedral chromite; most facies are ad- to meso-cumulate. The orthopyroxene/clinopyroxene ratio is varied, generally with dominant orthopyroxene, and the facies include orthopyroxenite, clinopyroxenite, websterite, harzburgite, and lherzolite. The mineralogical composition can change very rapidly, even within a single dyke.

## MINERALIZATION

The Pt mineralization at Pirogues is found systematically in chromite-rich rocks. These form: 1) 'stratiform' chromite concentrations in the basal dunite and pyroxene peridotite cumulates; and 2) irregular, commonly elongate, chromitite pockets, systematically PGE-enriched, that can be as much as 1-m long and 10-cm thick with generally sharp and unusual textures. In these pockets, chromite crystals are small (<100 µm) and euhedral. Pt-Cr-rich dykes are distributed within an area of about 1000 by 500 m. Pt in the chromite-rich rocks varies from 500 ppb to 36.5 ppm and roughly correlates with $Cr_2O_3$. Pt systematically dominates the other PGE with a Pt/(ΣPGE) ratio generally ranging between 5 and 15. The PGE form PGM that (>90%) are included in, or attached to, chromite crystals, with the most common phases being Pt-Fe alloys (isoferroplatinum, tetraferroplatinum, tulameenite), followed by cooperite, laurite, bowieite, malanite, cuprorhodsite and a few base-metal sulphides (BMS) with PGE in solid solution.

Like all of New Caldeonia, the Pirogues sector has undergone strong lateritic alteration. Study of PGM in weathering profiles showed Pt mobility with dissolution figures of Pt-Fe grains, as well as images of concentrically zoned PGM grains that were first interpreted as secondary formed parti-

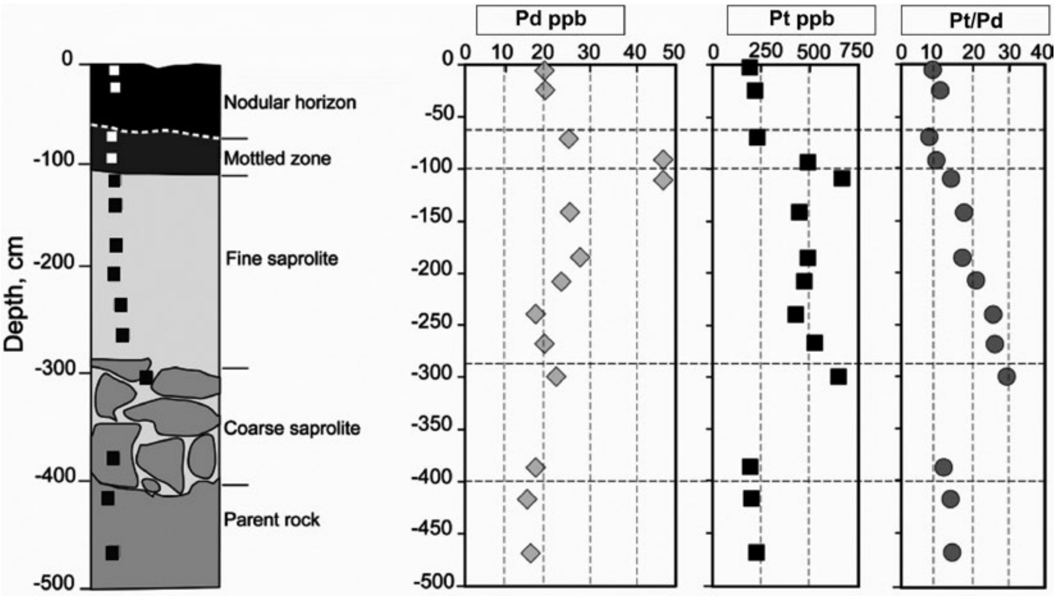

*Fig. 1.* Pd, Pt and Pt/Pd ratio of samples collected in the weathered profile of the Pirogues mineralized area. Position of the samples in the profile is indicated by squares (after Traoré et al., 2008)

cles, similar in texture to iron pisolites. Microprobe analyses of these grains revealed for the first time the natural occurrence of PGE oxides (Augé & Legendre, 1994), which were initially interpreted as formed under surface conditions after remobilization and reconcentration of PGE (and their crystallization as oxides). This model was further supported by that fact that laterite was enriched in Pt, disconnected from any Cr enrichment. Detailed investigation of the weathering profiles confirmed that Pd is more mobile than Pt (Traoré et al., 2008, Fig. 1). However, it also showed that PGM liberated during the supergene dissolution of chromite can accumulate in the lower parts of the profiles, fine Pt-rich particles being driven by water percolation through the connected pore space and accumulating in the lower part of the profile where porosity decreases, thus explaining the decoupling between Pt and Cr concentrations. However, the origin of the Pt-Fe oxides remains partly unknown, with for example two-phase grains composed of a Pt-Fe alloy associated with a Pt-Fe oxide. Further work on characterizing such grains (Hattori et al., 2010) explained the formation of the O-bearing Pt-Fe with the following process. In Stage 1 within ultramafic rocks, highly reducing alkaline waters can remove Fe$^0$ from isoferroplatinum as Fe$^{2+}$. The removal of Fe$^0$ likely produces the porous texture and shrinkage cracks of isoferroplatinum grains, common in the area. During this stage, Pt$^0$ is stable and likely remains in isoferroplatinum. Further erosion of the rocks leads to an incursion of oxygenated alkaline surface water that dissolves Pt$^0$ and washes Pt away as soluble Pt$^{2+}$-OH complexes. Fe$^{2+}$in solution starts to precipitate in voids as Fe$^{3+}$-O-OH. This simultaneous dissolution of Pt$^0$ and precipitation of Fe$^{3+}$-O-OH likely produced a delicate mixture of isoferroplatinum and Fe$^{3+}$-O-OH, which initially was interpreted as PGE oxide.

## CONCLUSIONS

The Pirogues River ultramafic sequence in the New Caledonia ophiolite has many unique aspects. It is a quite uncommon occurrence of Pt-rich chromite mineralization in ophiolite, generally characterized by an Os-Ir-Ru PGM mineralization in podiform chromitite. In addition, it is also a spectacular example of the effect of strong lateritic weathering on Pt-mineralization and Pt minerals.

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# MINERAL CHEMISTRY AND ISOTOPIC COMPOSITION OF OPHIOLITIC Os-RICH ALLOYS AND Ru-Os SULFIDES: SYNTHESIS OF NEW DATA

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**ABSTRACT**. The study presents textural and mineral chemistry data, as well as whole-rock and mineral separate Os-isotopic compositions for PGM assemblages from deep portions of the oceanic mantle. The extensive data set of Os-isotope compositions of intimately intergrown grains of Os-rich alloy and Ru-Os sulfide from ophiolite-type massifs of different ages is firstly evaluated. The Os-isotope results identify a restricted range of 'unradiogenic' $^{187}Os/^{188}Os$ values for coexisting laurite and Os-rich alloy pairs that form 'primary' PGM assemblages at Hochgrössen, Shetland, and Verkh-Neivinsk. Similarly 'unradiogenic' $^{187}Os/^{188}Os$ values have been identified in the chromitite and mineral separates from 'primary' and 'secondary' PGM assemblages, implying that the whole-rock Os-isotope budget is largely controlled by the laurite-alloy pair.

Osmium isotopes are an important tracer of the evolution of highly siderophile elements in the upper mantle. The depleted upper mantle, as sampled by abyssal peridotites and the mantle sections of ophiolites, constitutes one of the most important geochemical reservoirs, which is not yet well constrained. Primary Os-rich platinum-group minerals (PGM) (e.g., laurite-erlichmanite series ($RuS_2$-$OsS_2$) and Os-Ir-Ru alloys), which form inclusions in chromites, are particularly well protected by the host mineral and are thus likely to retain initial Os isotopic values of the source, from which they were derived.

The extensive data set of bedrock and detrital PGM grains from ophiolite-type massifs of different ages (i.e., Neoproterozoic Kunar in northern Taimyr, Russia, and Hochgrössen in Eastern Alps, Austria, Paleozoic Verkh-Neivinsk in Middle Urals, Russia, and Shetland in northern Scotland) permits an evaluation of mineral chemistry and Os-isotopic composition of Ru-Os sulfides and Os-Ir-Ru alloys by a combined analytical approach using electron microprobe analysis and laser ablation (LA) attached to multiple-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS), respectively. The investigation also employed isotope dilution (ID) ICP-MS after high pressure acid digestion to evaluate platinum-group element concentrations and Os-isotopic composition of chromitites that host distinct PGM assemblages.

Two distinct platinum-group mineral (PGM) assemblages have been recognized: a 'primary' euhedral PGM assemblage, which occurs as inclusions in chromite, and a modified 'secondary' subhedral to anhedral PGM assemblage observed in cracks filled by chlorite or serpentine, interstitially to chromite grains (Badanina et al., 2013). The 'primary' PGM assemblage at Shetland and Hochgrössen is represented by solitary grains of laurite or iridian osmium and composite grains of laurite+osmian iridium±iridian osmium, whereas a 'secondary' PGM assemblage is defined by laurite, Os-rich laurite, irarsite, osmium and Ru-pentlandite. The 'primary' PGM assemblage at Verkh-Neivinsk and Kunar is dominated by Ru-Os-Ir alloy grains that commonly mantled by 'secondary' Ru-Os sulfide overgrowths.

Whole-rock platinum-group element (PGE) concentrations give negatively sloped chondrite-normalized PGE patterns, typical of podiform chromitite, where refractory PGE (Os, Ir and Ru) prevail over less refractory PGE (Rh, Pt and Pd).

The osmium isotope results identify (1) a restricted range of 'unradiogenic' $^{187}Os/^{188}Os$ values for coexisting laurite and Os-rich alloy pairs

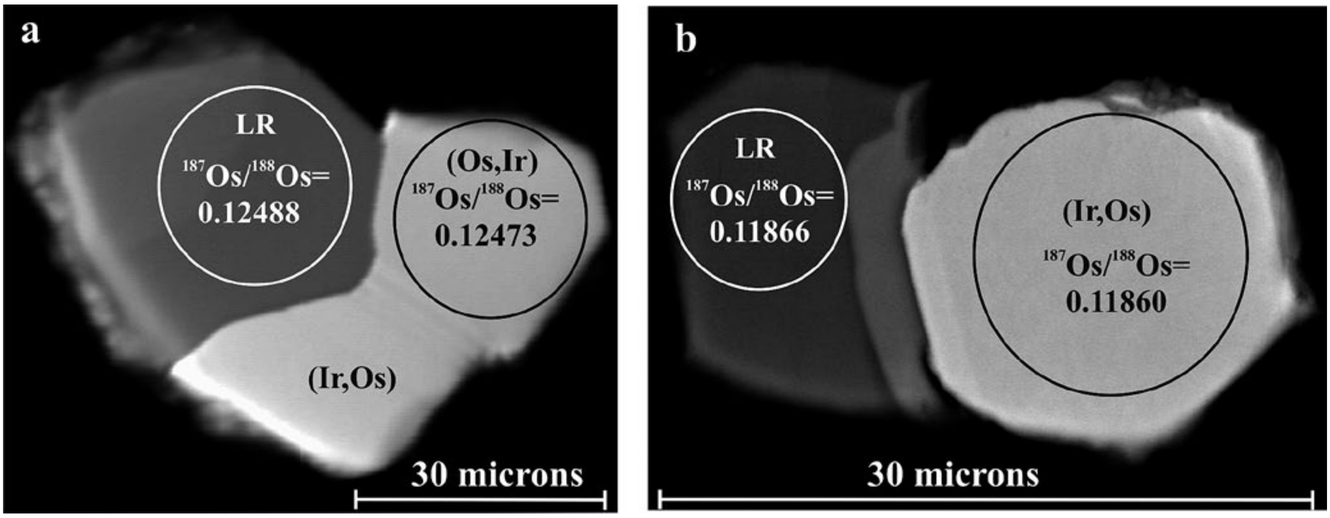

*Fig. 1.* Back-scattered electron images of euhedral composite PGM grains from podiform chromitite at Unst (a) and Hochgrössen (b). LR – laurite, (Ir,Os) – osmian iridium, (Os,Ir) – iridian osmium, circles denote areas of laser ablation MC-ICP-MS analyses

that form 'primary' PGM assemblages at Hochgrössen and Shetland (0.11860–0.11866 and 0.12473–0.12488, respectively, Fig. 1); (2) similar 'unradiogenic' $^{187}$Os/$^{188}$Os values for both 'primary' and 'secondary' PGM assemblages at Shetland (with a weighted mean of 0.12419 and 0.12464, respectively) and Verkh-Neivinsk (with several mean $^{187}$Os/$^{188}$Os values of 0.1164, 0.1178, 0.1188 and 0.1207), and (3) a wide scatter of subchondritic $^{187}$Os/$^{188}$Os values for 'primary' PGM assemblages at Kunar (i.e., $^{187}$Os/$^{188}$Os 0.11848–0.11239), Verkh-Neivinsk (0.11619–0.12565), and Hochgrössen (0.11860–0.12450).

The whole-rock Os-isotope budget of chromitite at Shetland (0.1240±0.0006) is largely controlled by laurite-dominant assemblages. At Shetland and Verkh-Neivinsk, the 'secondary' PGM assemblage inherited the 'unradiogenic' Os-isotope signature of the 'primary' PGMs. No evidence for other source contributions during later thermal events has been observed. However, a wide range of subchondritic $^{187}$Os/$^{188}$Os values has been found in the 'primary' PGM assemblages (e.g., laurite and Os-rich alloys) from the ophiolite-type complexes worldwide (Malitch, 2004; González-Jiménez et al., 2014 and references cited therein). This wide range would be consistent with a model, in which a prolonged history of melting events of parent ultramafic source rocks took place in the mantle. This variability is in agreement with the conclusion that the Os-isotope system of PGMs records multiple events during the chemical differentiation history of the mantle (Carlson, 2002) and could have been controlled by deep geodynamic processes (Dobretsov & Kirdyashkin, 1998). On the other hand, the observed Os-isotope heterogeneity may be also attributed to the presence of subcontinental lithospheric mantle (SCLM), characterized by highly unradiogenic $^{187}$Os/$^{188}$Os values (i.e., <0.1220), that has subsequently been incorporated into asthenospheric mantle with more radiogenic $^{187}$Os/$^{188}$Os values (0.1220-0.1230).

*Acknowledgments. The study was supported by the Russian Foundation for Basic Research (grant 12-05-01166-a) and the Ural Branch of Russian Academy of Sciences (project 12-P-5-1020).*

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# PLATINUM GROUP ELEMENT GEOCHEMISTRY IN GRANITOIDS AS A FERTILITY INDICATOR FOR GOLD AND COPPER MINERALIZATION

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**ABSTRACT**. Platinum group element geochemistry has been used to identify sulfide saturation in two ore bearing and three felsic magma systems. The results show that the barren suites were subject to a high rate of sulfide precipitation early in their evolution when compared to the ore-bearing suites. The timing and rate of sulfide precipitation determine whether or not a suite is ore bearing, and if it is ore bearing, whether the mineralization is Cu, Cu-Au or Cu-Au-Pd.

## INTRODUCTION

The link between copper, copper-gold and felsic rocks is well known (Robb, 2005). What is not known is why some felsic suites are ore-bearing while other, apparently similar suites, are barren. What is the fundamental difference between barren and fertile granitic systems? Our starting hypothesis was that if a magma becomes saturated with an immiscible sulfide melt prior to becoming volatile-saturated, the chalcophile elements (Cu, Au, Pt, Pd, etc.) will be locked in a sulfide phase in an underlying magma chamber where they are less available to dissolve in a hydrothermal fluid and form a Cu or Cu-Au deposit. Alternatively, if the magma becomes volatile-saturated before it becomes sulfide-saturated, the chalcophile elements remain in the melt and are available to be collected by a degassing volatile phase and/or ore-forming hydrothermal fluid.

## RESULTS

We have tested this hypothesis by analysing the platinum group of elements (PGEs) in two ore-bearing and several barren suites of felsic rocks. Preliminary results are most encouraging. Fig. 1 shows a plot of Pd against MgO for a suite of Cu-bearing felsic rocks from El Abra in Chile, and the Cadia Cu-Au porphyry from NSW, compared with three barren suites; the ilmenite and magnetite series granites from Japan, and the Rachite suite from Argentina. Note that for samples with MgO > 3wt.%, the Pd content of samples from the ore-bearing suites are at least an order of magnitude higher than for samples from barren suites. The reason for this difference is that the barren Japanese and Rachite suites became sulfide-saturated early in their evolution, at MgO > 6 wt.%, whereas the ore-bearing El Abra suite did not become sulfide-saturated until the MgO content of the magma fell to 2.7 wt.% MgO. Although Cadia may have reached sulfide-saturation at an early stage of fractionation, the rate of sulfide precipitation was markedly less than for El Abra.

## DISCUSSION AND CONCLUSIONS

The El Abra study showed that our original hypothesis was incorrect. Sulfide saturation in the El Abra suite occurs at 2.5 wt.% MgO whereas volatile saturation, as determined from the composition of the ore-associated porphyries, is delayed until 1.2 wt.% MgO. Why can the El Abra system precipitate an immiscible sulfide melt prior to volatile saturation and still produce an economic Cu deposit? The factor we overlooked is that it is not just the timing of sulfide saturation but also the rate of sulfide precipitation. The effect of varying the rate of sulfide fractionation has been modelled assuming the following sulfide/silicate partition coefficients: $D_{Cu}=10^3$, $D_{Au}=10^4$ and $D_{Pd}=10^6$ (Mungall & Brenan, 2014). The results show that if the fraction of sulfide melt to precipitate is 1%, Cu, Au and Pd in the silicate melt are all rapidly depleted by fractional crystallisation so that by 20% fractionation, the Cu content of the melt has

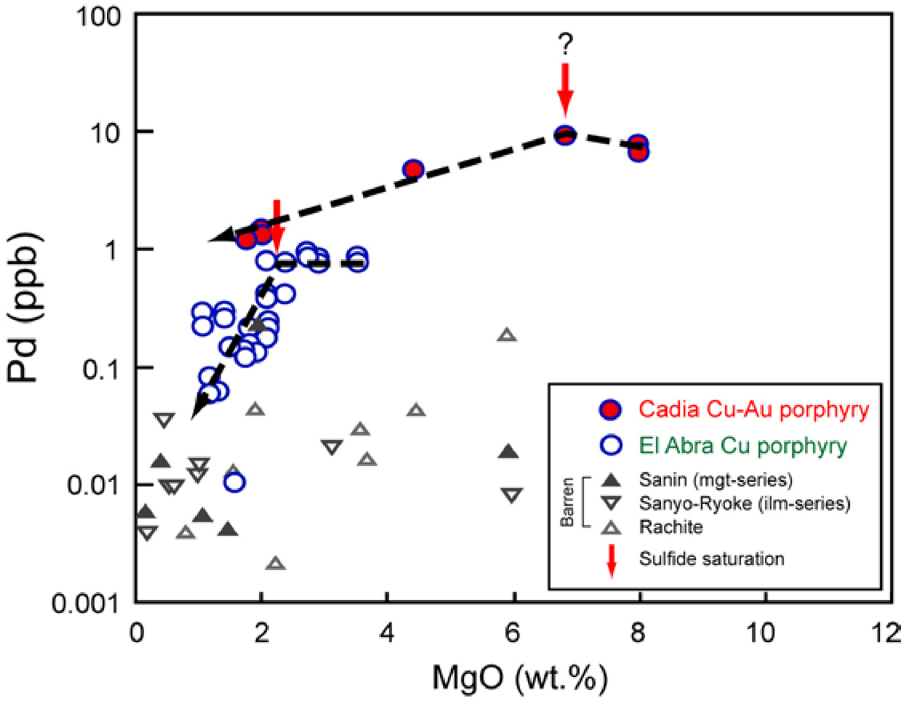

*Fig. 1.* A plot of Pd against MgO (as a measure of fractionation) for samples from the El Abra Cu deposit in Chile, the Cadia Cu-Au porphyry deposit in NSW, and three barren granitic suites. Note: (i) the low Pd content of samples from the barren suites with MgO > 2.5 wt.%, (ii) the rate of decline in Pd, following sulfide saturation, is less for Cadia than it is for El Abra, implying a much lower rate of sulfide precipitation

fallen to about 10% of its original value and the gold content has become negligible. A magma precipitating 1% sulfide is unlikely to form an economic Cu deposit and/or Au deposit if sulfide saturation precedes volatile saturation. If the amount of precipitating sulfide is 0.3% the Cu content of the melt falls to 70% of its original values by 20% fractionation and the Au content becomes negligible. This magma could produce a Cu deposit if it became volatile-saturated at 20% fractionation after sulfide saturation, but the ore would be Au-poor producing a Cu-only deposit like El Abra (Fig. 1). For 0.1 wt.% sulfide-melt fractionation, the Cu content of the melt is unaffected but Au falls to 18% of its initial concentration by 20% fractionation. Finally, 0.03 wt.% sulfide melt precipitation lowers the Au content of the melt to only 65% of the original value by 20% fractionation. Such a magma could produce a Cu-Au deposit. Note that in all of the calculations, even if the amount of sulfide fractionation is as low as 0.03 wt.%, Pd has fallen to negligible concentrations by 3% sulfide fractionation. This suggests that for Cu deposits with significant Pd, volatile saturation occurred before the melt became saturated with an immiscible sulfide melt or the amount of sulfide to precipitate was <<0.03 wt.%. We suggest that Cadia is a Cu-Au deposit either because it became volatile-saturated before it became sulphide-saturated, or if sulfide saturation did occur at ~6 wt.% MgO (Fig. 1), the amount of sulfide to form was trivial, enough to remove some Pd but not enough to affect Cu or Au.

