

IZOKLAKEITE FROM VENA, SWEDEN, AND THE KOBELLITE HOMOLOGOUS SERIES

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ABSTRACT

Izoklakeite from Vena, Sweden occurs in aggregates up to a few mm in diameter, intergrown with jaskólskiite, native bismuth, galena, pyrrhotite and, rarely, native antimony. The average of 19 electron-microprobe analyses is Pb 50.01, Bi 19.20, Sb 11.67, Cu 0.88, Ag 0.59, Fe 0.19, S 16.91, sum 99.45 wt%. Based on 96 cations and 114 S the analytical formula of izoklakeite from Vena is $Pb_{51.29}Sb_{20.37}Bi_{19.52}Cu_{2.94}Ag_{1.16}Fe_{0.72}S_{114}$ or, ideally, $(Cu,Fe)_2Pb_{26.5}(Sb,Bi)_{19.5}S_{57}$. The unit cell is orthorhombic, with a 34.07(1), b 37.98(1), c 4.072(1) Å, $V = 5269.1$ Å³, space group $Pnmm$, $Z = 2$. Structurally any crystal in the kobellite homologous series (the Pb-Bi-Sb-Cu-Fe-Ag sulfosalts) consists of two types of rods, which are interested in a pseudotrigonal pattern. The rods alternate in both a and b directions. The larger type of rod is based on a PbS-like archetype and has general formula $M_{6(N+1)}S_{7N+9}$; the smaller type represents a 2Å-sheared PbS structure, with general formula $M_{4N}S_{4(N+1)}$. Two strings of tetrahedrally co-ordinated (Cu,Fe) atoms for each pair of rods are added at the interfaces of the rods. The complete formula is $2(Cu,Fe)_2M_{10N+6}S_{11N+13}$ for a 4Å repeat subunit of the structure. The order N of the homologue expresses the width of the smaller rods as a number of (Sb,Bi) co-ordination pyramids with common vertical edges, strung across the rod. Natural phases of the kobellite homologous series include kobellite and tintinaite with $N = 2$, and giessenite and izoklakeite with $N = 4$.

Keywords: izoklakeite, new mineral species, Pb-Cu-Sb-Bi sulfosalts, kobellite homologous series, Vena, Bergslagen, Sweden.

SOMMAIRE

L'izoklakéite de Vena (Suède) se présente en agrégats qui peuvent atteindre plusieurs mm de diamètre, en intercroissance avec jaskólskiite, bismuth natif, galène, pyrrhotine et (rarement) antimoine natif. La moyenne de 19 analyses à la microsonde électronique donne Pb 50.01, Bi 19.20, Sb 11.67, Cu 0.88, Ag 0.59, Fe 0.19, S 16.91, total 99.45 % en poids. Avec 96 cations et 114 S, la formule s'écrit $Pb_{51.29}Sb_{20.37}Bi_{19.52}Cu_{2.94}Ag_{1.16}Fe_{0.72}S_{114}$ soit, idéalement, $(Cu,Fe)_2Pb_{26.5}(Sb,Bi)_{19.5}S_{57}$. La maille structurale est orthorhombique, avec a 34.07(1), b 37.98(1), c 4.072(1) Å, $V = 5269.1$ Å³, groupe spatial $Pnmm$, $Z = 2$. Structurellement, tout cristal de la série homologue de la kobellite (sulfosels Pb-Bi-Sb-Cu-Fe-Ag) consiste en deux types de bâtonnets, dont l'agencement réciproque crée une symé-

trie fortement pseudotrigonale. Les bâtonnets alternent à la fois dans les deux directions a et b . Le type de bâtonnet le plus grand résulte d'un archétype PbS et donne la formule générale $M_{6(N+1)}S_{7N+9}$; le type le plus petit représente la structure PbS tronquée à 2 Å, de formule générale $M_{4N}S_{4(N+1)}$. Deux enfilades d'atomes (Cu,Fe) tétraédriquement coordonnés sont ajoutés à l'interface des bâtonnets pour chaque paire de ceux-ci. La formule complète, $2(Cu,Fe)_2M_{10N+6}S_{11N+13}$ est celle d'un motif de 4 Å. L'ordre N de l'homologue exprime la largeur du petit bâtonnet, qui est égale au nombre de pyramides de coordination (Sb,Bi) à arêtes verticales communes dirigées transversalement au bâtonnet. Les phases de la série de la kobellite qui se présentent dans la nature comprennent kobellite et tintinaïte ($N = 2$), ainsi que giessenite et izoklakéite ($N = 4$).

(Traduit par la Rédaction)

Mots-clés: izoklakéite, nouvelle espèce minérale, sulfosels Pb-Cu-Sb-Bi, kobellite (série homologue de la), Vena, Bergslagen (Suède).