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# NOBLE METALS IN HIGH-TEMPERATURE VOLCANIC GASES (KAMCHATKA AND KURILES, RUSSIA)

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**ABSTRACT**. The Kuril-Kamchatka arc stretches for nearly 1900 km. 29 active volcanoes are known presently on Kamchatka, and about 40 on the Kuriles. Mineralizations of Au (Vergasova et. al., 2001; Yudovskaya et al., 2006), Re (Znamensky et.al., 2004) and Pt (Korzhinsky et.al., 1996) found in products of fumaroles show that volcanic gases are capable of transporting noble metals. High-temperature volcanic gases considered as close analogues of ore-forming fluids were sampled on Kudriavy (up to 870°C), Gorely (830–900°C) and Tolbachik (1030°C) volcanoes. Our data on acid gas condensates show that concentrations of some PGE, Au in volcanic fluids may reach a few ppb, 79 ppb Re, and 39 ppb Ag.

The Kudriavy volcano is located in the caldera Medvezhia in the northern part of Iturup Island (Kuriles). Its stratovolcanic edifice of basaltic andesite composition is superimposed on an eroded dacitic cone that was extruded in a post-caldera stage. Since the last magmatic eruption (1883) there is only stationary fumarolic degassing and rare phreatic explosions on Kudriavy. The Maximum temperature (940°C) measured in 1992 dropped to 870°C after small phreatic eruption in 1999. Since 1991, volcanic gases, condensates and mineralization have been sampled almost every year (the data for 2001–2013 will be presented). Gorely is a ridge-like volcanic edifice composed of 3 basaltic andesite cones hosted in a Paleocene caldera (South Kamchatka). Holocene activity of Gorely included explosive eruptions alternating with periods of lava flow eruptions. After the last eruption (1984–86) a hot lake was formed. In 2010–2013 a strong jet-like gas eruption took place emitting ~11000 t of gas per day (Aiuppa et al., 2012). The Large Tolbachik fissure eruption of 1975–76 is famous for its post-eruptive mineralization including numerous copper minerals and an amazing occurrence of exhalative gold. New basaltic eruption in the Tolbachik region, which began after 36 years of silence and lasted from Nov 27, 2012 to September 28, 2013, allowed to obtain gas condensate samples (1030°C) from vents in the roof of active lava channels. Therefore samples represent 3 types of magmatic degassing: long-lasting field degassing (Kudriavy), short-living jet-like gas eruption (Gorely) and degassing active lava flows (Tolbachik).

ICP-MS analyses of filtered condensates showed that concentrations of PGE are usually less than 1 ppb (Os was not analysed). Only Pd shows concentrations up to 6 ppb (Kudriavy). Au concentrations range from 0 to 8.3 ppb with higher values in samples from Gorely and Tolbachik. Concentrations of Ag are 3–5 times higher compared to those of Au reaching 39 ppb in Tolbachik condensate. Re is present in all samples and average values are even higher for Gorely and Tolbachik than for Kudriavy volcano that is known for rhenium disulfide mineralization. PGE and Re have been also analysed by the isotopic dilution ICP-MS method (Meisel et al., 2003) in ammonia solutions from Giggenbach bottles, which are commonly used for sampling volcanic gases (samples from Kudriavy volcano). Os was extracted from solutions as $OsO_4$ by Ar flow and sparged into ICP-MS. PGE and Re were analysed after separation from matrix elements in a cation-exchange column. According to these data, Ru, Rh, Pd are at a level of a few tens ppt, Os – few ppt, Ir and Pt are up to 5 and 7 ppb, respectively. Re concentrations may reach 66 ppb.

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# PLATINUM GROUP ELEMENTS IN FELSIC SUITES ASSOCIATED WITH THE El ABRA AND GRASBERG PORPHYRY DEPOSITS

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**ABSTRACT**. Recent advances in the inductively coupled plasma mass spectrometry (ICP-MS)-NiS fire assay-isotope dilution method make it possible to measure the PGEs at concentrations as low as 1 to 20 ppt, so that felsic rocks can now be analyzed. As a consequence, PGE geochemistry can show the onset of sulfide saturation in evolving felsic magmas. We present results from studies of PGE in felsic magmas associated with two porphyry systems: El Abra and Grasberg. Abundances of Pt and Pd in felsic rocks from the El Abra suite drop rapidly below 2.5 wt. % MgO, following sulfide saturation of the magmas, which occurs slightly before volatile saturation and formation of the copper deposit. We suggest that the amount of sulfide melt that formed was enough to strip the PGE and Au from the magma but not Cu, because of the lower partition coefficient of Cu relative to the precious metals, which explains why El Abra is a Cu only porphyry deposit rather than a Cu-Au deposit. The same trend is not seen in the Grasberg samples suggesting that these magmas did not reach sulfide saturation and so that Cu, Au, Pt and Pd were all available to enter the volatile phase.

## INTRODUCTION

The extreme silicate melt-sulfide melt partition coefficients of platinum group elements (PGE; Ru, Rh, Pd, Os, Ir, and Pt), which are appreciably higher than those for Cu and Au, make them valuable indicators of sulfide saturation in evolving melts. PGE have been successfully used to identify sulfur saturation in mafic systems, but analytical difficulties have limited their application in felsic systems until the recent modification of the NiS fire assay. We used this modified NiS fire assay isotope dilution ICP-MS method (Park et al., 2012) to analyze PGE abundances in samples from the El Abra-Pajonal, Chile, and Grasberg, Papua, intrusive complexes that are associated with Cu-only and Cu-Au porphyry deposits respectively. We hypothesized that if a fractionating magma system becomes sulfide saturated before it becomes fluid saturated most of the Cu and Au will be trapped in sulfides in a plutonic chamber and be unavailable to enter a magmatic hydrothermal fluid. Alternatively, if fluid saturation occurs before sulfide saturation most of the Cu and Au will be available to partition into the hydrothermal fluid, which could lead to the formation of an economic Cu and/or Au deposit.

## RESULTS

Pd and Pt results are plotted against MgO in Fig. 1. El Abra Pd abundances, in samples >2.5 wt.% MgO, are higher than samples with lower MgO but show no clear trend. The Pd abundances decrease rapidly in samples below 2.5 wt. % MgO. The abundance of Pt decreases continuously with decreasing MgO but the rate of decrease becomes more rapid once the MgO drops below 2.5 wt. %. Grasberg Pd and Pd abundances are scattered but are typically much higher than in El Abra samples and the decreasing trends seen in El Abra are not visible in the Grasberg suite.

## DISCUSSION AND CONCLUSIONS

The rapid decrease in Pd and Pt abundances at 2.5 w.t% MgO in the El Abra suite suggests that sulfide saturation occurred shortly before volatile saturation at ~ 1.2 wt. % MgO. However only a small amount of immiscible sulfide melt formed, enough to remove most of the Pd and Pt and Au from the silicate melt but little of the Cu. Therefore a Cu-only porphyry deposit was still able to form. Sulfide saturation did not occur at Grasberg and so all the Pd, Pt, Au, and Cu was available to partition into the volatile phase and form a Cu-Au-(Pd) type deposit.

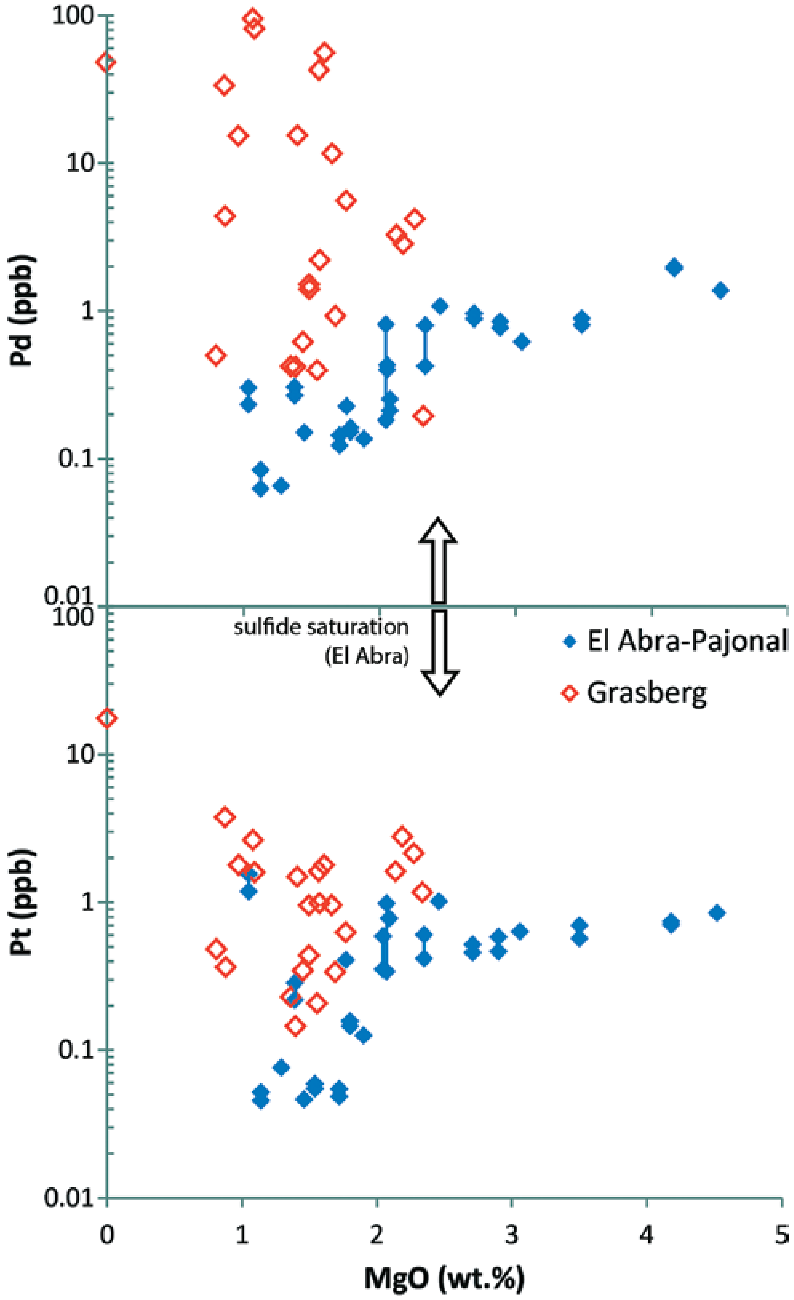

*Fig. 1.* Pd (top) and Pd (bottom) results for El Abra (closed diamonds) and Grasberg (open diamonds) samples plotted against MgO. Vertical lines connect duplicate samples.

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# METALLOGENY OF THE POYI MAGMATIC Cu-Ni DEPOSIT: REVELATION FROM THE CONTRAST OF PGE AND OLIVINE COMPOSITION WITH OTHER Cu-Ni SULFIDE DEPOSITS IN THE EARLY PERMIAN, XINJIANG

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**ABSTRACT**. Permian mafic–ultramafic intrusions in the Beishan rift have been the focus of several recent studies. Some of them host economic magmatic sulfide deposits such as Poyi, which is a large magmatic Cu-Ni sulfide deposit related to ultramafic rock. The ore bodies are controlled by hornblende-peridotite, whereas dunite and wehrlite are country rocks. This paper compares PGE and olivine compositions in magmatic Cu-Ni deposits of three tectonic units (Altay, East Tianshan, Beishan) to better constrain the metallogenic process of the Poyi magmatic Cu-Ni deposit.

Regarding the Ni/Cu and Pd/Ir ratios, the Cu-Ni deposits in Altay are closely related to flood basalts, while East Tianshan and Beishan are located in the high-Mg basalt area (Fig. 1). There is a trend from Altay to East Tianshan and to Beishan, continuously approaching the komatiite and primitive mantle fields. This correlates with high positive εNd values, high Mg content of dunite and hornblende-peridotite and high Fo of olivine. We believe that a mantle plume was responsible for the Permian magmatic Cu-Ni deposits. The rocks within the Beishan rift underwent higher degrees of partial melting and thus were closer to the central part of the Permian mantle plume.

The degree of sulfide segregation (DSS) of Poyi was around 0.01% (Fig. 2), the value of R (the ratio of the mass of silicate magma to the mass of sulfide) ranges from 500-5000 (2333 on average); the R value of Cu-Ni sulfide deposits in the East Tianshan ranges from 100-500, and the DSS was about 0.013%. The Poyi Cu-Ni deposit is not as rich as the magmatic Cu-Ni deposits in East Tianshan, probably because the DSS of the former (0.01%) is lower than the latter (0.013%). From Beishan area via East Tianshan to the Altay Region, the R values change from 2333 to 100-500, and then to 100. According to the theory of Naldrett (2011), where R is low, i.e. in the range of 100 to 2000, the Ni and Co contents of the sulfides will be typical of most Ni sulfides ores, and the Pt concentrations will be relatively low, corresponding to those observed in ores such as those at Sudbury; where R is in the range of 10,000 to 100,000 the Ni and Co contents will not be much higher than at lower R values, but the Pt (and other PGE ) concentration will be higher and in the range of those characterizing the Merensky Reef. The R values of Poyi is 2333, this is probably the reason why there is no enrichment of PGE in Poyi.

Compared to East Tianshan, the olivines of Poyi have higher contents MgO and SiO$_2$, at lower FeO and CaO. From the equations (1) and (2), where P is in kbars, T is in degrees Kelvin, $X_S$ is mole fraction of sulfur, and $X_i$ is mole fraction of other components (i) in the silicate melts, the sulfur content at anhydrous（equation 1） and hydrous（equation 2）saturation in silicate melts as proposed by Li and Ripley (2009) based on

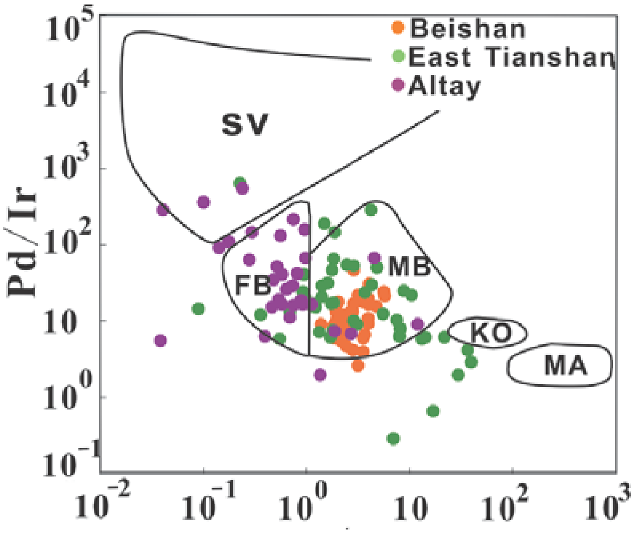

*Fig. 1*. (Pd/Ir) vs (Ni/Cu) ratios copper-rich sulfide veins (SV), flood basalts (FB), high-Mg basalts (MB), komatiites (KO), mantle rocks (MA). After Barnes et al. (1988). Data sources are the same as in Fig. 2

available experimental results and an updated empirical equation may be calculated. It can be emphasized that a magma with higher contents of MgO and $SiO_2$, and lower FeO and CaO is more favorable to reach sulfur saturation. Thus, at Poyi conditions for sulfur saturation were more favorable than in the other areas.

$$\ln X_S = 10.07 - 1.151\,(10^4/T) + 0.104\,P - 7.1\,XSiO_2 - 14.02\,XMgO - 14.164\,XAl_2O_3 \qquad (1)$$

$$\ln X_S = -1.76 - 0.474\,(10^4/T) - 0.021\,P + 5.559\,XFeO + 2.565\,XTiO_2 + 2.709\,XCaO - 3.192\,XSiO_2\ 3.049\,XH_2O \qquad (2)$$

However, due to the lack of sulfur, it is very hard for dunite and wehrlite to reach sulfur saturation. This leads to the higher Ni content in olivine of Poyi among the Permian magmatic Cu-Ni deposits in Xinjiang.

*Acknowledgments. This study was financially supported by the project of Pobei Cu-Ni sulfide deposits metallogenic regularity and location prediction of rich ore, Xinjiang (Grant XGMB2012012).*

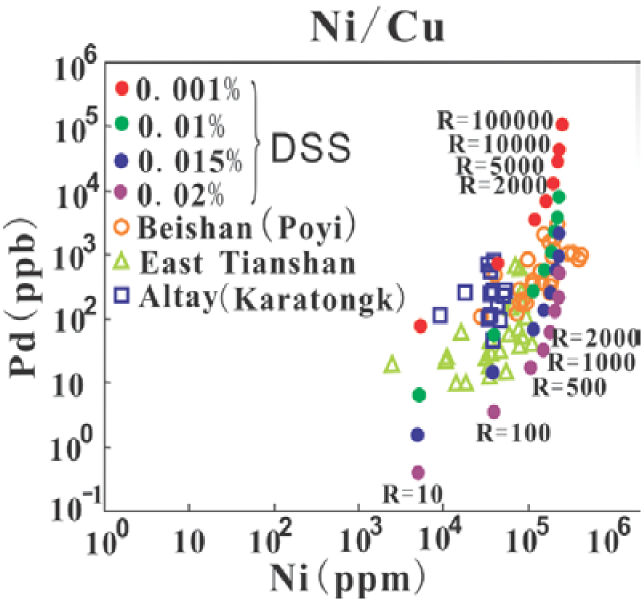

*Fig. 2.* The degree of sulfide segregation (DSS) and R value of magmatic Cu-Ni deposits from three tectonic units. Data sources: Liu et al (unpublished); Liu, 2011; Yang, 2011; Xia et al., 2013; Fu , 2012; Qian et al., 2009; Chai, 2006; Tang et al.,2009; Xiao et al., 2013; Wang et al., 2012; Chai et al., 2006. The Ni and Pd contents of both disseminated ores and sulfide rich ores are corrected to 100% sulfide content after Barnes & Lightfoot (2005)

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# CLOSED-SYSTEM BEHAVIOUR OF THE Re-Os ISOTOPE SYSTEM IN PRIMARY AND SECONDARY PGM ASSEMBLAGES: EVIDENCE FROM THE NURALI ULTRAMAFIC COMPLEX (SOUTHERN URALS, RUSSIA)

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**ABSTRACT.** This study presents the first in situ Os-isotopic compositions of distinct platinum-group mineral (PGM) assemblages from the metamorphosed chromitites of the Nurali ultramafic complex (Southern Urals, Russia). 'Primary' Ru-Os sulfides are commonly replaced by a 'secondary' unnamed Ru-Os-Fe-Ir oxide, providing evidence for different stages of desulfurization and oxidation of primary laurite (e.g., with relics of laurite or without laurite). The osmium isotope data define a restricted range of similarly 'unradiogenic' 187Os/188Os values for 'primary' and 'secondary' PGM supporting the conclusion for closed system behaviour of the Re-Os isotope system during postmagmatic hydrothermal or metamorphic events. The Os-isotope data provide further support for an Enstatite Chondrite Reservoir (ECR) model for the convective upper mantle as defined by Walker et al. (2002).

Recent Os-isotope studies have clearly shown that the Os-isotope system of minerals like chromite, base-metal sulfides, Ru-Os sulfides and Os-rich alloys may contribute to a better understanding and more accurate interpretation of the processes leading to fractionation of Os isotopes in different environments in the mantle. Taking into consideration that these minerals, encapsulated in chromian spinel, retain their primordial Os-isotope signatures it has been suggested that they are the best targets to avoid existing ambiguity in the interpretation of whole-rock Os isotope results.

In this study we present for the first time the results of laser ablation (LA) attached to multiple- collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) for distinct platinum-group mineral (PGM) assemblages from the metamorphosed chromitite of the Nurali ultramafic complex (Southern Urals, Russia).

The Nurali lherzolite-gabbro complex belongs to a belt of tectonically dismembered ophiolite allochtons confined to the Main Uralian Fault in the Southern Urals (Russia) between N53° and 55°. It consists of a mantle tectonite formed by lherzolite, harzburgite and dunite, overlain by a dominantly ultramafic layered unit recognized as the Moho transition zone changing upward to amphibole gabbro and diorite. Effects of low-grade hydrothermal metamorphism are widespread: the ultramafic rocks have been serpentinized, whereas gabbro underwent partial to total rodingitization. An U-Pb age of zircon from a gabbro-diorite (399±2 Ma, Fershtater et al., 2000) has been interpreted as the age of a second intrusive phase of the complex (Savelieva et al., 1997).

The investigated samples characterize a massive chromitite body (CHR 1 chromitite, Zaccarini et al., 2004) occurring in the southern part of the complex, within the dunite-wehrlite-clinopyroxenite layered unit. Similar to previous studies (Zaccarini et al., 2004; Garuti et al., 2007), two distinct platinum-group mineral (PGM) assemblages have been recognized: a 'primary' euhedral PGM assemblage, which occurs as inclusions in chromite cores, and a modified 'secondary' euhedral to anhedral PGM assemblage observed either in chromite rims associated with cracks that are filled by chlorite or serpentine, or interstitially to chromite grains in silicates (chlorite, serpentine, prehnite). The 'primary' PGM assemblage is represented by solitary grains of laurite and composite grains of erlichmanite+osmium, laurite+Ru-bearing pentlandite±PGE-bearing heazlewoodite, whereas a 'secondary' PGM assemblage is defined by either relics of laurite mantled by the erlichmanite±oxide-bearing Ru-Os-Fe-Ir mineral or by as yet unnamed and poorly characterized Ru-Os-Ir-Fe oxide.

‘Primary’ laurite grains preserved in the chromite cores have $^{187}Os/^{188}Os$ values between 0.12485 and 0.12553, with a weighted mean of 0.12517±0.00021 (2 sigma, $n = 22$), and $^{187}Re/^{188}Os$ lower than 0.00006. ‘Secondary’ PGMs clearly inherited these primary Os-isotope signatures ($^{187}Os/^{188}Os$ values range from 0.12474 to 0.12549 with a mean of 0.12516 and a standard deviation of 0.00019, n=36). The osmium isotope results identify a restricted range of similar $^{187}Os/^{188}Os$ values for ‘primary’ and ‘secondary’ PGMs being consistent within uncertainty with ‘unradiogenic’ $^{187}Os/^{188}Os$ values defined for the chromitite (0.1254±0.0002, Tessalina et al., 2005). This implies that later thermal events, which led to desulfurization and oxidation of laurite, have not affected the Os-isotope system of the investigated PGMs. The subchondritic osmium isotope signature of laurite is clearly preserved in the secondary Ru-Os-Fe-Ir oxide.

The formation of oceanic crust in the Urals has been previously dated as Middle Ordovician to Early Devonian (from 470 to 390 Ma, see references in Tessalina et al., 2005). By comparing the independent chronological data available for the Nurali complex (Fershtater et al., 2000) and the Os-isotope results for chromitite (Tessalina et al., 2005) with associated primary and secondary PGMs (this study) we can distinguish between the various proposed mantle evolution curves following the approach of Shi et al. (2007). The $T_{MA}$ and $T_{RD}$ model ages, calculated for PGMs and chromitite using the Enstatite Chondrite Reservoir (ECR) model (Walker et al., 2002; Shi et al., 2007), give clusters at ca. 420±30 Ma and 385±30, respectively. These estimates agree within the ECR model uncertainty with the U-Pb age of zircon (399±2 Ma, Fershtater et al., 2000) recovered from the gabbro-diorite. Os-isotope data for chromitite and the associated PGMs thus provide further support for the ECR-like Os-isotope evolution for the convective upper mantle as defined by Walker et al. (2002). This estimate is significantly less radiogenic than the primitive upper mantle (PUM, Meisel et al., 2001) and more radiogenic than the Carbonaceous Chondrite Reservoir (CCR, Walker et al., 2002) and the depleted MORB mantle (Snow & Reisberg, 1995).

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# WITWATERSRAND PLATINUM-GROUP MINERALS AS A KEY TO UNRAVELLING MANTLE PROCESSES OF THE YOUNG EARTH

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**ABSTRACT**. The compositionally diverse platinum-group minerals (PGM) from the Evander Goldfield, in the eastern part of the Witwatersrand Basin (South Africa), have been studied by a number of modern techniques including SEM, EMPA, N-TIMS and LA MC-ICP-MS. The characteristic feature of PGMs from Evander is an extensive presence of Ru and Os-rich alloys (i.e., Ru-Os-Ir, Ru-Os-Ir-Pt, Ru-Ir-Pt, Ru-Pt), which prevail over iridium, Ru-Os sulfides, Pt-Fe, Pt-Ru-Fe and Pt-Ir-Os alloys. Unradiogenic $^{187}Os/^{188}Os$ values are clearly indicative of a subchondritic mantle source of the platinum-group elements. Compositional and Os-isotope evidence suggest that the Os-rich alloy grains were formed under mantle conditions. The model $^{187}Os/^{188}Os$ ages obtained for the main set of PGM (4.1-2.9 Ga, n=108) imply that the PGM are detrital, supporting a scenario in which the majority of PGM were incorporated into the Witwatersrand basin by their release from Archean ultramafic or mafic source-rocks during weathering.

Understanding mantle processes of the young Earth have to rely mainly on evidence obtained by investigating greenstone belts and ophiolite sequences. Samples of the Archean mantle, such as podiform chromitites, are extremely rare (Moores, 2012). An alternative source of information about chemical differentiation of the early Earth's mantle are Os-enriched PGM from the Archean paleoplacers of the Witwatersrand Basin. Os isotopic compositions of PGM have been shown to retain a record of mantle depletion events, owing to their high Os content, low Re content and their resistance to alteration.

The Late Archean paleoplacers of the Witwatersrand Basin are not only unparalleled in their gold-uranium deposits, but are also a leading source for osmium production as a by-product of gold mining from rocks underlying the Ventersdorp Supergroup, which is about 2.7 Ga old (Altermann & Lenhardt, 2012). The detrital PGM have source areas which are hundreds of kilometers apart and are likely to have been geologically distinct, resulting in systematic differences in PGM. This variability is reflected in the Os-isotopes of individual grains and requires a careful evaluation of the relationships of mineral compositions, textures, and osmium isotopes.

The Evander Goldfield, situated in the eastern extremity of the Witwatersrand Basin, differs from the other six goldfields (i.e., East Rand, Central Rand, West Rand, Carletonville, Klerksdorp, and Welkom) in its higher in situ concentration of PGM and the lower than typical bulk (Os+Ir)/(Ru+Pt+Rh) and Ru/Pt values (Cousins, 1973). Based on mineral chemistry we show that within the Evander Goldfield (1) the Os–Ir–Ru alloys have systematically higher Ru contents and (2) there are different modal proportions of chemically distinct PGMs. Equilibrium phase-relationships of osmium and ruthenium alloys at Evander, based on the restricted solid solution in the binary systems Os–Ir, Os–Ru and Ir–Ru (Massalski, 1993), and the presence of a ruthenium-enrichment trend in Os–Ru–Ir–Pt alloys, are indicative of high temperatures and pressures, which could only be reached under mantle conditions. We therefore propose that these PGM likely represent examples of slightly differentiated PGE alloys, which were formed in the Archean mantle.

Although the exact ages of the PGM in the Witwatersrand basin are at present not well constrained (only samples from the Kimberly Reef have been investigated using modern techniques; Malitch & Merkle, 2004; Dale et al., 2010; this study), it stands to reason that PGM older 2.7 Ga must have formed before the deposition of the sediments in which they occur today. The $^{187}Os/^{188}Os$ values measured by N–TIMS and LA MC–ICP–MS in PGM grains of different composition (*e.g.*, osmium, ruthenium, rutheniridosmine, Pt–Ir–Os, Ru–Ir–Pt, Ru–Pt and Pt–Fe alloys) span a range from 0.10987 to 0.1095. The Os-isotope

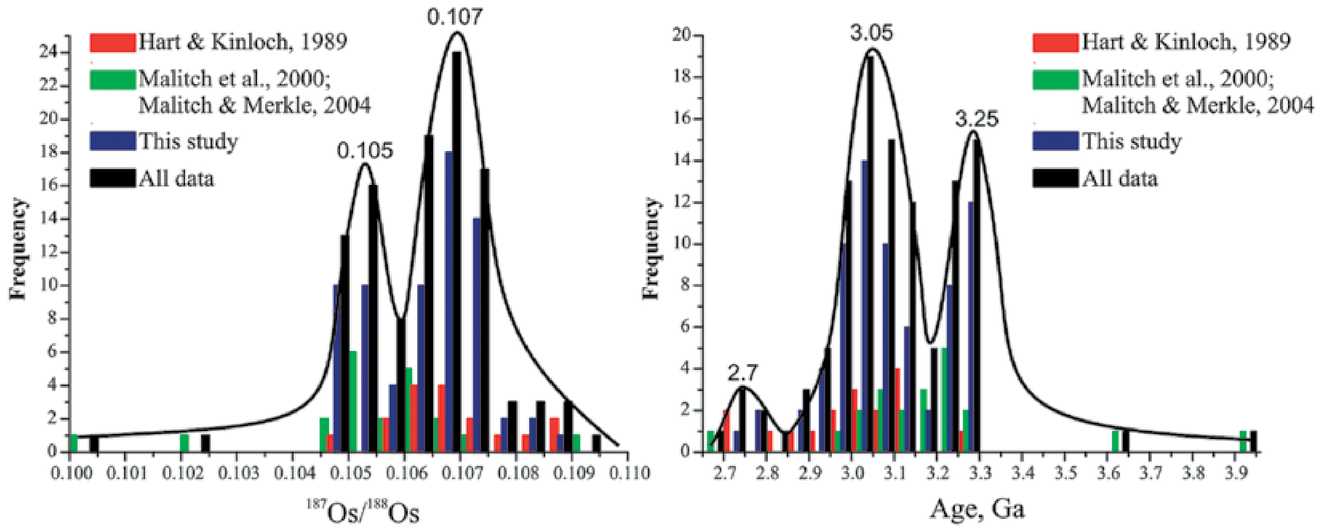

*Fig. 1.* Histograms of $^{187}$Os/$^{188}$Os values and ages of Os-rich PGM from the Witwatersrand Basin

results identify a restricted range of unradiogenic $^{187}$Os/$^{188}$Os values for coexisting Os-rich alloy and laurite pairs that form primary PGM assemblage. Excluding three PGM nuggets with the lowest $^{187}$Os/$^{188}$Os values (<0.1024) and one sample with the highest $^{187}$Os/$^{188}$Os value (i.e., 0.1095), for the major set of PGM at least two groups with distinct $^{187}$Os/$^{188}$Os values were distinguished (0.105 and 0.107, respectively, Fig. 1). Accordingly, Os-rich alloys yielded model $^{187}$Os/$^{188}$Os ages of 3.25 and 3.05 Ga (Fig. 1). Three PGMs, however, appear to imply ages of 4.1±0.1, 3.9±0.1 and 3.6±0.1 Ga, respectively. These samples arguably represent the oldest source of information on mantle processes that can probably in no other way be reconstructed. The data obtained imply that the source for the PGM was the Archean mantle, slightly differentiated with respect to PGE. Our results support a scenario in which the majority of PGM were incorporated into the Witwatersrand Basin as detrital material, derived most probably from a variety of greenstone belts of different ages (e.g., Barberton, Murchison, etc.) and Archean ultramafic rocks of yet unidentified affinity.

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# PGE IN DEVONIAN MAFIC ROCKS AND THE ORIGIN OF QUATERNARY PLATINUM PLACERS (EASTERN PART OF SIBERIAN PLATFORM)

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**ABSTRACT**. The native sources of low-grade placers of Rh-bearing ferruginous platinum in the eastern part of the Siberian platform are unknown. It is supposed that the Devonian mafic rocks containing PGE, especially in the middle stream of the Vilyui River, may represent these sources, and Pt was released from volcanics during long-term processes of weathering, transportation and precipitation.

Determination of the PGE content in combination with additional geochemical signatures of 21 samples of mafic rocks (18 volcanic and 3 intrusive) from the Middle Paleozoic Patom-Vilyui aulacogen (eastern part of the Siberian platform) shows that these lithologies belong to mineralogically and chemically distinct groups (Masaitis, 2006) that differ in the abundances and inter-elemental ratios of PGE. Among these mafites the following types are distinguished:

1) rocks of normal alkalinity, comprising olivine basalt, plagiobasalt, basalt and dolerite,

2) subalkaline rocks, including low-Ti olivine trachybasalt and high-Ti andesine trachybasalt.

The abundances of PGE in effusive mafites of normal alkalinity positively correlate to the Mg# and may be caused by partial melting (maximal ~10%) of depleted mantle (olivine basalt and plagiobasalt), and subsequent fractionation (basalt). The PGE content of the olivine trachybasalts also correlates to the Mg#, suggesting that their initial melt resulted from partial melting of depleted mantle (~10% or slightly more) in high pressure environments. The highest abundances of PGE were determined in olivine basalts (average ΣPGE of 21.75 ng/g), followed by plagiobasalts (avg. ΣPGE of 16.7 ng/g), and olivine trachybasalts (avg. ΣPGE of 13.98 ng/g), while basalts are characterized by significantly lower PGE contents (avg. ΣPGE of 7.36 ng/g). Dolerites are characterized by intense fractionation of an initial melt similar in composition to that of the basalts, although this process probably occurred in extensive vertical conduits with a significant role of volatiles. The abundances of PGE in dolerites (avg. ΣPGE of 19.2 ng/g) are close to those of olivine basalts, but Pd prevails over Pt. The PGE content and ratios of dolerites are quite different compared to the basaltic group, as the correlation of the PGE content with the Mg# is negative, and the Pd/Ir ratio is the highest of the characterized mafites. Andesine trachybasalts originated by low degrees of partial melting (~1%) of primitive metasomatized mantle, with very low PGE contents in these rocks (avg. ΣPGE of 3.12 ppb) and Pd prevailing over Pt much stronger than in dolerites. The trends ΣPGE vs. mg# for three groups of mafic rocks differ significantly (Fig. 1).

The composition of the mantle subjected to partial melting in the various volcanic regions of the aulacogen was not homogeneous and various domains with different mineralogical and chemical characteristics can be recognized. This type of volcanic eruptions (long-term activity of multiple volcanic centers that produced several lavas over a geographically spread area with frequent interruptions, etc.) accompanied with a gradual subsidence and divergence of the crust and accumulation of thick sequences of shallow-sea sediments indicate that during the Middle Paleozoic several magma reservoirs existed at different depths, providing melts of diverse composition and characterized by strongly differing PGE contents. The majority of mafic rocks were formed from S-undersaturated melts that underwent subsequent crystallization, fraction-

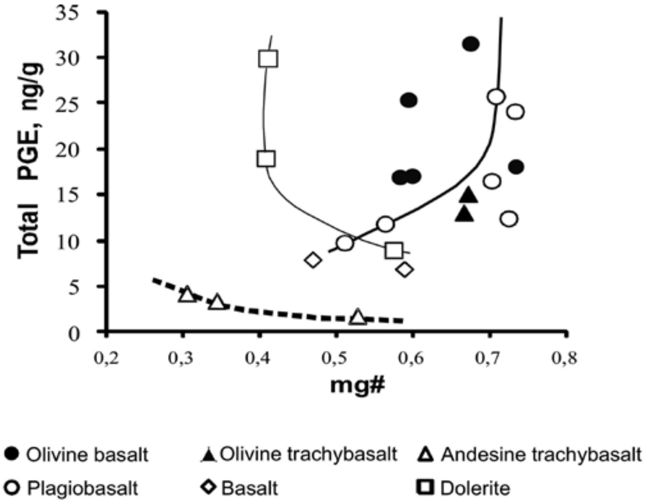

*Fig. 1.* ΣPGE plotted against mg# for the mafic rocks of Patom-Vilyui aulacogen. Thick line – trend for olivine basalts, plagiobasalts, basalts and olivine trachybasalts; thin line – trend for dolerites; dotted line – trend for andesine trachybasalts

ation and probably insignificant contamination by crustal material.

The vast territory of PGE-bearing mafites coincides with the area where low-grade platinum placers occur (Vysotsky, 1933, Okrugin, 2000), of which the native sources are unknown. The widely distributed effusive and intrusive mafic rocks, in some places enriched in PGE, could be the source of local placers. This assumption is based on the following:

1) the Re-Os model age of the Os-Ir-Ru minerals from the placer (Okrugin et al., 2006) coincides with the time of extrusion of the Devonian basalts;

2) the vast territory of the volcanic province where placers occur indicates that their source may be of regional nature and not local, similar to some kind of ore-bodies, e.g. chromitite or Cu-Ni sulfide;

3) the enrichment of detrital platinum group minerals in Ru, Rh and Pd indicates that the source melt was S-undersaturated (Okrugin, 2000) similar to Mg-enriched mafites;

4) the highest content of ferruginous platinum in riverbeds can be found in the Vilyui valley; these grains are also characterized by the highest content of Rh;

5) exactly at this position the olivine basalts and plagiobasalts, most enriched in ΣPGE, are outcropping.

It is possible that the PGE were released from the solid rocks during long-term geochemical and physical transformations: laterite weathering, dissolution, transportation, precipitation and subsequent rewashing in the course of geological evolution in Mesozoic and Cenozoic. It is possible that the precipitation of PGE in the course of the origin of the Vilyui-type placer platinum province was supported by bioreducing bacteria. Thus the PGE-bearing Middle Paleozoic mafites are the most probable source of the placers.

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# FIRST DISCOVERY OF SPERRYLITE IN ARCHAEAN PATCHEMVAREK GABBROANORTHOSITE (KOLA REGION, RUSSIA)

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**ABSTRACT**. Sperrylite, a platinum arsenide, has been found in the sulphide mineralization zone of the Patchemvarek intrusion. This pioneer discovery opens perspectives for future metallogenic investigations of Archaean gabbroanorthosites.

In the Early Palaeoproterozoic (2550-1980 Ma) epoch of the long ESCLIP evolution history, a few stages separated by breaks (conglomerates) sedimentation and magmatism have been distinguished. The Sumi (2550-2400 Ma) stage was of fundamental significance in the metallogeny of Pt-Pd ores related to the intrusive siliceous highly Mg boninite-like and anorthositic magmatism (Mitrofanov, 2010; Sharkov, 2006). According to Bayanova et al. (2009) the ore-bearing intrusions formed earlier in the Kola belt (Fedorov-Pana and other intrusions, 2530-2450 Ma) and at some later stage in the Fenno-Karelian belt (2450-2400 Ma). The Archaean anorthositic units (2760-2770 Ma) associate with titanomagnetite deposits and ore prospects (Tsaga and Acha deposits). The Patchemvarek gabbroanorthosite (2925 ± 7 Ma) earlier demonstrated zones of sulphide mineralization with increased Au, Pt and Pd concentrations (Kudryashov & Mokrushin, 2011).

The Patchemvarek gabbroanorthosite is located in a deep-seated fault zone at the junction between the Keivy terrane, Murmansk domain, and the Kolmozero-Voron'ya greenstone belt. The Patchemvarek gabbroanorthosite is a lenticular intrusion (up to 2 km thick) consisting of variably altered leucogabbros and fairy uniform medium-grained metagabbroanorthosites. The Patchemvarek gabbroanorthosite have massive structure and granoblastic texture with the following mineral composition (in vol. %): plagioclase 75-80, hornblende 5-10, actinolite-tremolite mass 5-10, and epidote 1-5. The rock mainly consists of relics of primary and secondary, significantly recrystallized plagioclase. The composition of plagioclase varies from bytownite to labradorite. Mafic minerals represented by amphibole and epidote that are embedded in the actinolite-tremolite fibrous mass. Accessory minerals are zircon, titanite, apatite, and Ti-magnetite.

The sulphide mineralization occurring in narrow shear zones in marginal parts of the Patchemvarek intrusion has been studied in details. The collected samples of rocks were analyzed using an optical microscope Leica DM2500P and scanning electron microscope Hitachi SU6600 with EDS at the Optical and Electron Microscopy Laboratory in the Department of Geology and Lithosphere Protection (UMCS, Lublin, Poland).