INTRODUCTION

Izoklakeite described in the present paper was encountered in the abandoned Vena Cu-Co mine, Bergslagen metallogenic province, Sweden, almost simultaneously with the discovery of izoklakeite in Canada (Harris *et al.* 1986). A joint proposal to the Commission of New Minerals and Mineral Names of IMA, based on combined data from both occurrences, was accepted in 1983. It appears probable that izoklakeite was the major component of the material from Vena (Hvena) analyzed by Flink (1915) and interpreted to be Sb-kobellite. Flink's results were reinterpreted by Doelter & Leitmeier (1926), who assumed the material to be lillianite.

The chemistry and the results of X-ray investigations indicate a close relationship between izoklakeite and giessenite. Both minerals belong to the kobellite homologous series, which was (tentatively) proposed by Makovicky (1981) on the basis of the close relationship between kobellite and giessenite. This relationship was confirmed, and the crystal-chemical implications were worked out in detail by Makovicky & Mumme (1985). The mineralogical significance of the kobellite homologous series is outlined and discussed below.

THE MINERALOGY OF IZOKLAKEITE

Occurrence

The Vena ore field is a *fahlband*-type chalcopyrite-cobaltite deposit typical of the Ämmeberg-Tunaberg belt, which is located in the southern part of the Proterozoic Bergslagen metallogenic province in central Sweden. The geology and ore deposits of this province have been described by Grip (1978). The Vena deposit is particularly well known in the mineralogical literature for the occurrence of kobellite (Setterberg 1839), "Sb-kobellite" (Flink 1915) and jaskólskiite (Zakrzewski 1984).

The specimens examined in this study contain aggregates up to a few centimetres across of a lead-grey sulfosalt intergrown with galena. Under reflected light two Pb-Cu-Sb-Bi sulfosalts were recognized: izoklakeite and jaskólskiite $Pb_{2+x}Cu_x(Sb,Bi)_{2-x}S_5$. Izoklakeite is the major constituent, followed in decreasing abundance by pyrrhotite, chalcopyrite, arsenopyrite, galena, jaskólskiite, cobaltite, pyrite, sphalerite, native bismuth, cubanite, freibergite, gudmundite, marcasite, native antimony, costibite or paracostibite, and mackinawite. Additional investigations on material from

Vena by De Haas (1985) have shown the occurrence of izoklakeite associated with antimonian bismuthinite, and Bi-rich izoklakeite associated with kobellite.

Physical and optical properties

Izoklakeite occurs mainly as aggregates up to a few millimetres in diameter intergrown with jaskólskiite, galena, native bismuth and pyrrhotite. Jaskólskiite seems to be an earlier mineral than izoklakeite. In several cases, micrometre-size grains of native antimony are also found associated with izoklakeite. At the contacts with calcite, izoklakeite is terminated by crystal faces (Fig. 1). The crystal used for the structure determination by Makovicky & Mumme (1985) is bounded by faces that appear to belong to the surrounding minerals.

Izoklakeite has a grey color and a metallic lustre. The streak is dark grey. In reflected light the mineral is grey, similar to galena, with weak reflection-pleochroism. Anisotropism is moderate without distinct colors. The reflectance measurements are listed in Table 1. The polishing hardness is higher than that of galena and lower than that of jaskólskiite. Microindentation hardness VHN_{100} , based on ten indentations on several distinct grains, gave 132–146, equivalent to a Mohs hardness of $3\frac{1}{2}$. The mineral reacts with $HNO_3(1:1)$ immediately, but no observable reaction occurs with $HCl(1:1)$, $KOH(40\%)$, or $FeCl_3(20\%)$.

Izoklakeite could not be isolated in sufficient amounts for a direct determination of density, but Flink (1915) obtained a result of 6.535 g/cm^3 for the "Sb-kobellite" from the same locality. The possible identity of Sb-kobellite and izoklakeite was a working assumption, and these calculations, and those of *N*, appear to support its validity. However, this question of identity is not central to the present paper. A comparison of Flink's chemical data with the present microprobe results indicates that the material of Flink was contaminated with native bismuth, galena, pyrrhotite and chalcopyrite. After correction for this contamination, an extrapolated value of 6.57 g/cm^3 is obtained. A density of 6.68 g/cm^3 , calculated for a formula $Pb_{51.29}Sb_{20.37}Bi_{19.52}Cu_{2.94}Ag_{1.16}Fe_{0.72}S_{114}$ and $Z = 1$, approximates this value as well as the estimated value obtained by comparison with the density of other sulfosalts with a Pb/(Sb + Bi) ratio similar to that of izoklakeite. Among these minerals, there is a decrease in density