Inclusion of platinum arsenide (sperrylite $PtAs_2$) in a grain of labradorite (Fig. 1) has been

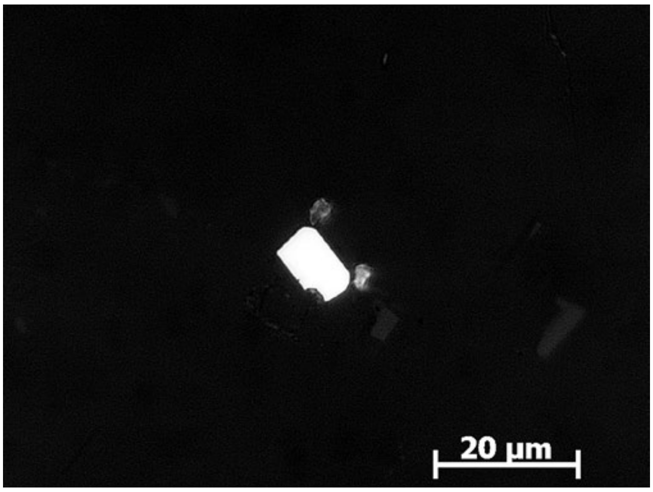

*Fig. 1*. Photograph of sperrylite inclusion in plagioclase

found in one of the samples. First discovery of sperrylite suggests a possible presence of platinum-group element mineralization in Archaean gabbroanorthosites, and requires further study.

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# PLATINUM-GROUP ELEMENT (PGE) AND CHROMIAN SPINEL GEOCHEMISTRY IN THE CHROMITITES FROM THE ABDASHT ULTRAMAFIC COMPLEX, KERMAN, SOUTHEASTERN IRAN

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**ABSTRACT**. The Abdasht complex is a major ultramafic complex in south-east Iran (Esfandagheh area). It is composed mainly of dunite, harzburgite, lherzolite, chromitite, and subordinate wehrlite. A detailed electron microprobe study reveals very high Cr#, Mg# and very low $TiO_2$ contents for chromian spinels in chromitites. The Abdasht chromitites contain up to 264 ppb total PGE, and display a systematic enrichment in IPGE relative to PPGE, with a steep negative slope in the PGE spidergrams and very low PPGE/IPGE ratios, a feature typical of ophiolitic podiform chromitites worldwide. The mineral chemistry data and PGE geochemistry of the Abdasht chromitites indicates that the Abdasht ultramafic complex was generated from an arc-related magma with boninitic affinity in a supra-subduction zone setting.

## GEOLOGICAL SETTING

The Abdasht ultramafic complex is located in the south-east of Iran, within the Sanandaj-Sirjan metamorphic zone in the ophiolitic mélange belt of the Esfandagheh region, southern Kerman province. This belt is situated at the SE edge of the main Zagros thrust and is part of the Tethyan ophiolite belt of the Middle East which links the Mediterranean ophiolites of the Hellenides and Dinarides with Himalayan ophiolites. The Abdasht ultramafic comlex comprises dunite, chromitite, harzburgite, lherzolite, and subordinate wehrlite.

## MINERAL CHEMISTRY AND PGE IN CHROMITITES

The composition of chromian spinels in chromitites varies within the following ranges: $Cr_2O_3$: 59-60.1 wt.% (average 59.3 wt.%), $Al_2O_3$: 12-12.8 wt.% (average 12.3 wt.%), MgO: 13-13.8 wt.% (average 13.4 wt.%), NiO: 0.01-0.09 wt.% (average 0.06 wt.%), FeO: 13.1-13.7 wt.% (average 13.3 wt.%) and $Fe_2O_3$: 0.6-1.2 wt.% (average 0.9 wt.%). In the massive chromitites of the Abdasht complex, chromian spinels exhibit a uniform and restricted composition around a high-Cr variety and are characterized by Cr# [=Cr/ (Cr+Al) atomic ratio] usually in a very narrow range from 0.76 to 0.77, Mg# [=Mg/ (Mg+$Fe^{2+}$) atomic ratio] from 0.63 to 0.65 and $TiO_2$<0.2 wt. % (average 0.17 wt.%) (Fig. 1a).

The total PGE contents of the Abdasht chromitites vary from 105 to 264 ppb, with an average of 176 ppb (similar to 172 ppb recently reported by Jannessary et al., 2012) in correlation with the range of PGE in other ophiolites (144-1064 ppb) (Tab. 1). All chromitite samples from the Abdasht complex display a steep negative slope in the PGE spidergrams, being enriched in the Ir-group (IPGE: Os, Ir and Ru) (98-252 ppb) and extremely depleted in the Pt-group (PPGE: Rh, Pt and Pd) (<20 ppb) (ΣIPGE/ΣPPGE=8-18) except Rh, so that except one sample, Pt and Pd contents are below detection limit (Fig. 1b) The relative enrichment of IPGE in chromitite samples is also reflected by highly negative slopes from Ru to Pt. These patterns and the low PGE abundances are typical of ophiolitic chromitites elsewhere (Fig. 1b) and indicating a high degree of partial melting (about 20-24%) of the mantle source very similar to the nearby mafic-ultramafic complex of Soghan (Najafzadeh and Ahmadipour, 2014). The binary plots of $TiO_2$ wt.% vs. Cr# show that the massive and most disseminated

Table 1

**Analyses of bulk-rock PGE in part per billion (ppb) of chromitites from the Abdasht ultramafic complex, Iran**

| Sample | Os | Ir | Ru | Rh | Pt | Pd | Au | Total PGE |
|---|---|---|---|---|---|---|---|---|
| N-A-4A | 28 | 38 | 110 | 10 | <2 | <2 | <5 | 186 |
| N-A-4B | 22 | 34 | 103 | 10 | 2 | <2 | <5 | 171 |
| N-A-5A | 18 | 34 | 107 | 17 | <2 | <2 | <5 | 176 |
| N-A-5B | 16 | 32 | 91 | 13 | <2 | <2 | <5 | 152 |
| N-A-6 | 60 | 56 | 136 | 12 | <2 | <2 | 18 | 264 |
| N-A-12 | 10 | 21 | 67 | 7 | <2 | <2 | 5 | 105 |

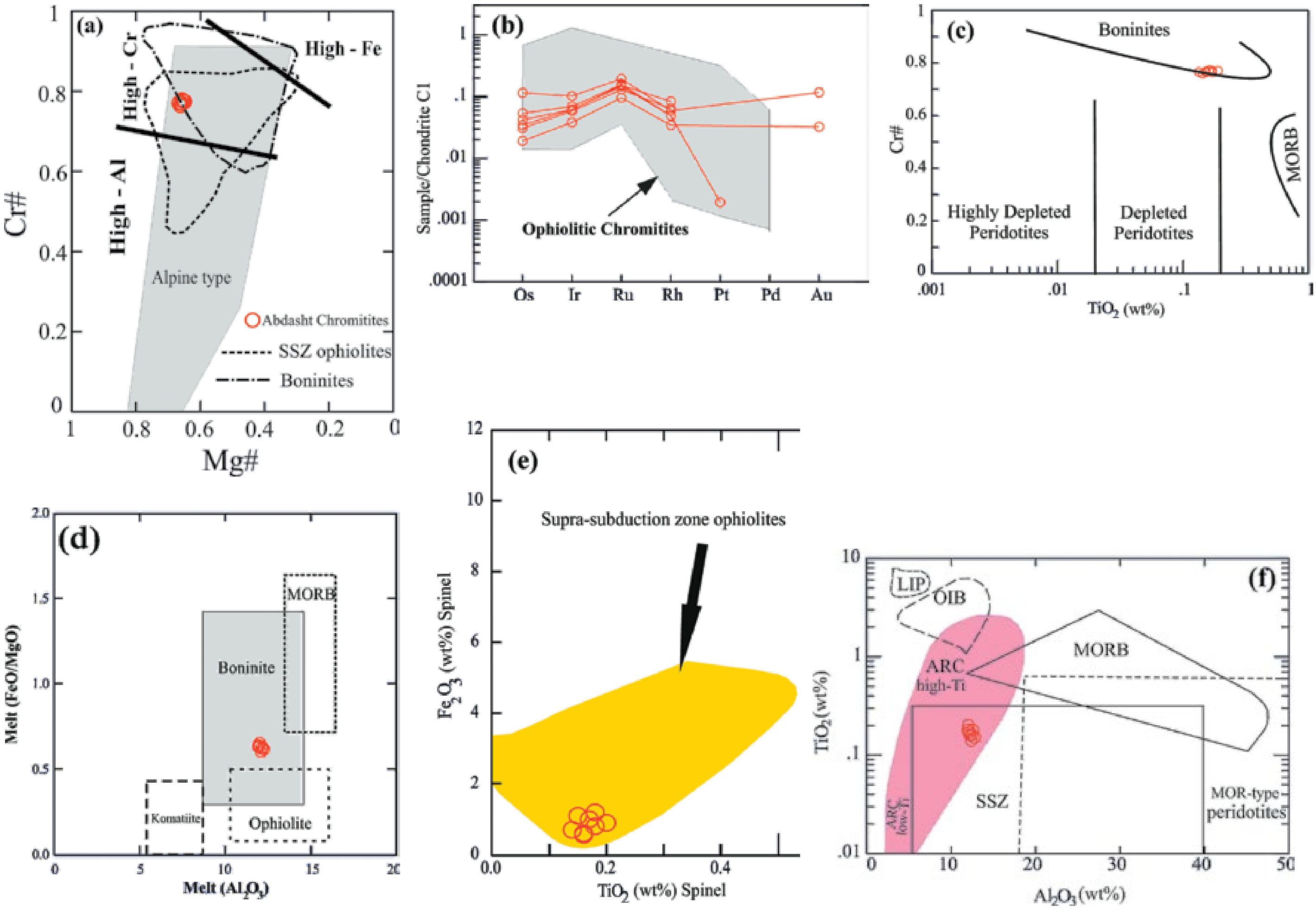

*Fig. 1.* a) Plot of Cr# vs. Mg# for chromian spinel in chromitites from Abdasht complex. b) Chondrite-normalized PGE spidergrams of chromitites from the Abdasht complex. c) $TiO_2$ vs. Cr# in chromian spinels, showing fields of boninites and MORB (mid-ocean ridge basalts). d) Estimated variation of the parental melt composition in terms of FeO/MgO vs. $Al_2O_3$ wt.% in the Abdasht complex. e) Plot of $TiO_2$ vs. $Fe_2O_3$ of chromian spinels of the Abdasht complex. f) Plot of $TiO_2$ versus $Al_2O_3$ in chromian spinel from the Abdasht complex with respect to modern-day tectonic settings. SSZ; Supra-subduction zone; LIP, large igneous province; MORB, mid-ocean ridge basalt; OIB, ocean island basalt

chromian spinels fall in the boninitic field (Fig. 1c). The $(Al_2O_3)_{melt}$ and $(FeO/MgO)_{melt}$ average values for the massive chromitites are estimated as 12.1wt.% and 0.61 respectively, also corroborating a boninitic parentage (Fig. 1d). Furthermore, massive chromitite on $Fe_2O_3$ vs. $TiO_2$ wt.% (Fig. 1e) and $TiO_2$ wt.% vs. $Al_2O_3$ wt.% plots (Fig. 1f) occupy mainly the field of supra-subduction zone and arc related peridotites.

## CONCLUSIONS

The mineral chemistry data and PGE geochemistry, along with the calculated parental melts in equilibrium with chromian spinel of the Abdasht chromitites indicates that the Abdasht ultramafic complex was generated from an arc-related magma with boninitic affinity above a supra-subduction zone setting.

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# SURFACE OF PLACER PLATINUM UNDER THE ELECTRON MICROSCOPE

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**ABSTRACT**. The surface of platinum grains is investigated under the scanning electron microscope with different magnification including in high resolution level. The objects of study are platinum grains from placers of the northern and middle Urals. Specific surface forms are found in every level of magnification. The details of placer platinum surface commonly discovered under the binocular microscope are cracks, cavities, coatings, inclusions, etc. Under the electron microscope, on the initial level of observation (magnification up to 5000-10000), pores, fissures, prints of obliteration and furrows of micron sizes are visible. At the next level (magnification up to 50000- 100000 and more) nano-forms of the platinum surface give hints to the genesis and influence of exogenic factors.

Methods of electron microscopy are widely applied in investigations of platinum grains. They give the opportunity to distinguish the surface forms, connect with the internal structure and reflect the influence of external (exogenic) factors. In particular, electron microscopy was applied for the study of platinum surface from placers of the Urals, Siberia, Komi Republic, USA and others (Mochalov et al., 2002; Rodionov et al., 2005; Mudalar et al., 2007; Melnikov, 2010; Osovetsky, 2011). Use of atom-forced microscopy revealed the fibrous nano-elements of internal structure in platinum of Chukotka (Grechkina et al., 2009).

The objects of our investigation are platinum grains from several placers of the northern and middle Urals. The images of platinum surfaces were made using a field emission scanning electron microscope JSM 7500F (JEOL) with cool emission. The chemical composition of some specimen was determined on an ED-spectrometer INCA x-act (Oxford Instruments) attached to an SEM 6390LV (JEOL). In total more than 100 platinum grains were studied under different levels of magnification.

Specific micro-forms of platinum surfaces reflecting the *influence of exogenic factors* are the prints of obliteration, pores, cavities, coverings, and inclusions of micron size. The micro-sized furrows, scratches and thin cuts are especially spread on the surface of platinum grains transported over large distances from source rocks. Micro-pores are the usual defects of platinum surfaces subjected to weathering. They reflect the intensity of chemical etching processes (Fig. 1). The presence of large amounts of cavities and caverns is connected with the zones of essential mechanical crushing of the platinum surface layer. The films and coverings on platinum surfaces are composed of various products of weathering (ferriferous, manganese, clayey, titanium, etc.) and absorbed complexes (compounds of gold, copper, mercury, zinc, arsenic). Inclusions in the platinum surface layer may be pressed grains during transportation or paragenetic minerals. The first ones are usually represented by quartz micro-grains, the second – by the platinum group minerals.

The micro-forms of platinum surfaces reflecting the *internal structure* of the metal include layering,

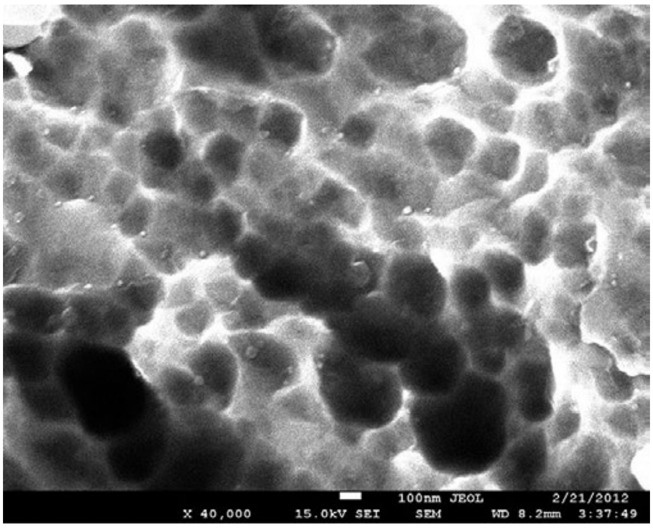

*Fig. 1.* Micropores on the platinum grains

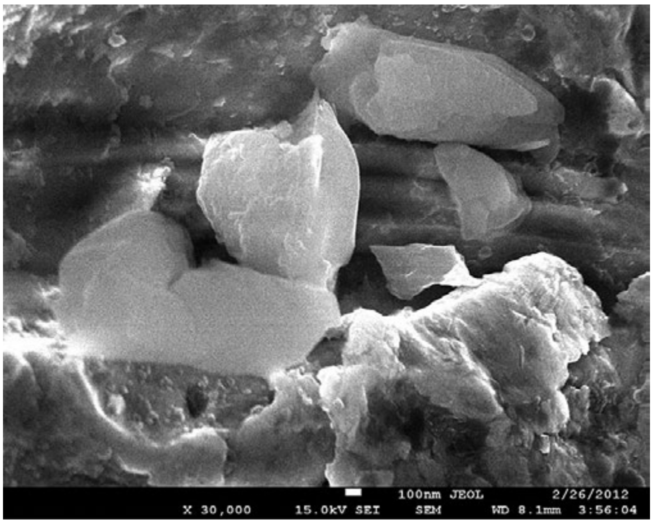

*Fig. 2.* Fibrous elements of platinum internal structure

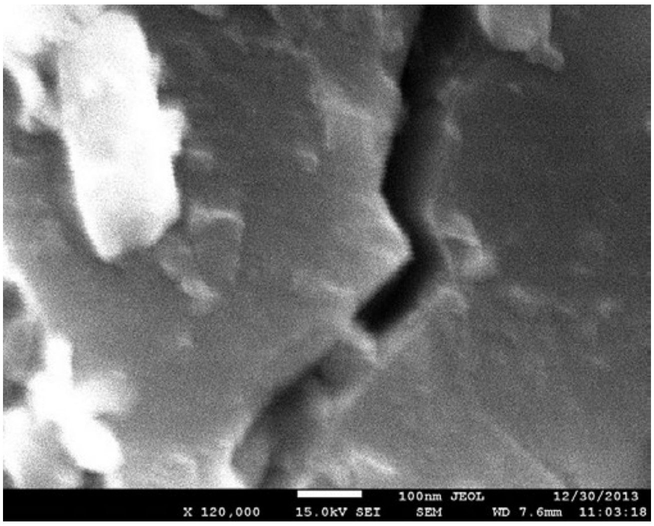

*Fig. 3.* Nano-fissure on the surface of platinum

fibrous or granular elements and fissures. The layering is often observed on the surface of platinum grains from placers situated proximal to source rocks. The most characteristic sign of a layered structure is a stepped surface. The fibrous elements are found in the surface layer of platinum with admixture of palladium from the Ekatherininskaya placer. They are up to 200 nm wide (Fig. 2). The granular structure is a typical peculiarity of platinum and gold grains (Osovetsky, 2012; Barannikov & Osovetsky, 2013). The micro-fissures on the platinum surface first of all reflect the peculiarities of the internal structure of the metal. Usually they correspond to defects in the crystal lattice. But in the process of migration along the rivers the initial fissures widen and new fissures may appeared.

Nano-forms of platinum surfaces are often found in combination with corresponding micro-forms. But they are sometimes concentrated into independent accumulations. The surface parts with abundant nano-pores mimic the short-term influence of aggressive environmental agents or the inhomogeneous composition of the metal. Nano-fissures are also typical surface forms. They predominate on local segments very often fixing defect zones of the crystal lattice (Fig. 3).

Thus, surface micro- and nano-forms of placer platinum provide useful information on genesis, internal structure and distance of transport from source rocks. In comparison with gold of these placers (Osovetsky, 2012; Barannikov & Osovetsky, 2013) the surface of platinum particles differs in having less deep furrows and cuts and less intensive mechanical processing of the surface layer due to the higher hardness of platinum.

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# EARLY PLATINUM ALLOY CRYSTALLISATION AND LATE SULFIDE SATURATION IN ARC-RELATED SUBMARINE LAVAS ASSOCIATED WITH MODERN VMS DEPOSITS

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**ABSTRACT**. Platinum group element (PGE) concentrations of the Pual Ridge lavas (arc-proximal in the Eastern Manus Backarc Basin) and the Niuatahi-Motutahi reararc lavas (northernmost Tonga Arc), were measured to investigate their variations and the timing of sulfide saturation during magma differentiation. Both of the submarine lava suites, which are related to magmatic hydrothermal mineralization, show similar PGE geochemistry. Palladium behaves incompatibly during the early stage of magma differentiation whereas Pt, Rh, Ru and Ir behave compatibly, showing positive correlations with MgO (fractionation index). These trends can be attributed to co-crystallization of Pt-alloy and Cr spinel. After prolonged magma evolution, the concentrations of all of the PGE as well as Pd/Cu decrease abruptly at ~3 % MgO, correlative with sulfide saturation. Late sulfide saturation resulted in the magmatic system becoming enriched in ore metals such as Cu and Au by the time of volatile saturation, which allowed the ore metals to partition into the exsolved magmatic gas and form magmatic hydrothermal deposits on the seafloor.

## INTRODUCTION

Magmatic hydrothermal Cu and Au deposits are closely associated with arc-related magmas and the ore metals are thought to originate from a coeval magma system. Therefore, the abundance of Cu and Au in the magma at the time of volatile exsolution is a critical factor for the formation of a Cu-Au deposit. The behaviour of these elements is largely controlled by sulfide phases during magma evolution because of their strong affinity with sulfide phases. The platinum group elements (PGE) can be used as a sensitive indicator of sulfide saturation because their partition coefficients into immiscible sulfide melts are several orders of magnitude higher than those of Cu and Au, and they are less mobile than these elements during low temperature alteration.

We investigated the PGE geochemistry of two submarine volcanic suites, the Pual Ridge lavas and Niuatahi-Motutahi (N-M) lavas, which are associated with Cu and Au mineralization, to understand variations in the chalcophile elements during magma evolution in ore-associated magmatic systems. The Pual Ridge is a recent submarine volcanic complex in the Eastern Manus Backarc Basin (Papua New Guinea). The Pual Ridge lavas show typical geochemical features of island arc lavas and vary in composition from basalt to rhyolite. The Cu-Pb-Zn hydrothermal deposits, which are mainly composed of chimneys that are a few tens of meters high, occur associated with dacite and andesite (Moss et al., 2001). The sulfide from this deposit contains high Au contents averaging 11.3 ppm, which is the highest among samples recovered from the sea floor (Moss et al., 2001). The N-M is an active volcanic caldera in the northern Tonga reararc. The N-M lavas mainly comprise dacite, but are genetically associated with basalt that occurs in the adjacent volcanic complex (~ 5 km west). Active hydrothermal vents are located in the central cone of the caldera. Molten sulfur collected from venting sites contains 1.7 % of Cu and 1.7 ppm of Au (Kim et al, 2011).

## RESULTS AND DISSCUSSION

The PGE geochemistry of the Pual Ridge and N-M lavas are both characterized by incompatible behaviour of Pd and compatible behaviour of Pt, Rh, Ru and Ir in the early stage of magma differentiation (Fig. 1). We suggest that these trends can be explained by crystallization of a Pt-rich alloy based on the following evidence: (i) Pt is not compatible in any silicate or oxide mineral but does occur in magmatic Pt-alloys reported from arc basalts, picrites, and cumulate rocks (Fig. 1). Furthermore, Pt-alloys contain minor IPGE

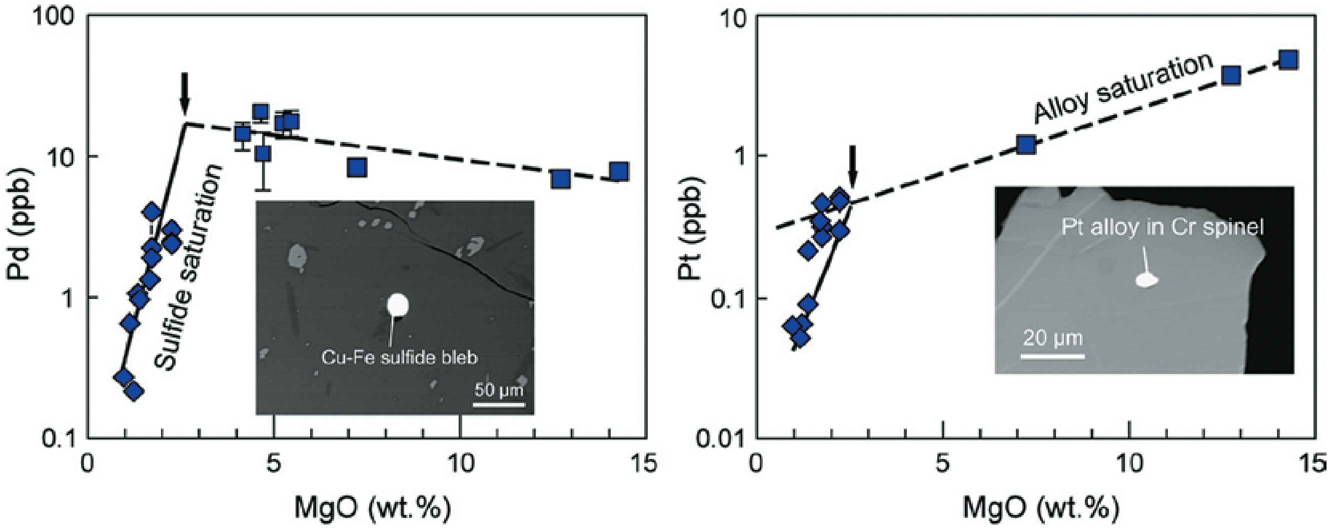

*Fig. 1.* Plots of Pd and Pt against MgO for samples from Nivatahi-Motutahi. Solid lines and dashed lines are trend lines of the samples before and after sulfide saturation, respectively. Black arrows represent the timing of sulfide saturation. Vertical dotted lines link duplicate analyses data. Inserted photos are a Cu-Fe sulfide bleb trapped in glassy matrix of N-M dacite (Left) and a Pt-alloy in Cr spinel from an Ambae picrite, Vanuatu (Right)

(Ru, Ir, Os), which can therefore account for some of the depletion of these elements with fractionation; (ii) Experimental studies of the Pt solubility in silicate melts suggest that, at the condition under which the Pual Ridge and N-M basalts crystallized, the measured Pt concentrations in the basalts were close to Pt-alloy saturation; (iii) Differences in duplicate analyses of the Pual Ridge basalts point to the presence of alloy nuggets and can be used to infer the composition of the nuggets. The results agree with the Pt-alloys found in arc picrites and cumulate rocks. The compatible behavior of Rh and IPGE (but not Pt) can also be partly attributed to Cr spinel crystallization because they partition strongly into Cr spinel under the oxidizing conditions that prevailed during solidification of the Pual Ridge and N-M lavas.

The abundances of all the PGE, together with Pd/Cu, begin to decrease sharply at ~3 wt. % MgO in both suites, which indicates sulfide saturation at this point and is consistent with the presence of a Cu-Fe sulfide bleb in N-M dacites with MgO<3 wt.% (Fig. 1). Sulfide nugget effects are also observed in both lavas with MgO below ~3 wt.%. Given that the mineralization is associated with dacites and andesites, volatile saturation is likely to have occurred slightly before or immediately after sulfide saturation in the Pual Ridge where Cu concentration of the melt reached up to ~250 ppm. The timing of volatile exsolution in the N-M was constrained by the Cl contents of melt inclusions and the results showed that it occurred at ~ 2% MgO, which is slightly after sulfide saturation. The Cu contents vary from 240 to 100 ppm in the N-M dacites, which are significantly higher than average Cu contents of arc dacites (~30 ppm; Stanton, 1994). We suggest that the late sulfide saturation in Pual Ridge and N-M lavas result in them being enriched in chalcophile ore metals such as Cu and Au until the point of volatile saturation and so that they could form magmatic hydrothermal deposits.

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# PGE IN MASSIVE SULFIDE DEPOSITS OF THE SOUTHERN URALS (NEW DATA)

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**ABSTRACT**. New data on PGE (platinum group elements) concentrations in ores of VMS (volcanic-hosted massive sulfides) deposits of the Southern Urals are given. The questions of geochemical specialization of the ores and behaviour of Au and PGE in their technological processing are discussed.

The main resources of non-ferrous metals of the Southern Urals are hosted by VMS deposits, including copper-pyritic, copper-zinc and polymetallic gold-copper ores. Large-tonnage copper-pyritic deposits such as Uchaly, Sibay, Podolsk, Yubileinoe, Novo-Uchaly, Zapadno-Ozernoe, Oktyabrskoe represent a considerable part of the reserves of non-ferrous metals for the metallurgical industry of the Russian Federation. In the last decades some information on the concentrations of PGE in pyritic deposits was published, owing to an improvement of analytical methods of PGE determination and a general growth of interest to the problem (Salikhov et al, 2001, Vikentyev et al., 2004, Pašava et al., 2007 and others). However, the need for further investigation is evident.

We obtained new data on PGE contents in ores, concentrates and tailings from the majority of VMS (pyritic) deposits of the Southern Urals (Table 1). The main conclusions are as follows:

1) Practically all ores of the studied deposits have elevated PGE content, represented mainly by Pt and Pd, which determine a platinum-palladium specialization of the pyritic ores.

2) The study of the PGE distribution in sulfide minerals of pyritic deposits has shown that the highest concentrations occur in galena and decrease from chalcopyrite over sphalerite to pyrite. This opens a way to some conclusions concerning the form of PGE and the conditions of their origin in the general process of the genesis of pyritic ore.

3) During processing of the pyritic ores Pt, on one hand, and Au and Pd on the other, behave in an opposite way. In the process of ore dressing, an accumulation of Au and Pd in concentrates takes place, while the quantity of Pt decreases. Platinum, however, increases in tailings, which can be explained by specific mineral forms of these platinoids and their dimensions.

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Table 1

**Contents (ppm) of precious metals in ores, concentrates, and tailings of pyritic deposits of the Southern Urals**

| | *Pt* | *Pd* | *Rh* | *Au* |
|---|---|---|---|---|
| Uchaly and Novo-Uchaly deposits | | | | |
| Ores (18) | 0.3–1.75 | – | – | 0.69–1.85 |
| Concentrates (8) | 0.29–0.62 | – | – | 1.72–4.6 |
| Dressing tailings (8) | 0.34–0.72 | – | – | 0.25–2.44 |
| Sibay deposit | | | | |
| Ores (24) | 0.0–1.05 | – | – | 0.0–1.97 |
| Concentrates (2) | 0.0–0.2 | – | – | 0–2.14 |
| Dressing tailings (4) | 0.22–2.19 | – | – | 0.62–1.21 |
| Bakr-Uzyak deposit | | | | |
| Ores (9) | 0.12–2.64 | – | – | 0.1–2.90 |
| Podolsk deposit | | | | |
| Ores (3) | 0.10–0.92 | – | – | 0.50–2.52 |
| Concentrates (4) | 0.32–1.09 | – | – | 1.65–19.7 |
| Dressing tailings (4) | 0.06–1.36 | – | – | 0.45–0.80 |
| Yubileinoe deposit | | | | |
| Ores (9) | 0.05–2.0 | 0.06–1.7 | – | 0.60–4.20 |
| Tash-Tau deposit | | | | |
| Ores (9) | 0.002–1.2 | 0.003–0.25 | – | 3.24–18.8 |
| Concentrates (6) | 0.07–1.22 | 0.06–1.8 | – | 3.46–9.28 |
| Tailings of flotation (3) | 0.22–2.19 | 0.009–0.48 | – | 0.90–2.32 |
| Bakr-Tau deposit | | | | |
| Ores (3) | 0.0–0.22 | 0.0–0.03 | 0.0–0.002 | 2.90 |
| Concentrates (6) | 0.0–0.80 | 0.015–0.03 | 0.003–0.01 | 9.8–12.5 |
| Balta-Tau deposit | | | | |
| Ores (3) | 0.12–0.35 | 0.07 | – | 0.47–3.08 |
| Oxidized ores (2) | 0.40–1.10 | – | – | 7.60–11.52 |
| Uzelga deposit | | | | |
| Copper-zinc ore | 0.20 | – | – | 1.20 |
| Copper concentrate (2) | 0.30–0.36 | – | – | 0.96–3.92 |
| Zinc concentrate | 0.12 | – | – | 3.68 |
| Tailings of flotation (2) | 0.44–0.68 | – | – | 0.84–1.28 |
| Collective tailings | 0.48 | – | – | 0.92 |
| XIX Partsyezd deposit | | | | |
| Zinc-pyritic ore | 0.40 | – | – | 12.3 |
| Molodezhnoye deposit | | | | |
| Copper concentrate | 0.18 | – | – | 2.52 |
| Tailings of flotation | 0.80 | – | – | 2.32 |
| Collective tailings | 0.38 | – | – | 0.48 |
| Aleksandrinka deposit | | | | |
| Zinc–pyritic ore | 0.34 | – | – | 2.36 |
| Tuba-Kain deposit | | | | |
| Oxidized ores | 0.008–0.011 | 0.002–0.043 | 0.003–0.040 | 0.56–22.0 |

*Footnote*. In brackets –number of analyses. PGE were determined by atomic absorption and kinetic methods in the chemical-spectral laboratory of TsNIGRI (analyst T.V.Puchkova) and ICP-MS method in the Central Laboratory of VSEGEI (analysts V.A. Shishlov and V.L. Kudryavtsev); the lower limits of detection of PGE and Au – 0.002 ppm).

# MANTLE PARTIAL MELTING, SULFIDE SEGREGATION AND METALLOGENIC POTENTIAL IN THE HONGSHISHAN MAFIC-ULTRAMAFIC COMPLEX, XINJIANG, NORTHWEST CHINA – IMPLICATION FROM PGE GEOCHEMISTRY

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**ABSTRACT**. The parental magma of the Hongshishan complex, classified as picritic magma, is originated from about 15% partial melting of the primitive mantle. The estimated degree of sulfide segregation is 0.015%-0.20%, with the R-factor is 2940-4140. The potential for PGE prospection is low, while Ni requires attention.

## GEOLOGIC SETTING AND PGE GEOCHEMISTRY

The recently discovered Hongshishan mafic-ultramafic complex hosting low grade Ni-Cu mineralization is located on the northeastern Tarim plate and west of the Beishan rift. The complex consists of diorite, gabbro, olivine gabbro, troctolite, peridotite, pyroxene peridotite and dunite. The main facies, a gabbro unit with a LA-ICP-MS zircon age 272.5±3.5Ma, occurs along the margins of the complex, while the mineralized pyroxene peridotite and dunite are restricted to the center, and the olivine gabbro in the middle. The orebody is a layer or lens with a low grade (0.2% Ni). A series of disseminated sulfides including pyrrhotite, pentlandite, chalcopyrite, and pyrite is enclosed by olivine and pyroxene.

Except of troctolite, the samples of peridotite, pyroxene peridotite and dunite, although low in Ni, collected from drill core ZK16-5 for PGE analysis are rich in sulfide compared to the whole complex. The total PGE content of 11 samples ranges from 0.85 ppb to 14.79 ppb and is lower than the primitive mantle (23.5 ppb). The content of PGE decreases successively from dunite, peridotite, troctolite, to pyroxene peridotite. An obvious correlation exists between the PGE and sulfide contents as well as the content of mafic minerals. The primitive mantle normalized patterns of PGE-Ni-Cu of every rock type of the complex are similar, i.e. slightly tilted to the left showing weak differentiation between PPGE and IPGE, with a weak negative anomaly of Ir and positive anomaly of Ru.

## MANTLE PARTIAL MELTING CALCULATION AND SULFIDE SEGREGATION SIMULATION

The lack of PGE enrichment may be attributed to the following two reasons. (1) At low degrees of partial melting, the PGE remain in the mantle. (2) Sulfides segregating at depth remove most of the PGE from the parental magma. Considering the obvious correlation between the PGE and sulfide, the PGE content is restricted by the sulfide content, and therefore fractional crystallization does not seriously affect the PGE content. Accordingly, the PGE content is calculated for different degree of partial melting. According to the simulation (Fig. 1), the primitive mantle suffered about 15% partial melting. The Ni/Pd ratio is lower than the primitive mantle, implying no sulfide segregation at depth; otherwise

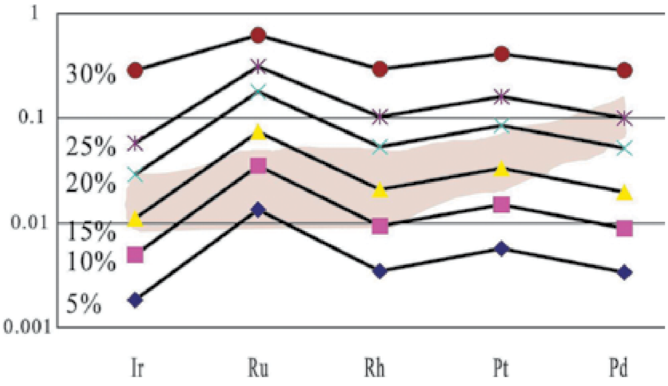

*Fig. 1.* Comparison of model composition with sample data. Dashed area represents sample compositions

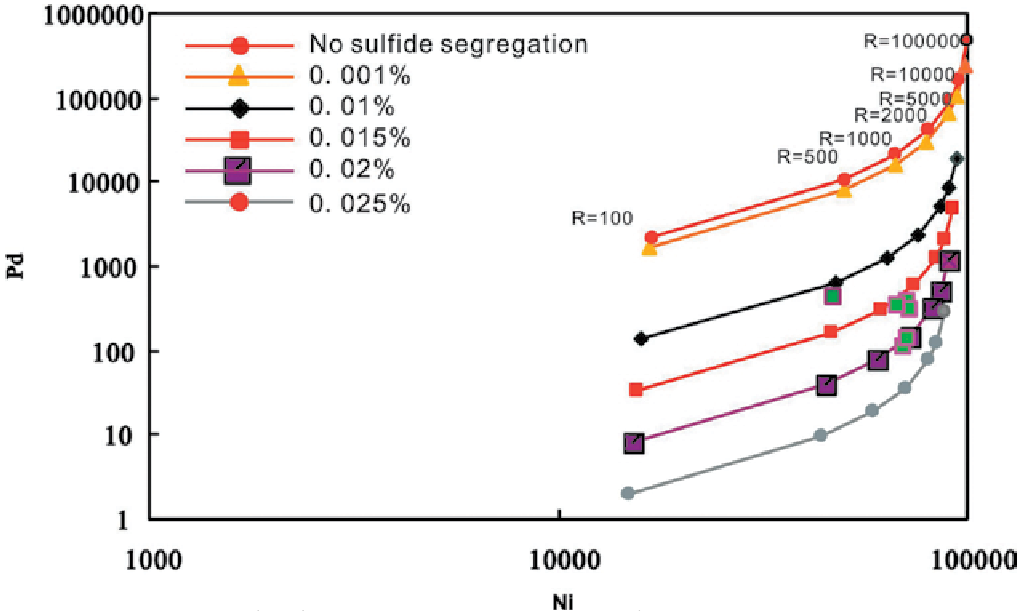

*Fig. 2.* The simulation of sulfide segregation degree and R-factor in the Hongshishan complex

the Pd content will greatly reduced and the Ni/Pd ratio will be higher than in primitive mantle. To estimate the degree of sulfide segregation and the R-factor, the metal content in 100% sulfide in ore has been calculated. Using the scatter diagram of Ni-Pd, the parental magma underwent 0.015%–0.02% sulfide segregation at an R-factor of about 2000 (Fig. 2). According to the formula published by Campbell & Naldrett (1979) $C_{isul}=C_{isil}\times D_l\times R+1)/(R+D_l)$ the R-factor is 2964 taking Cu as the standard to calculate and 4141 taking Ni, which are still within the same magnitude.

## METALLOGENIC POTENTIAL

According to Naldrett (2004), Ni enrichment and low contents in PGE occur when R=100~2000, like at Sudbury. Cu, Ni and PGE in the ores increase, while the PGE is not of economic grade, at R=2000~10000. Cu and Ni in sulfide change little, whereas the PGE contents increase quickly when R=10000~100000, such as in the Merensky Reef. The Hongshishan complex should be enriched Ni, with R-factors of 2940-4140 according to the existing metallogenic theory. Meanwhile, the PGE content with 0.18-0.97 g/t (Pt+Pd), averaging to 0.63 g/t in 100% sulfide, is still below the economic grade. The PGE prospecting potential is low, while the Ni requires attention, especially in the bottom of the pyroxene peridotite. This is supported by massive or vein sulfide, with maximum 1.7% Ni, found at 1100m in drill cores ZK11-2 and ZK40-1.

## CONCLUSIONS

The parental magma of the Hongshishan complex, classified as picritic magma, originated from about 15% partial melting of the primitive mantle. In addition, the degree of in situ sulfide segregation is simulated at 0.015%-0.020%, and moreover, the R-factor is estimated at 2940-4140. The low PGE content is mainly attributed to the low degree of partial melting. Given the partial melting, degree of sulfide segregation and the R-factor of other typical PGE/Ni-Cu deposits, the potential for PGE prospection is low, while Ni requires attention, especially in the bottom of the pyroxene peridotite.

*Acknowledgments. We thank Qi L. for the laboratory assistance. We appreciate No. 6 Geological Party, Xinjiang Bureau of Geology and Mineral Resources, China, for their careful help and critical suggestions in the field work. Funds from the key scientific research project of Xinjiang Bureau of Geology and mineral resources (No. XGMB2012012).*

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# NOBLE METALS GEOCHEMISTRY AND MINERALOGY IN SULPHIDE MINERALIZATION OF GABBRO-DOLERITE BODIES (PAY-KHOY, RUSSIA)

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**ABSTRACT**. The results of geochemical, mineralogical study of noble metals mineralization and form of its location in the copper-nickel sulphide ores from gabbro-dolerites bodies of Pay-Khoy hengursk complex are presented. Formation stages of PGE mineralization are proposed with characterization of mineral assemblages and processes that lead to its formation.