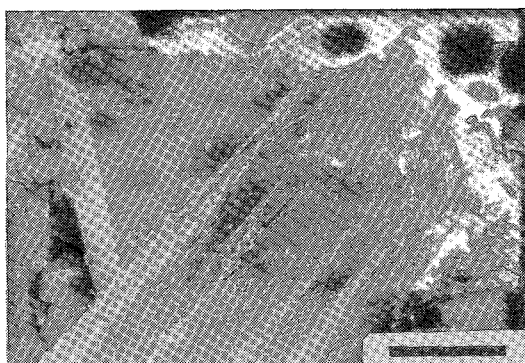


FIG. 1. Scanning electron micrographs of izoklakeite from Vena. Bar represents 0.1 mm.

TABLE 1. REFLECTANCE VALUES FOR IZOKLAKEITE FROM VENA

Wavelength	R ₁	R ₂
470 nm	41.1	45.1
546	39.0	43.0
590	38.4	42.3
650	36.7	40.2

Standard: WC-6 (Zeiss). Reflectance expressed in %.

corresponding to an increase in the Sb/(Sb + Bi) ratio: for boulangerite, with Sb/(Sb + Bi) = 1, the calculated density is 6.13 g/cm³; jaskólskiite (0.67, 6.50 calculated, Zakrzewski 1984); Bi-rich izoklakeite (0.40, 6.61 calculated, Armbruster *et al.* 1984, recalculated from anal. 11, Table 5 to 6.82); giessenite (0.20, 6.89 calculated from anal. 14, Table 5); nuffieldite (0, 7.0 calculated and measured, Kingston 1968) and neyite (0, 7.02 measured, Drummond *et al.* 1969). The measured (6.47 g/cm³) and calculated (6.505 g/cm³) values of density of izoklakeite from Izok Lake (Harris *et al.* 1986) are somewhat lower than expected purely from the Sb/(Sb + Bi) ratio of 0.54, probably because of a greater extent of Ag substitution.

Chemical composition

Electron-microprobe analyses (Table 2) were obtained with a Cambridge Instruments Microscan 9 electron microprobe, using as standards galena (for Pb), stibnite (for Sb,S), chalcopyrite (for Cu), troilite (for Fe) and metallic Bi and Ag (for these elements). Apparent concentrations have been corrected using the Microscan 9 on-line data-reduction program.

The average unit-cell content is Pb_{50.61}Sb_{20.10}Bi_{19.26}Cu_{2.91}Ag_{1.15}Fe_{0.72}S_{110.58} on the basis of the calculated molecular weight using the extrapolated density of Flink (1915). Based on 96 cations, as indicated by structure analysis (Makovicky & Mumme 1985), the results of the microprobe analyses can be recalculated to Pb_{51.29}Sb_{20.37}Bi_{19.52}Cu_{2.94}Ag_{1.16}Fe_{0.72}S_{112.06} in a unit cell. The averaged analysis shows only a small deficiency in S, within one standard deviation of the ideal content of 114 atoms in a unit cell. Cu, Fe and 0.34 Ag are assigned to the tetrahedral positions. The rest of the Ag content (0.82) must be assigned to the large co-ordination polyhedra

according to the substitution scheme $Ag + (Bi,Sb) \rightleftharpoons 2Pb$.

In order to compare the analytical results with the structural formulae of the kobellite homologous series (see below), we convert the rest of Ag as well as the corresponding contents of (Bi,Sb) into Pb: Pb_{52.93}(Sb,Bi)_{39.07}(Cu,Fe,Ag)₄S₁₁₄. This formula assigns 4.93 positive charges per unit cell to the tetrahedrally co-ordinated metal atoms. The excess over 4 positive charges is within analytical accuracy assignable to Fe²⁺. The possible Cu²⁺ contents are very small at best. The idealized chemical formula of the Vena material is Cu₃FePb₅₃Sb₂₀Bi₁₉S₁₁₄, leaving five positive charges to be provided by the tetrahedrally co-ordinated metal atoms.

The calculated density for the formula with the empirical metal-ratios and 114 S atoms in a unit cell is 6.68 g/cm³. That from the idealized formula is 6.71 g/cm³.

X-ray-diffraction studies

The space-group symmetry was established and preliminary cell-parameters for izoklakeite from Vena were calculated from Weissenberg and rotation photographs. Izoklakeite is orthorhombic, space group *Pnmm*, as determined from the systematic extinctions and the symmetry of the weighted reciprocal lattice. The alternative space-group, *Pnn2*, is excluded because all corresponding reflections *hk0* and *hk2* are equal in intensity, confirming the presence of a mirror plane at $z = \frac{1}{2}$. This symmetry is valid for the (sub)structure with a periodicity $c \sim 4$ Å. On overexposed rotation-photographs, extremely weak 8-Å levels are discernible. They are so weak that overexposed Weissenberg photographs show only about 5 to 10 barely recognizable reflections, thus giving no information on the extinction rules valid for the very weak 8-Å cell.