The Hengursky gabbro-dolerite complex is located in the central part of the Yugorski Peninsula (north-east of Europe, between the Barents and Kara Sea, in the Nenets Autonomous District) and characterized by the wide-spread occurrence of intrusive bodies associated with copper-nickel sulphide ores bearing noble metals mineralization. The results of a chemical and mineralogical study of rocks, ores and silicification zones in the Pay-Khoy area are presented in the abstract.

The presence of noble metals in the mineralized gabbro-dolerite bodies in the Pay-Khoy area was revealed in 1969 during the geological survey. Up to 1 ppm platinum (Pt+Pd to 0.83 ppm) and up to 0.22 ppm gold were reported. According to our data, the content of noble metals in the gabbro-dolerite varies from 0.14 to 2.29 ppm. In particular, Pt+Pd does not exceed 0.47, gold <0.24 silver <1.85 ppm, and Os and Ir content in most of the samples is significantly lower than bulk earth values (not higher than 0.001 and 0.02 ppm, respectively). It is noted that with the increasing of the platinum content concentrations of palladium and ruthenium also increase, while the concentrations of osmium and iridium decrease; moreover, a negative anomaly of Ir is observed when the Pt content is close to Pd. This fact shows a higher-than-normal degree of geochemical differentiation of the mineralized magmatic rocks. The results of correlation analysis of noble metals content showed that gabbro-dolerite from Pay-Khoy differ significantly from the igneous rocks of PGE ore deposits. The iridium deficit, as it turns out, is not unique to ores from the Pay-Khoy gabbro-dolerites, but is characteristic (less than 0.02 ppm) for ore deposits such as Insizwa, J-M reef, Pechenga, Langmuir, Mount Keith, Sudbury, Voisey`s Bay and others (Shaybekov, 2013a).

We found that higher concentrations of PGE are confined to the most differentiated coarsely crystalline dolerites. Almost in all analyzed samples the ratio of Pt/Pd is <1 with fluctuations from 0.05 to 0.95 ppm. In sulphide-rich samples the value of Pt/Pd fluctuates from 1.10 to 1.74 ppm and this value depends directly on the content of sulphides.

Microprobe analysis using a scanning electron microscope revealed the mineralogy of noble metals in rocks and ores. In some cases, noble metals are finely dispersed in pyrrhotite, chalcopyrite, arsenopyrite, pentlandite, galena, cobaltite, sphalerite, whereas and in others they mainly occur as separate micron-sized mineral phases, such as gold, electrum, kotulskite, hessite, sperrylite, Pt-Pd telluride (Fig. 1). This distribution can be explained by different conditions of mineral formation and results from fluid-hydrothermal conversion of magmatic ore, accompanied by a redistribution of noble metals. In addition, quartz veinlets ranging from a few millimeters up to 1–2 meters are present in the gabbro-dolerite bodies. Often, higher concentrations of gold and silver are found in these veinlets in association with chalcopyrite (Shaybekov, 2013b, 2013c).

The distribution of gold, silver and platinum in the Pay-Khoy gabbro-dolerite bodies was also studied using X-ray microprobe technique. It was

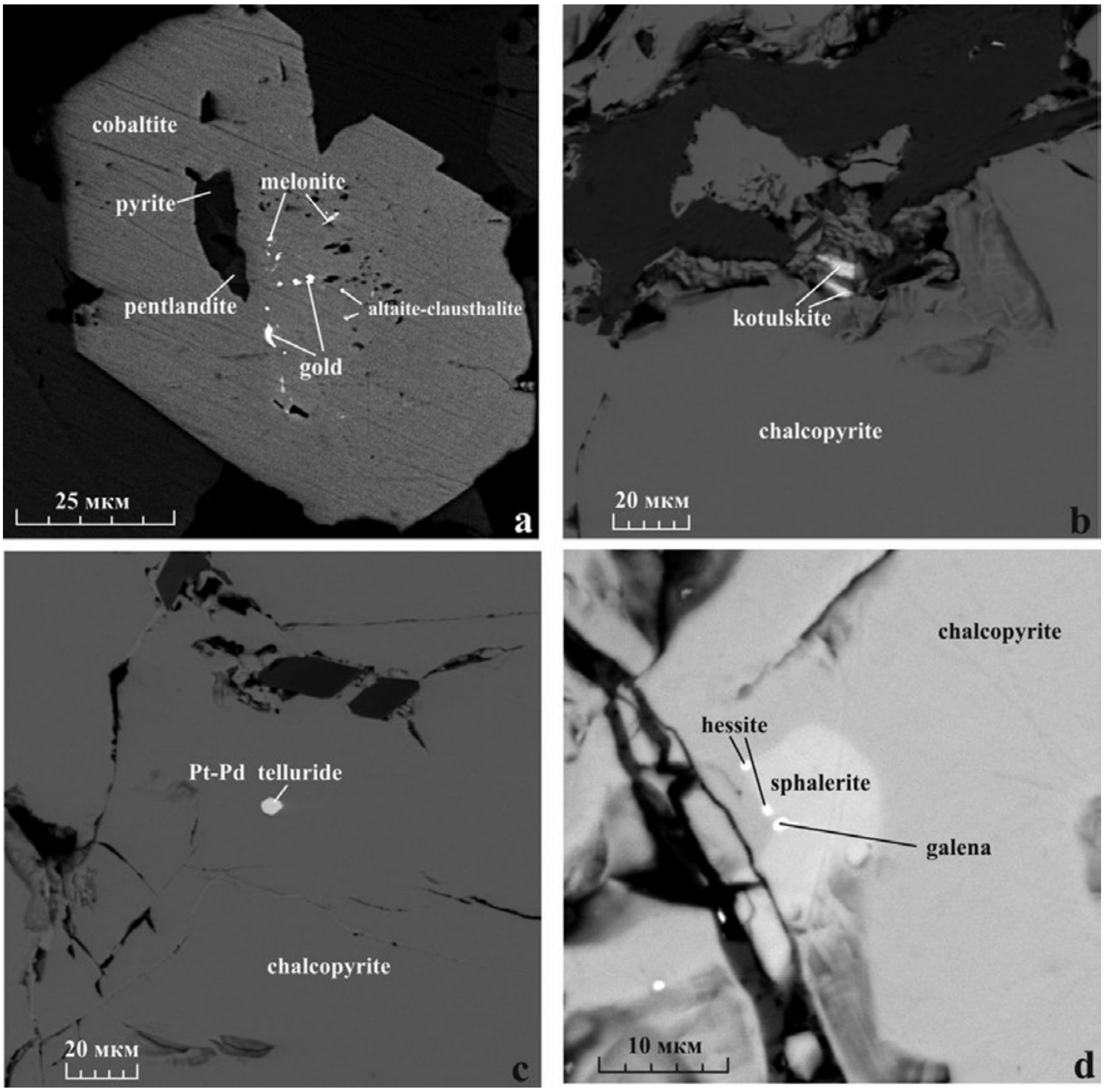

*Fig. 1.* Scanning electron-micrographs with sulphide mineralization in Pay-Khoy gabbro-dolerite bodies: a – gold, altaite-clausthalite, melonite and pentlandite in cobaltite, b – kotulskite on the periphery of chalcopyrite; c – Pt-Pd telluride in chalcopyrite, d – galena and hessite on the border of chalcopyrite and sphalerite

found that these elements are distributed unevenly between the three mineral assemblages:

1) early (magmatic) chalcopyrite-pentlandite-pyrrhotite;

2) intermediate (magmatic) sulfide-telluride-sulfarsenide;

3) late (hydrothermal) telluride-arsenide.

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# PdTe AND $PdTe_2$ IN BORNITE OF THE VOLKOVSKY DEPOSIT (CENTRAL URALS): STUDY BY SEM, EDS AND “IN SITU” MICRODIFFRACTION

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**ABSTRACT**. The complex data on chemical composition and structural studies of PdTe and $PdTe_2$ analyzed “in situ” in bornite of the Volkovsky deposit by microprobe analysis, and back-scattered electron (BSE) microdiffraction, are presented. The findings of PdTe and $PdTe_2$ have the best stoichiometry and single crystalline structure. It was experimentally defined that the monocrystals of PdTe have hexagonal symmetry by morphological observations supported by electron microdiffraction.

Palladium tellurides occur in magmatic, hydrothermal and metamorphosed Cu-Ni-PGE deposits as minerals with a variable ratio of elements: moncheite – (Pt, Pd) $(Te, Bi)_2$, merenskyite – (Pd, Pt, Ni) $(Te, Bi)_2$, kotulskite – Pd(Te, Bi). An important feature of palladium tellurides is the common presence of essential amounts of platinum and bismuth. Stoichiometric monotelluride and ditelluride of palladium still were not found in the nature though these phases were successfully produced by experimental synthesis (Stolyarova & Osadchii, 2011).

In Russia palladium tellurides were reported from the Kola Peninsula, the Norilsk area and the Urals in connection with Cu-Ni ores in ultramafic and mafic intrusive rocks. In the Urals region, Kulikova & Varlamov (2002) described rare palladium tellurides of variable elemental composition, also containing a large portion of bismuth and platinum, but also nickel and other metals. Bismuth-bearing kotulskite and keithconnite ($Pd_{3-x}Te$) also were reported from the Baron PGE deposit of the Volkovsky massif in the Central Urals (Anikina & Alexeev, 2010).

During mineralogical studies of copper ores of the Volkovsky deposit hosted by gabbro-diorite (Central Urals), single crystalline PdTe and $PdTe_2$ microcrystals of 5 µm in size were detected in bornite (Fig. 1). The chemical composition of the grains and the host bornite were analyzed by SEM TESCAN VEGA3 with EDS Oxford instruments X-Max. The structure of the particles and the host bornite was studied “in situ” in polished sections with accompanied diffraction equipment (Oxford instruments Nordlys). Based on EDS analysis the Pd:Te atomic ratio in tellurides is equal to 1 : 1.01 and 1 : 1.96 demonstrating perfect stoichiometry, i.e. very close to the ideal PdTe and $PdTe_2$ compositions. According to “in situ” back scattered electrons diffraction PdTe is characterized by a hexagonal structure that is in a good correspondence with the synthetic analogue (Stolyarova & Osadchii, 2011). The absence of Bi within the studied tellurides, and the co-existence of PdTe and $PdTe_2$ within the same bornite host grain are noteworthy.

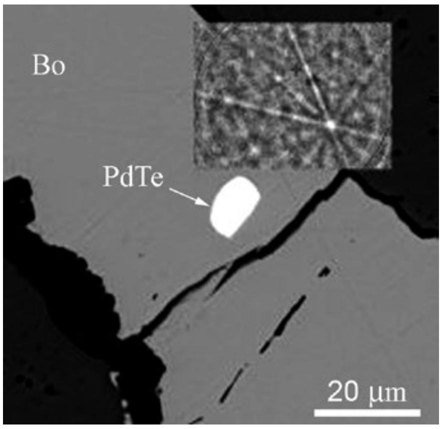

*Fig. 1.* BSE image of PdTe within bornite, inset – “in situ” diffraction pattern of back scattered electrons from the PdTe grain

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# NORIL'SK ORE FIELD: EPIGENETIC METAMORPHOGENIC-HYDROTERMAL Sn-Pt-Pd-Ag MINERALIZATION

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**ABSTRACT**. In the Noril'sk ore field, there are metamorphogenic-hydrothermal veins and nests of anhydrite, calcite, dolomite, prehnite, datolite, apophyllite, quartz, hisingerite, and zeolites, which contain magnetite, mackinawite, valleriite, Ni-pyrite, millerite, bornite, chalcocite, heazlewoodite, hematite, wurtzite, sphalerite, Ag, Bi, Pb, Mn, and Cd sulfides and selenides, as well as Ni-Co-Fe arsenides and antimonides. Hydrothermal minerals include silver (Au < 0.01 wt.%), often with 1–10 wt.% Hg, as well as argentopentlandite and chalcopyrite–lenaite $AgFeS_2$ solid solution. Metamorphosed ores contain dispersed PGM including vysotskite, Ag-paolovite, palladoarsenide, kharaelakhite and malyschevite. Vysotskite occurs in metamorphosed sulfide ores in association with actinolite, Fe-chlorite, prehnite, pumpellyite, ilvaite, millerite and babingtonite. Pneumatolytic paolovite was replaced by cassiterite, Sn-containing hydrogrossular-andradite and sobolevskite, whereas sperrylite was replaced by platinum.

In magmatogenetic sulfide ores the main part of Ag is dispersed in base metal sulfide (BSM), and a significant amounts of Ag is found in the form of hessite $Ag_2Te$; Au is contained in pneumatolytic Pt – Pd intermetallides, Au – Cu and Au – Ag minerals. A small part of Pd is dispersed in BSM (pentlandite), whereas significant Pd and Pt are contained in pneumatolytic PGM. Among the pneumatolytic PGM of the Noril'sk ores sulfide minerals are absent. Instead, pneumatolytic Pd and Pt minerals comprise intermetallides of Pd and Pt with Fe, Cu, Sn, Pb, Bi and also tellurides, arsenides, and antimonides (Kulagov, 1968; Spiridonov, 2010).

The area of the East Siberian Platform that was covered with 4 km thick flood basalts and was saturated with the trap formation intrusions underwent post-trap subsidence. The trap formation (basalts, gabbro-dolerites, Ni-Cu ores, 251 Ma), postore minettes (250 Ma) and subtrap strata were subjected to epigenetic burial metamorphism under conditions of zeolite facies (ZF) (Rb/Sr ages of apophyllite are 232-212 Ma), then prehnite-pumpellyite facies (PPF) (Rb/Sr ages of apophyllite are 212-196 Ma) and, again, zeolite facies (Rb/Sr ages of metabasalts and apophyllite are 187-122 Ma) (Spiridonov, Gritsenko, 2009). The maximum metamorphic grade is 2.5 kb and 310° C. Metabasalts and metadolerites of the trap formation contain occurrences of the opper-zeolite formation, such as agate, datolite, and Iceland spar (Zolotukhin & Ryabov, 1975; Spiridonov & Ladygin, 2000).

Each sample of the sulfide ores contains micro veins with hydrothermal magnetite and mackinawite. In the magmatogenic ores the following minerals are developed as single crystals, nests, micro- and macro-veins and bands, also including large blocks: magnetite, pyrite-magnetite aggregates, millerite, mackinavite, bornite, Ni-pyrite, valleriite, chalcocite, heazlewoodite, hematite, wurtzite, sphalerite, galena; thiospinels and arsenides of Fe, Ni, Co; native silver; breithauptite, parkerite, ullmannite and others. Anhydrite, calcite, dolomite, quartz, prehnite, serpentine, smectites, chlorites, hydrogarnets, datolite, apophyllite, hisingerite and zeolites are associated with them. The sequence of epigenetic ore formation is:

1) millerite+chalcopyrite+pyrite±greenalite (ZF),
2) chalcopyrite + pyrrhotite + stilpnomelane (ZF-PPF),
3) associations with bornite, magnetite, anhydrite (PPF),
4) associations with chalcocite and heazlewoodite (ZF),
5) associations with valleriite, Ni-pyrite (ZF),
6) U-Ag-Bi-Co-Ni formation with arsenides and antimonides, native silver, arsenic and bismuth, Ag, Bi, Pb, Mn, and Cd sulfides and selenides; uraninite (ZF),
7) associations with marcasite, quartz, calcite, hisingerite, tochilinite (low T path of ZF) (Spiridonov & Gritsenko, 2009).

During the process of low-grade metamorphism of the Noril'sk ores Ag is more mobile, whereas Pd is less mobile and Pt is even less mobile. No evidences of Au mobilization have been detected (Spiridonov, 2010). The Pb isotope composition of metamorphogenic-hydrothermal mineralization corresponds to the Pb isotope composition of the Earth's crust (Spiridonov & Gritsenko, 2012).

Hydrothermal minerals include native silver (Au < 0.01 wt. %), often with 1–10 wt. % Hg, as well as argentopentlandite, chalcopyrite–lenaite $AgFeS_2$ solid solution, and others. Metamorphosed Noril'sk ores contain the holotype of vysotskite (Genkin, Zvyagintsev, 1962) in association with actinolite, chlorite, prehnite, pumpellyite, ilvaite, millerite, and babingtonite. The vysotskite contains up to 1 % Fe and but no Pt – $(Pd_{0.79}Ni_{0.18}Fe_{0.02})S$. In localities with abundant parkerite or hisingerite, pseudomorphs of Ag-paolovite (without Sb, Pt, Au) after pneumatolytic Sb-paolovite are present. Orcelite from pseudomorphs after pneumatolytic PGM contains up to 10 wt. % Pd, and breithauptite up to 4 % Pd. Veinlets which usually comprise chlorite, serpentine and calcite contain palladoarsenide when they crosscut mayakite PdNiAs grains (Spiridonov & Korotaeva, 2011). Malyschevite $PdCuBiS_3$ occurs only in ores with abundant veinlets of bornite. Cassiterite, Sn-containing hydrogrossular-andradite and sobolevskite replaced pneumatholytic paolovite. Sometimes kharaelakhite $(Pt,Cu,Pb,Fe,Ni)_9S_8$ occurs in the metamorphosed ores, and is occasionally overgrown by cooperite PtS. Occasionally native palladium or cooperite are found as overgrowth on the replacement rim of platinum around sperrylite. The metamorphosed magmatogenic ores which were rich in Pd minerals and hessite are composed of native silver, laflammeite, telargpalite and sopcheite in association with Se-bearing galena and agvilarite. The development of vysotskite and cooperite in low grade metamorphosed ores is correlated with the experiments on crystallization of PdS and PtS from low-temperature hydrothermal solutions (Evstigneeva et al., 1995). Thus the metamorhogenic-hydrothermal PGM of the sulfide ores are significantly different from the pneumotolytic PGM.

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# HSE DISTRIBUTION AND Os ISOTOPE SYSTEMATICS IN HYDROTHERMAL DEPOSITS

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**ABSTRACT**. Concentrations and sources of HSEs (PGEs+Au+Re) in hydrothermal deposits through time are considered. Even though PGE concentrations in hydrothermal sulphides are generally low (about 3 times of magnitude lower than that in magmatic counterparts), it is important to better understand their recycling between crust and mantle via hydrothermal and magmatic fluids. Several examples of VHMS deposits through time are discussed, including VHMS in the Urals. Contribution of HSEs from magmatic fluid is addressed using the example of the HSEs contents within modern magmatic fluid (volcanic gas condensates) from subduction zone setting.

The seafloor hydrothermal acivity is an important mechanism of metals cycling between mantle and continental crust, producing Volcanogenic Hydrothermal Massive Sulphide (VHMS) deposits in various tectonic settings through time. The metals in sea-floor hydrothermal systems may arise purely from the interaction of circulating seawater with host rocks, or there may be an admixture from the fluid escaping from magma at depth.

Concentrations and sources of Highly Siderophile Elements (HSE: Ru, Rh, Pd, Re, Os, Ir, Pt Au) were studied in hydrothermal VHMS deposits from Archean to present using new and published Re-Os isotopic data and the HSE concentrations. In general, concentrations of HSE, as normalised to C1-chondrite, are situated slightly above the mantle values, with the exeption of higher Au contents; and they are approximately 3 orders of magnitude lower compared to magmatic sulphides.

Remarkably, the Re/(Common Os) ratio significantly increases from Archean deposits in intracratonic settings to the Palaeozoic VHMS deposits in island arc settings, reaching the highest values in modern sulphides from MORB settings, with simultaneous decrease in common Os values. These observations may be related with a change of the main metal sources related to different tectonic settings through time.

In Urals, the PGE and Re elemental and Re-Os isotope compositions have been studied within three distinctly different Urals VHMS deposits (Gannoun et al., 2003; Tesalina et al., 2008). The PGE are enriched in first-stage high-temperature portions of hydrothermal systems and correlate with Co and Au contents. The Re has more affinity with lower temperature polymetallic assemblages and correlates positively with Zn and Mo. In general, the Re/Os ratio decreases from the interior (hydrothermal-metasomatic ore facies) to the exterior (clastic and seafloor altered ore facies) of the hydrothermal system and reflects the progress of mixing between hydrothermal fluid and seawater.

The initial $^{187}Os/^{188}Os$ ratios increase with depth in the hydrothermal system in the following order: seafloor altered sediments – clastic sulphides – massive sulphides – stockwork zone – sulphide chimney. The straight linear correlation between initial $^{187}Os/^{188}Os$ and 1/Common Os shows the mixture of two components, which could be identified as hydrothermal fluid and seawater. Thus, our studies of ancient Devonian hydrothermal systems confirm that the Os isotopic composition in the ore facies is controlled by the mixture of at least two end-members – seawater and hydrothermal fluid, as has been shown for the TAG mound (Brugmann et al., 1998).

Rhenium enrichment in modern VHMS deposits may be related with higher Re contents in present day seawater, which along with the hydrothermal fluid is one of the main sources of metals in VHMS deposits. Modern seawater is characterised by a high Re/Os ratio of ~730, whereas hydrothermal fluid has a much lower Re/Os ratio. In general, the Re/Os ratio increases and Os contents decrease by 2 order of magnitude from the stockwork toward the seafloor sulphides, reflecting a fluid – seawater mixing process. The same pattern has been observed across hydrothermal chimneys, with higher Re/Os ratio and lower Os contents toward the outer part of the chimney. This pattern is confirmed by $^{187}$Os/$^{188}$Os isotopic mixing between these two end-members, as it was shown for modern and ancient VHMS systems.

The contribution of magmatic fluids was proposed for the VHMS deposits (including the Urals) based on melt inclusions and isotopic evidence. How would this influence the PGE contents in hydrothermal fluids? To answer this question, we address the PGE concentrations and Os isotopic compositions of modern magmatic fluids (volcanic gas condensate) in the Kurile-Kamchatka subduction zone setting (Tessalina et al., 2008; Yudovskaya et al., 2008). Gas condensates of the Kudryavy volcano are enriched with Re, Os and Au (to 210 ppb Re, 0.907 ppb Os, 2.4 ppb Au, 0.49 ppb Pt, 0.4 ppb Pd, 0.04 ppb Ir, 0.07 ppb Rh, 0.009 ppb Ru). The measured enrichment factors demonstrate that Os is the element that is most strongly compatible with this fluid. Fluid compatibility decreases in the sequence: Os>Re>Au>Pt>Pd over the temperature range from 480 to 850 °C. The $^{187}$Os/$^{188}$Os isotope ratio of fumaroles (0.122-0.152, up to 1.82) is typical for the DMM and close to that of Kamchatka peridotite xenoliths. The addition of such a PGE-rich fluid will significantly increase the PGE concentrations of hydrothermal deposits. However, the Os isotopic composition of magmatic fluids will be close to that of the mantle wedge, and will influence the Os isotopic composition of the hydrothermal fluids.

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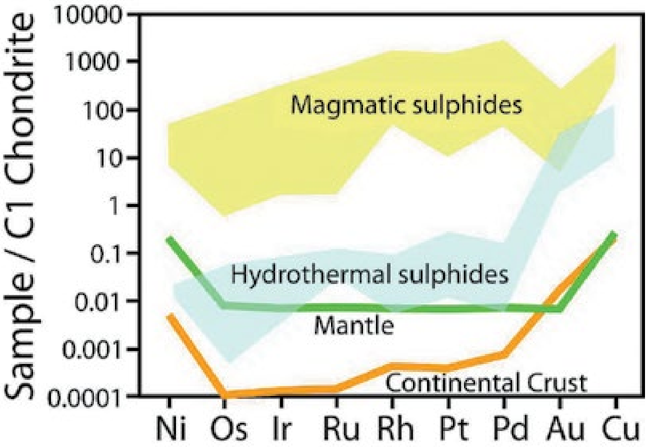

*Fig. 1.* Chondrite normalized HSE (plus Ni and Cu) pattern for hydrothermal sulphides (see text). Continental crust, mantle and magmatic sulphides are shown for comparison.

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# MINERALOGY, GEOCHEMISTRY AND IN SITU Re-Os DATING OF SULFIDES FROM MEGACRYSTALLINE PYROPE PERIDOTITES FROM THE UDACHNAYA PIPE, SIBERIAN CRATON

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**ABSTRACT**. Re-Os isotopic compositions for 2 types of "primary" Fe-Ni MSS sulfides from harzburgite-dunite xenoliths from Udachnaya kimberlite pipe have been determined by laser ablation MC-ICP-MS. Calculated $T_{RD}$ ages for sulfides fall into two main intervals – 3.0 – 3.5 Ga and 2.8 – 2.98 Ga and are well correlated with previous results for subcontinental lithospheric mantle under Siberian Craton.

The Udachnaya kimberlite pipe has brought to the surface a very wide range of uniquely fresh mantle xenoliths. One of the most interesting types is the megacrystalline pyrope harzburgite-dunites, which consist primarily of ultracoarse olivine (up to 10 cm), orthopyroxene and subcalcic Cr-pyrope; some of them also contain diamond±chromite. Their constituent minerals are very similar in composition to the mineral inclusions in Udachnaya diamonds. Based on this observation it was proposed that harzburgite-dunite xenoliths with high-chromium subcalcic pyrope represent fragments of the host rocks of Siberian diamonds (Pokhilenko et al., 1977; Sobolev et al., 1984; Pokhilenko et al., 2014; Malkovets et al., 2007).

The lithospheric mantle of the Siberian craton experienced melting in the Archaean (Pearson et al., 1995; Griffin et al., 2014) and is characterized by extreme depletion of incompatible major elements indicating extensive (~40%) melt extraction (Boyd & Mertzman, 1987). Mantle that has experienced such high-degree melting usually would not be expected to have residual sulfides. However, our first detailed mineralogical study of the megacrystalline pyrope harzburgite-dunite xenoliths has revealed abundant enclosed and intergranular sulfides. The sulfides can be subdivided into several groups:

1) "primary" Fe-Ni MSS sulfides enclosed in olivine (no cracks around sulfides have been found);

2) Fe-Ni MSS sulfides enclosed in olivine but with djerfisherite rims (these sulfides are located in cracks cutting olivine crystals);

3) interstitial Fe-Ni MSS sulfides with djerfisherite rims;

4) numerous interstitial grains of djerfisherite. Sulfides of the first three groups reach 500 microns in diameter, while most interstitial djerfisherites rarely reach 100 microns.

The Os concentrations of the Fe-Ni MSS sulfides of different groups vary over a wide range from 4 to 2475 ppm. Chondrite-normalised PGE abundance patterns are generally characterized by depletion in PPGE relative to IPGE. There is no difference in the concentrations of PGE between Fe-Ni MSS cores and their djerfisherite rims. This suggests that the kimberlitic fluid responsible for crystallisation of the djerfisherite rims around primary Fe-Ni MSS sulfides did not transport significant amounts of PGE.

Re-Os isotopic compositions have been determined by laser ablation MC-ICP-MS for 13 sulfides (4 of group 1 and 9 of group 2) in eight xenoliths. All Group 1 sulfides have very low $^{187}Re/^{188}Os$ (<0.09), whereas Group 2 sulfides have a wider range (0.02-1.2). Modelling by Griffin et al. (2002) suggested that sulfides with $^{187}Re/^{188}Os$ <0.07 are unlikely to have been disturbed by any metasomatic events.

For Group 1 sulfides $T_{CHUR}$ ages fall mainly between 3.2 and 3.9 Ga and $T_{RD}$ (Re-depletion) ages between 3 and 3.51 Ga (±0.03 Ga, mean 2s analytical uncertainty). $T_{RD}$ model ages for Group 2 sulfides fall into two intervals: 2.83-2.98 Ga and 1.87-2.12 Ga.

A previous study of sulfide inclusions in megacrystic olivines from the Udachnaya pipe suggested that most of the SCLM beneath the Daldyn kimberlite field formed at 3-3.5 Ga, and that lithosphere formation culminated at ca 2.9 Ga (Griffin et al., 2002). The occurrence of Group 1 and Group 2 sulfides with different model ages within a single xenolith suggests a later metasomatic input at 1.87-2.12 Ga, which may be related to the amalgamation of several Archean terrains to form the Siberian craton.

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# PGE IN MINERALS OF VOLCANOGENIC MASSIVE SULFIDE DEPOSITS OF THE URALS: ORE GEOCHEMISTRY AND FIRST LA-ICP-MS DATA

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**ABSTRACT**. The distribution of noble metals has been studied in ores and sulfide concentrates from volcanogenic massive sulfide (VMS) deposits of the Urals. Gold, silver and PGE concentrations have been determined by instrumental neutron activation analysis and wet-chemical analysis with ICP-MS. The LA-ICP-MS method has been used for trace element analysis of sulfides from the Uchaly and Valentorsk deposits. The bulk of the gold and PGE occur invisibly in pyrite and chalcopyrite. Their contents range from ~0.01-42.8 ppm Au, 0.03-0.2 ppm Pd and 0.02-0.25 Rh ppm. The PGE enrichment (ppb, up to 1220 Pd, 375 Pt and 707 Rh for the Uzelginsk and 1800 Pd for the Gai deposits) was established in ultra heavy concentrates from Au rich ores. Late hydrothermal processes resulted in the redistribution of non-ferrous and precious metals and the formation of submicron-sized inclusions of Au-Ag alloys, Au (and PGE?) compounds with Te, Se, S, As, Sb and Hg.

Although the Urals is the largest VMS province in the world, the distribution and mineralogy of Au, Ag, and platinum group elements (PGE) in ores are poorly understood. Gold minerals form rare fine inclusions in common sulfides such as sphalerite, chalcopyrite and pyrite and can be found in recrystallized (mainly metamorphosed) ores. The ores and principal minerals of the Cu-Zn-pyritic deposits were studied, including the no unmetamorphosed Uzelginsk, Alexandrinsk, Galkinsk and Valentorsk deposits, the metamorphosed Safyanovsk and Uchaly deposits and the highly metamorphosed Gai and Tarnjer deposits. Microprobe analyses were carried out using an electron-probe microanalyser (EPMA) and a scanning electron microscope with EDS detector. The contents of Au, Ag, and base metals were examined by instrumental neutron activation analysis (INAA) for bulk samples and mineral concentrates (50-100 mg). PGE contents in 2-5g bulk samples, sulfide and ultra heavy concentrates were determined by wet-chemical analysis with ICP-MS (Table 1). Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS, LabMaTer at the Université du Québec à Chicoutimi) has been used for analysis of sulfides from the Uchaly and Valentorsk deposits.

Some technological concentrates are rich in PGE (ppb): zinc flotation tailings (590 Pt, 318 Pd, Uzelginsk and 1960 Pt, Uchaly) and collective tailings (19700 Pt, Uchaly) which consist mainly of pyrite (>90 vol.%) with minor chalcopyrite, fahlore and gangue minerals. High PGE contents were found in *ultra heavy concentrates* obtained from samples with initial Au contents of 22.8 and 11.1 ppm (Uzelginsk) and 73.4 ppm (Gai), respectively (Table 2). The Uzelginsk concentrates consist of pyrite (25 vol.%), galena (20), altaite (20), hessite (15), petzite (5), native gold (10) with minor native tellurium and base metal sulfides. The Gai concentrate consists of native gold (80 vol.%) with minor galena and tellurides. The PGE enrichment in the concentrates may be connected with both tellurides and native gold.

Pyrite is the dominant mineral of the ores (40-90 vol.%). Chalcopyrite and sphalerite are the major commercial minerals (1-10, up to 30 vol.%). Fahlore is a common mineral in most of the VMS deposits (0.1-1 vol.%) while galena occurs locally in smaller quantities (0.1-0.5 vol.%). A few other minerals are abundant in separate ore bodies (pyrrhotite in Uzelginsk, Tarnjer; bornite in Gai, Alexandrinsk, Valentorsk). A positive correlation between Au and Ag in ore sulfides and a high dis-

Table 1

**PGE and gold contents (ppm) in bulk sulfide samples of VMS deposits of the Urals**

| *Ore belt* | *Deposit* | *n* | *Pd* | | *Pt* | | *Au* | |
|---|---|---|---|---|---|---|---|---|
| | | | *av.* | *max* | *av.* | *max* | *av.* | *max* |
| Platinum Bearing Belt | Galkinsk | 5 | 0.04 | 0.08 | 0.02 | 0.02 | 1.37 | 2.87 |
| | Tarnjer | 15 | 0.92 | 13.4 | 0.91 | 12.14 | 17.07 | 200 |
| | | (14) | 0.03 | | 0.11 | | 3.94 | |
| Magnitogorsk zone | Safyanovsk | 16 | 0.01 | 0.10 | 0.01 | 0.04 | 1.79 | 4.5 |
| | Uchalinsk | 22 | 0.05 | 0.35 | 0.06 | 0.30 | 2.77 | 5.85 |
| | Uzelginsk | 23 | 0.02 (3) | 0.04 | 0.02 | 0.05 | 0.67 | 3.10 |
| | Alexandrinsk | 12 | 0.004 | 0.01 | 0.007 | 0.02 | 1.83 | 4.89 |

The detection limits (ppm): Pt 0.002, Pd 0.002, Rh 0.0005, Ru 0.0002, Ir 0.0005

Table 2

**PGE contents (ppb) in ultra-heavy concentrates of VMS ores rich in gold**

| *Deposit* | *Pt* | *Pd* | *Rh* | *Ru* | *Ir* | *Pd/Pt* |
|---|---|---|---|---|---|---|
| Uzelginsk | 375 | 804 | – | – | 1.8 | 2.1 |
| Uzelginsk | 354 | 1220 | 707 | – | – | 3.4 |
| Gai | 150 | 1800 | | 100 | | 12 |

persion of the contents (as shown by INAA) seems to reflect the occurrence of Au-Ag alloys. The elevated contents of S, Sb, As, Hg, Te, Se in gold-bearing sulfide ores can testify the occurrence of other Au (+Ag) compounds. The average Au contents are (INAA, ppm): 1-2 in *pyrite* (total range 0.01-23.5) and 1.5-2 in *chalcopyrite* (0.01-42.8). According to LA-ICP-MS data admixtures of Au, Ag and PGE in pyrite range between (ppm): 0.05-16 Au, 0.01-300 Ag, 0.03-0.2 Pd, 0.04-0.26 Rh for Uchaly and 0.1-5 Au, 0.03-14 Ag, 0.04-0.07 Pd, 0.02-0.25 Rh for the Valentorsk deposits.

A dominant variety of the *fahlore* is low-iron tennantite (0.1-0.6 wt.% Ag, EPMA), whereas Ag-bearing tetrahedrite (up to 8 wt.% Ag) is scarce. In addition, up to 0.14 Se (wt.%, EPMA), 0.38 Pd, 0.05-0.3 Hg and 0.2-4.5 Te were found in tennantite from Uzelginsk and up to 0.24 Pt (wt.%, EPMA), 0.07 Pd in that from the Gai deposits. *Galena* from the Uzelginsk deposit carries (EPMA, wt.%): 0.1-0.2 Se, 0.1-3.35 Te, 0.05-0.2 Au, up to 0.14 Pd and 0.25 Hg. The ore parageneses related with the late hydrothermal events enriched in Au mainly consist of Ag-bearing galena, fahlore, bornite, tellurides, and native elements. *Native gold* forms grains and aggregates with a size of 5-20 up to 250 μm. Admixtures (wt.%) of Te (up to 3.01), Pt (up to 2.23), Hg (up to 1.07) were detected at Uzelginsk, and Pd (0.66), Pt (0.2), Co (0.40), Ni (0.32) in the Gai deposits.

VMS deposits of the Urals are subduction-related and bear metals derived from the mantle (Fe, Cu, Zn, Co, Ni, Au and PGE). The late paragenesis with coarse gold probably results from late magmatic events and processes of regional metamorphism that redistribute the metals. As the PGE contents in the ores are rather low, remobilization does not facilitate a concentration sufficient enough to form discrete minerals unlike for other trace elements (Sb, As, Te, Ag, Au, Hg). At the same time the PGE enrichment is established in ultra heavy concentrates consisting of tellurides, galena and native gold, indicating that PGE could be redistributed together with Au and Te during late processes.

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# DIAMONDS AND HIGHLY REDUCED MINERALS IN OPHIOLITIC MANTLE ROCKS AND CHROMITITES

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**ABSTRACT**. We found microdiamonds, native elements and metal alloys in chromitites in Ray-Iz, Polar Ural and Luobusa, Tibet. The diamonds are different from those in kimberlites and UHP metamorphic rocks, and probably have formed in the Mantle Transition Zone.

Ophiolitic mantle rocks and chromitites are generally thought to have formed near the top of the upper mantle. However, our discovery of diamonds and highly reduced minerals in ophiolitic chromitites significantly challenges this model. Some recent results are summarized below:

1. A very significant milestone is that diamonds have now been confirmed to occur in situ within chromite grains from the Luobusa and Polar Ural chromitites. This discovery has ended all doubts about the diamonds being the result of contamination during samples processing. Previously such contamination could not be conclusively ruled out because all the diamonds had been obtained from mineral separates.

2. The C isotope compositions and mineral inclusions of the diamonds from Luobusa and the Polar Urals are very similar and are characterized by their light C isotopes ($\delta^{13}C$ -18 to -28‰) and typical Mn-bearing mineral inclusions, such as Mn-olivine, Mn-garnet, Mn-spinel and Co-Mn-Ni alloy. These features, along with their typical occurrence in oceanic mantle rocks, clearly distinguish them from kimberlite diamonds within cratons and UHP metamorphic diamonds at plate margins. Thus, we propose a new occurrence of diamond on Earth, termed ophiolite-hosted diamond.

3. We have greatly expanded the number of ophiolites known to contain diamonds. Diamonds and highly reduced minerals have now been confirmed in mantle peridotites or chromitites from 11 ophiolites in 5 orogenic belts in different parts of the world. These include the Luobusa, Zedang, Xigaze, Dangqiong, Parang and Dongbo massifs in the Yarlung-Zangbo suture and the Dingqing massif in the Bangong-Nujiang suture of Tibet, the Myitkyina massif in Myanmar, the chromitites in the Sartohai and Hegenshan massifs of the Central Asia Orogenic Belt, and the Ray-Iz massif in the Polar Urals. Thus, we propose that diamonds and their associated unusual minerals may be common within oceanic mantle, although not present in great abundance. If this can be proven in future studies, it will provide a previously unrecognized feature of the mantle and will lead to a better understanding of ophiolite and chromitite formation.

4. We discovered a new UHP mineral, named Qingsongite (cubic boron nitride, BN), which has been approved by the International Mineralogical Association (IMA2013-30). Experimental studies indicate that Qingsongite, which occurs as inclusions in coesite in the Luobusa chromitite, formed at 10-15GPa and 1300°C. The discovery of Qingsongite and stishovite pseudomorphs in the Luobusa chromitite has lead us to propose a model for the deep formation of ophiolite-hosted diamonds and chromitite. In this model, UHP minerals and chromite grains crystallized simultaneously at a depth near the mantle transition zone, and were later brought to shallow levels by upwelling mantle and emplaced in ophiolites.

# PROCESSES CONTROLLING HIGHLY SIDEROPHILE ELEMENT FRACTIONATIONS IN PERIDOTITE XENOLITHS AND THEIR INFLUENCE ON OS ISOTOPES

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**ABSTRACT**. Peridotite xenoliths having a similar range of major element compositions from three localities in the Xing'an Mongolian Orogenic Belt (XMOB), Northeast China, provide a good opportunity to explore effects resulting from both primary melting and secondary processes on Os isotopes and highly siderophile element (HSE) abundances. HSE patterns of peridotites from Shangzhi are similar to those of orogenic peridotite massifs worldwide. These patterns can be explained by relatively low degrees of melt extraction. By contrast, peridotite from nearby Shulan have major element compositions similar to the Shangzhi xenoliths, but are characterized by highly fractionated HSE patterns with lower total HSE abundance and Os, Pd and Re depletions relative to Ir. Some of the latter HSE characteristics must reflect secondary processes, such as removal of interstitial sulfide during interaction with a S-undersaturated melt/fluid. Peridotite xenoliths from Zhuoerhe also have major element compositions similar to the Shangzhi xenoliths, but are characterized by variable Pd and Re enrichment, which may be related to secondary sulfide addition during interaction with a S-saturated melt. The very poor correlation between $^{187}Os/^{188}Os$ and whole rock $Al_2O_3$ in the Shangzhi, Shulan and Zhuoerhe rocks, coupled with the poor correlation between Re/Os and whole rock $Al_2O_3$, suggest that the Re-Os isotopic systematic has been significantly disturbed by post-melting processes (such as sulfide addition or breakdown during lateral melt-rock reaction).

Peridotite xenoliths entrained by basalts or kimberlites are fragments of the lithospheric mantle that formed as residues produced by partial melting of asthenospheric mantle. In addition to melt extraction, lithospheric peridotites may also record the effects of secondary processes. Here, we consider the effects of both partial melting and secondary processes on the relative and absolute abundances of the HSE in lithospheric peridotites underlying northeastern China and what effects these processes have had on Re-Os isotopic systematics.

## PARTIAL MELTING

The peridotite xenoliths from Shangzhi, Shulan and Zhuoerhe delineate a sequence from fertile lherzolite to depleted harzburgite. Major element compositions are mainly controlled by melt extraction. The highest Re depletion age ($T_{RD}$=2.28 Ga) of these samples suggests that melt extraction took place in the Early Proterozoic (Fig. 1). Given the typical established relative order of the compatibility of HSE (Os~Ir~Ru>Pt>Pd>Re), melt extraction progressively results in depletions of PPGE and Re relative to the more refractory IPGE (e.g., Pearson et al., 2004). $(Pd/Ir)_n$ and Re/Os ratios of samples from Shangzhi, Shulan and Zhuoerhe are poorly correlated with $Al_2O_3$, and suggest that the inter-element HSE fractionations of XMOB peridotites can only partially result from a single stage of partial melting. The poor correlation between $^{187}Os/^{188}Os$ and $Al_2O_3$ for XMOB peridotites also may relate to secondary processes, rather than primary melt depletion.

## METASOMATISM VIA MELT-ROCK REACTION

The effects of melt/fluid-rock reactions are frequently observed in mantle peridotites. Metasomatism mainly results in variable degrees of enrichment of light rare earth elements (LREE) in refractory peridotites, but may not affect the major mineralogy and whole rock major element contents. In particular, metasomatism can potentially result in secondary sulfide precipitation or sulfide dissolution or breakdown. Trace element data, including variable degrees of LREE enrichment, suggest that melt/fluid-rock reaction occurred in most XMOB peridotite xenoliths. Zhuoerhe samples with abnormally high $(Pd/Ir)_n$ and Re/Os ratios may be interpreted by secondary sulfide addition during interaction with a S-saturated melt (Fig. 1). In contrast, a small number of Shangzhi and Shulan samples display abnormally low $(Pd/Ir)_n$ and Re/Os ratios, which may result from removal of interstitial sulfide during interaction with a S-undersaturated melt/fluid. The very poor correlation between $^{187}Os/^{188}Os$ and whole rock $Al_2O_3$ in XMOB peridotites, coupled with the poor

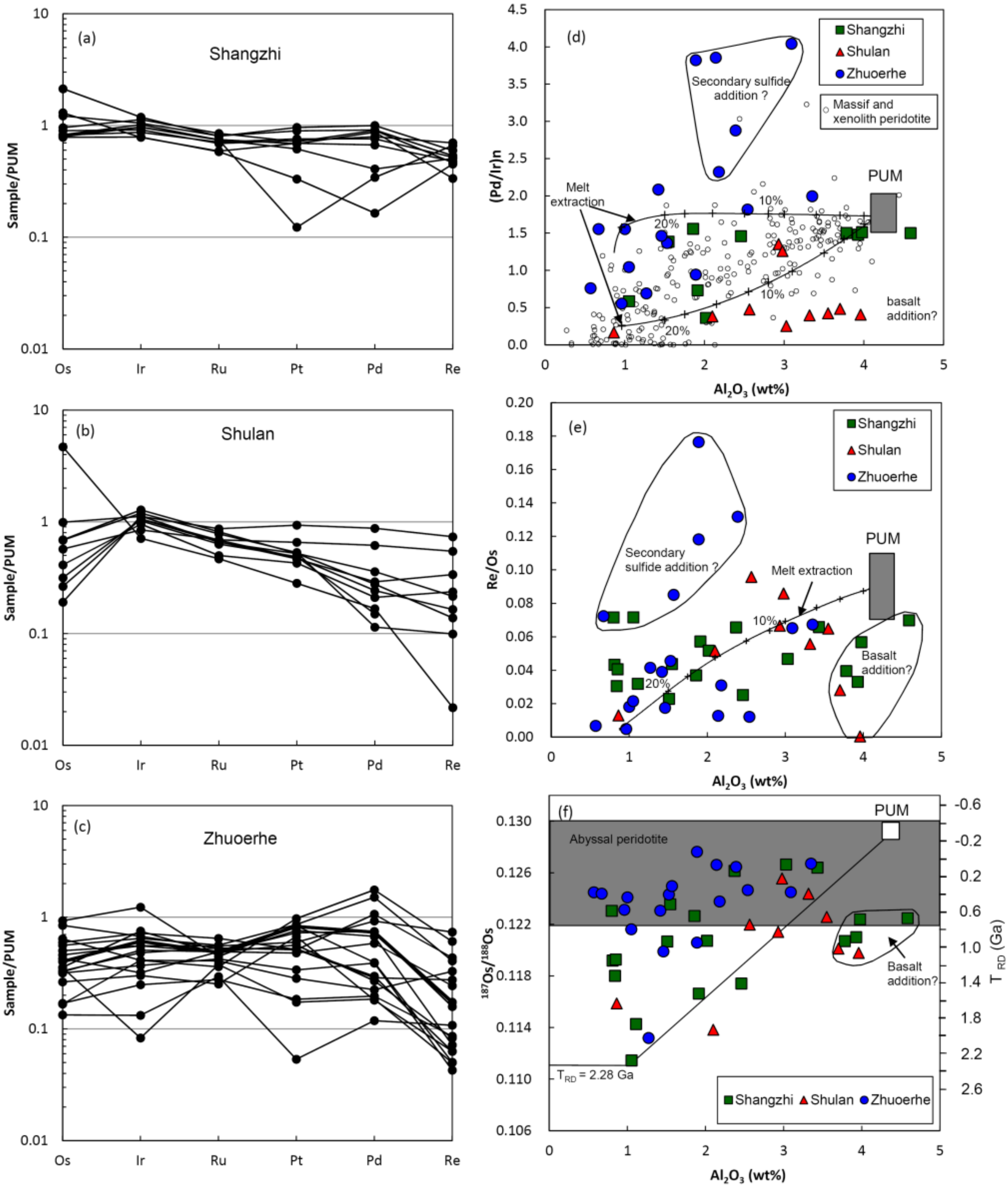

*Fig. 1.* (a-c), HSE patterns of whole rock peridotite normalized to the primitive upper mantle (PUM, Becker et al., 2006); (d), whole rock $Al_2O_3$ versus Pd/Ir ratios normalized to the CI chondrite (Anders and Grevesse, 1989); (e-f) whole rock $Al_2O_3$ versus Re/Os and $^{187}Os/^{188}Os$ ratios. Melt extraction curves in figure 2d and e were calculated for non-modal fractional melting using a PUM source containing 280ppm S. $T_{RD}$, Re depletion age

correlation between Re/Os and whole rock $Al_2O_3$, suggest that the Re-Os isotopic systematics have been significantly disturbed by secondary processes (such as sulfide addition or breakdown during lateral melt-rock reaction).

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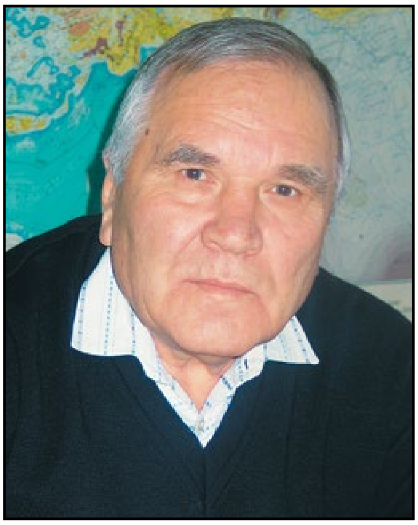

# IN MEMORIAM FELIX P. MITROFANOV

JUNE 22, 1935 – MAY 8, 2014

Felix Petrovich Mitrofanov was born on 22 June 1935 in Chkalov (presently known as Orenburg) and graduated with honors from Secondary School № 13 in 1952. At school he got the third senior degree in boxing. In 1937, his father, Pyotr V. Mitrofanov who held a high political position was killed, and mother, Nina Vasilievna was deported to labor camps and prisons for a period of 10 years. Felix P. Mitrofanov was brought up by his aunts, sisters from father's side.

During 1952-1957 Felix P. Mitrofanov studied in the A.A. Zhdanov Leningrad State University (LSU). He graduated the university with honors as a geochemist, and was offered a position in the Precambrian Geology and Geochronology Laboratory of the USSR Academy of Sciences (since 1967 known as the Institute of Precambrian Geology and Geochronology RAS, or IPGG RAS), where the outstanding national scientific school for Precambrian geology was founded by the academician A.A. Polkanov, and corresponding member K.O. Kratts. Felix P. Mitrofanov successfully blended in to the team to become one of its leaders while having progressed form a senior laboratory assistant to the director of the IPGG RAS.

The long-term research investigations of the Proterozoic and Early Proterozoic granitoids from the East Sayan and field materials collected during 1958-1962 were compiled to an extensive candidate thesis (Ph. D) devoted to the Proterozoic and Early Proterozoic granitoids of various structural and formation zones in the southeastern part of the East Sayan, which was defended by Felix P. Mitrofanov in 1963 in the A.A. Zhdanov Institute.

In 1973 Felix P. Mitrofanov was elected to a position of the Scientific Secretary of the Research Board in Precambrian Geology and Geochronology under the Department for Geology, Geophysics, and Geochemistry of the USSR Academy of Sciences (presently known as the Department for the Earth Sciences, ONZ RAS).

Felix P. Mitrofanov devoted his early scientific efforts to study granites as the oldest Earth's rocks, and in 1975, he successfully defended doctoral thesis (Habilitation) titled «Granitoids in the geological evolution of the Early Precambrian» being 40 years old.

After K.O. Kratts passed away in 1984, Felix P. Mitrofanov initiated annual Youth Scientific Conferences dedicated to the memory of his favorite mentor and honorable Precambrian geologist. These conferences were attended by young researchers, post-graduate students, and students of academic institutes and high schools to discuss various complex issues of the Precambrian geology. In 2014, the 30th jubilee meeting of young scientists will be taking place in Petrozavodsk, where K.O. Kratts headed the Institute for Geology of the Karelian Science Center RAS in 1962-1966.

During 1983-1988 Felix P. Mitrofanov was the leader of the 2nd International Geological Correlation Project (IGCP-2) from the Russian side together with A. Frischbuter (Germany) from the EU. The investigations titled "Precambrian in the Folded Domains" were aimed to study assemblages of the Archaean high-gradient magmatism in juvenile folded domains taking the Sayan and Mongolian areas as examples. This project produced a new sketch map for these areas that was published in a series of volumes: Precambrian in the Southeastern Part of the East Sayan and Khamar-Daban Ridge, Early Precambrian Granitoid Formations, Igneous Early Precambrian Formations in the USSR Territory (3 volumes), Precambrian in West Mongolia and South Tuva, Migmatization Migmatite and Granite Generation under Various PT-Conditions, Precambrian Correlation of the Western Part of the East European Platform. International geological field trips in East Sayan, and an International conference in Mongolia were organized for the first time with the involvement of leading world's experts (A. Krener, S. Bogdanov, Ye. Bibikova, V. Kozhukharov, Ye. Kozhukharova among others).

In 1986 Felix P. Mitrofanov became the Director of the Geological Institute of the Kola Science Center RAS, where he worked for over 20 years till 2008. In 1990, he was awarded with the title of a corresponding member of the USSR Academy of Sciences, and in 2000 honored as an academician of Russian Academy of Sciences.

During 1989-1994 Felix P. Mitrofanov leaded the 275th International Geological Correlation Project (IGCP-275) devoted to the Deep Geology of the Baltic Shield. The project was co-managed by Rostislav M. Gorbachev (Sweden), Cornellius Gillen (Great Britain), and Steven Daily (Ireland). This project resulted in a new edition of the Explanatory Note to the 1:500 000 Tectonic Map of the Northeastern Baltic Shield, and 1:500000 Geological Map of the Kola Region, which provided the basis for the compilation of the 1:500000 Mineral Resources Map of the Murmansk Region. The project investigations were recorded in the following volumes and a preprint: Precambrian Geology of the USSR, and Explanatory Note to the 1:500 000 Tectonic Map of the Northeastern Baltic Shield. The geochronological research for the reference sites in the Kola region was initiated and published in the preprint "New Data in the Precambrian Geochronology and Isotope Geochemistry of the Kola Peninsula". Felix P. Mitrofanov considered Palaeoproterozoic Pechenga, Federov-Pana, Monchegorsk, and Imandra layered intrusions with Cu-Ni ores as the most important rocks for the national mining potential. These intrusions were visited by the participants of the 7th International Platinum Symposium within a field trip for which the Guidebook of the Kola Belt of Layered Intrusions was compiled.

Since 1989 Felix P. Mitrofanov initiated and headed systematic targeted search for platinum-bearing mineralization in the layered Paleoproterozoic complexes of the Kola region. In addition, in 1990, the first ore horizon, or rift, was discovered, and in 1992, this resulted in the foundation of a small-scale innovation enterprise "Pana", which together with BHP Minerals started explorations and investigations of the Fedorov-Pana intrusion. By mid-1990-ies, 2 PGE deposits, Fedorovo, and East Kievey (Malaya Pana) were discovered to promote extensive platinum-group metal oriented investigations in the Kola Peninsula and adjacent territories. These efforts by early 2000-ies brought the region to the second PGE Province in Russia in terms of importance and resources. In particular, the Fedorovo deposit is the largest in Europe.

In addition to the study of layered PGE-bearing intrusions, and reference rocks of the Baltic Shield (e.g., anorthosites, alkaline granites, charnokites, TTG formations, etc.), Felix P. Mitrofanov was interested in diamond genesis and evaluating potential of the area near the White Sea. In opinion of Felix P. Mitrofanov this territory experienced denudation by glacial phenomena in the eastern part of the Kola region shoreline where kimberlite pipes were mapped. The results of long-term theoretical and practical investigations executed together with the Institute for Oceanology were published in the article thesis titled as the Diamond Genesis and Potential in the eastern Baltic Shield.

The issues of oil and gas prospectivities in the Barents Sea shelf were also in the range of scientific interests of Felix P. Mitrofanov, who devoted many years to study these hydrocarbon potential regions. Main results were published in a number of articles: New prediction aspects for large oil and gas-bearing areas, Upper Proterozoic sediments of the Kildin-White Sea-Mezen area as hydrocarbons prediction, Multimedia reference guide for the mineral resources database and mining complex of the Murmansk region, and major geological sights of the Kola Peninsula.

During 1994-2000 Felix P. Mitrofanov headed the investigations of the Kola super-deep drill hole, SG-3, which represented the Russia's national pride being the deepest window to the crystalline hearth of our planet (drilled down to a depth of 12 226 m). These investigations were undertaken in the framework of the following International projects: IGCP-488 Correlation of rock composition, structure, and physical properties along the cross-section of the Kola super-deep drill hole, SG-3 and surface homologues, and International INTAS-01-0314 Program, which was supervised by John Ladden, a Professor from Great Britain and Director of the Institute for Geochemistry in Nancy. Felix P. Mitrofanov, Dmitry M. Guberman, and John Ladden united scientists from 20 countries of the world around the SG-3 studies to grant them the status of an international research laboratory, and provide an opportunity to execute direct correlative examinations with the core from the deep boreholes in Europe. These studies in 1990-ies (Archaean Complex in the section of the Kola super-deep drill hole SG-3, Cross-section, structure and evolution of the Baltic Shield evolution, and Precambrian geology of the USSR) were resulted in compiling new article in studying deep substance and physical processes in SG-3 (Results of the deep substance and physical processes study in the section of the Kola super-deep drill holel down to a depth of 12 261 m [IGCP 408]). The long-term joint international studies were summarized by two extensive articles in Russian (New data on geology and mineral resources of the Kola Peninsula) and English (Structure of the lithosphere in the Russian part of the Barents Region).

During 2007-2010 Felix P. Mitrofanov headed the International Interreg-Tacis K-0197 Project (Strategic mineral resources of Lapland as basis for sustainable development of the North (Russia–Finland–Sweden), which combined efforts of leading scientists of Scandinavian countries (Sweden, Norway, and Finland) managed by Markku Iljina and Tuomo Alapieti (Finland), and created a new geodynamic model of plume magmatism related to the generation of largest PGE resources, and Cu-Ni-Ti-V ores within the eastern Fennoscandian Shield. The results of international joint research project were published in two article theses in Russian and English (Interreg-Tacis Project: Strategic mineral resources of Lapland as a basis for sustainable development of the North, Issues 1 and 2), and in two databases in deposits and metallogenic maps of various scale.

In 1996 Felix P. Mitrofanov founded the Kola scientific school for metallogeny of strategic mineral resources. The studies under his personal supervision were supported by grants of the RF President (No 96-15-98481, 98-3-15l/240, 00-15-98526, NSh 2305.2003.5, and NSh 1413.2006.5), State Contracts of the Ministry of Science and Education (NoNo. 02.445.11.7403, 02.515.11.5068, 16.515.11.5013), RFBR (over 40 projects), including grants for targeted fundamental research (09-05-12028 ofi-m, 11-05-12012 ofi-m, 13-05-12055 ofi-m), and other budgetary and non-budgetary foundations. These research investigations have resulted in the developed method for identifying platinum-palladium and/or copper-nickel content of mafic and ultramafic layered intrusions, which was patented under Number 2012132672/28(051780) dated 06/09/2013.

In 1996 Felix P. Mitrofanov initiated the foundation of the Academic Department for Geology and Mineral Resources in Apatity within the Murmansk State Technical University (MSTU AB), which devotedly trains young generation of geologists. For almost twenty years, 70 masters and 182 bachelors have graduated from the Department. Under the guidance of Felix P. Mitrofanov, over 12 doctoral and 24 candidate theses were prepared and defended in the field of geology, petrology, geochronology, and metallogeny of Precambrian shields. In addition, Felix P. Mitrofanov supervised PhD theses of scientists from the European countries, e.g., Charles Francois (France) and Milosh Huber (Poland). He was a member of editorial boards of different scientific journals such as Geotectonics, Lithosphere, and Karotazhnik (Well Log Analyst), and a few dissertation boards.

The research heritage of the academician Felix P. Mitrofanov is compiled in over 400 publications, including over 30 article theses in Russian and English. For the outstanding contribution to fundamental science, and discovery of platinum-bearing deposits at Kola Peninsula, the academician RAS Felix P. Mitrofanov was awarded with the Honorary Title of Merited Geologist of the Russian Federation (2011), Medal for Distinguished Labor (1981), Orders of Friendship (1995) and Honor (2006), P.L. Kapitsa Silver Medal of RAS (1998), State Award in Science and Technique (2011), A.D. Arkhangelsky (1999) and S.S. Smirnov (2009) RAS awards. The Scandinavian Association of Miners awarded Felix P. Mitrofanov with a special prize, Golden Geological Hammer (2007) and Honorary Diploma to distinguish his outstanding contribution to the Fennoscandian geology and metallogeny.

**Tamara B. Bayanova**

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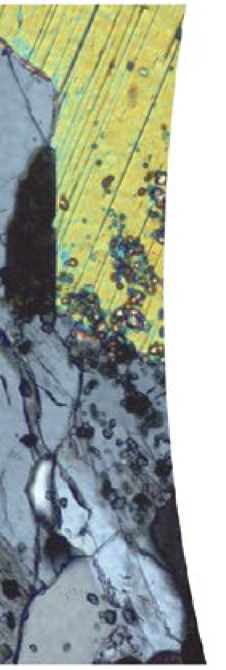

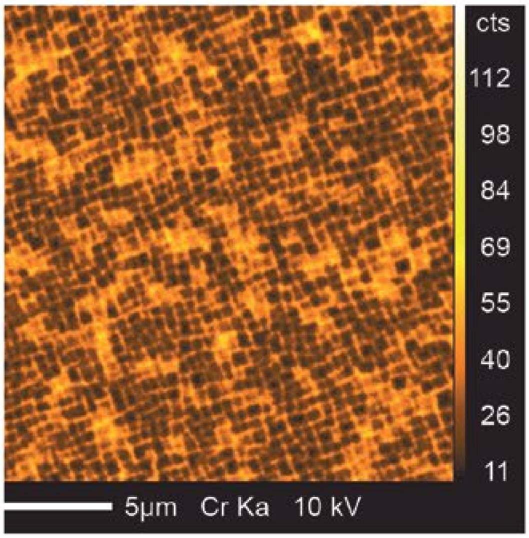
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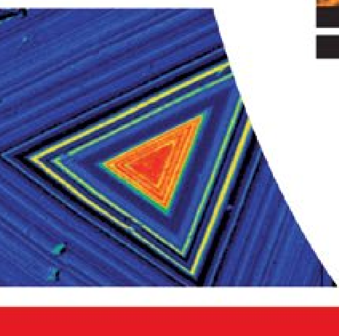


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