The preliminary cell-parameters were further refined by Dr. W.G. Mumme on the single-crystal diffractometer at the University of Melbourne, for the crystal used in the structure determination. The values obtained, a 34.07(1), b 37.98(1), c 4.072(1) Å, $V = 5269.1$ Å³, agree well with those obtained by Harris *et al.* (1986) for the Izok Lake material. Slightly different values of cell parameters can be obtained from the powder data but, owing to the factors described below, preference has been given to the results from the single-crystal unit-cell refinement.

X-ray powder-diffraction data (Table 3) for izoklakeite from Vena were obtained on a Guinier camera with CoK α_1 radiation and corundum as internal standard. They were indexed using the intensity data obtained from the weighted reciprocal lattice of izoklakeite, as revealed by single-crystal studies. The quality of the powder data is influenced by the presence of jaskólskiite in intimate intergrowths.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF IZOKLAKEITE FROM VENA

	Mean of 19			st. dev.	Point 4		Point 5
	weight %	st. dev.	at. prop.		weight %	weight %	
Pb	50.01	0.50	51.29	0.51	50.16	49.56	
Sb	11.67	0.18	20.37	0.32	11.54	11.63	
Bi	19.20	0.49	19.52	0.49	18.96	20.14	
Cu	0.88	0.05	2.94	0.17	0.87	0.96	
Fe	0.19	0.03	0.72	0.11	0.20	0.20	
Ag	0.59	0.08	1.16	0.15	0.67	0.68	
S	16.91	0.30	112.06	1.98	16.85	17.39	
Total	99.45				99.24	100.56	

Formula calculated on 96 cations and assumed 114 S

Mean of 19 Pb_{51.29}Sb_{20.37}Bi_{19.52}Cu_{2.94}Ag_{1.16}Fe_{0.72}S₁₁₄(112.06)

Point 4 Pb_{51.52}Sb_{20.17}Bi_{19.31}Cu_{2.92}Ag_{1.32}Fe_{0.76}S₁₁₄(111.84)

Point 5 Pb_{50.35}Sb_{20.11}Bi_{20.28}Cu_{3.18}Ag_{1.32}Fe_{0.75}S₁₁₄(114.16)

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR IZOKLAKEITE FROM VENA

$I_{est.}$	$d_{obs.}$	$d_{calc.}^*$	hkl	$I_{est.}$	$d_{obs.}$	$d_{calc.}^*$	hkl
5	25.4	25.36	110	10	3.134	3.131	371 ?
5	19.0	18.99	020			3.125	641
5	8.56	8.52	400			3.123	701
5	6.75	6.71	510	80	3.042	3.042	471 ?
5	5.96	6.00	530			3.041	281 ?
5	5.71	5.68	600			3.034	651
5	4.65	4.64	560	40	2.969	2.967	741
20	4.28	4.26	800	20	2.938	2.938	571
20	3.955	3.956	390	80	2.894	2.889	751
		3.955	121			2.888	291
20	3.900	3.923	670	30	2.839	2.839	12.0.0
		3.896	580	10	2.806	2.808	12.2.0 ?
30	3.840	3.852	131	30	2.744	2.744	851
		3.833	301			2.743	921
60	3.786	3.798	0.10.0	10	2.642	2.641	4.10.1 ?
		3.781	490	10	2.610	2.609	781
50	3.664	3.669	331	10	2.507	various incl.	881
		3.657	411	10	2.323		
40	3.615	3.602	3.10.0 etc.	10	2.253	2.255	15.2.0
50	3.565	3.569	151			2.253	1.14.1
		3.554	341	60	2.152	2.153	10.10.1 etc.
100	3.427	3.426	441	10	2.125	2.129	16.0.0
		3.422	351	80	2.038	various incl.	002.
		(3.407	10.0.0)	10	1.9921		
40	3.389	3.387	690	10	1.9065		
80	3.312	3.318	5.10.0	10	1.8500		
		3.307	451	20	1.8205		
30	3.1615	3.165	0.12.0 ?	20	1.7910		
		3.157	6.10.0	10	1.7706		
				30	1.7476		
				10	1.7116		

* calculated with cell parameters a 34.07(1), b 37.98(1), c 4.072(1) Å obtained from single-crystal diffractometer. Guinier camera, $\text{CoK}\alpha_1$ radiation, corundum used as internal standard, intensities estimated visually; lines belonging to admixed jaskólskite are omitted.

Multiple indexing of many peaks is in agreement with the near-coincidence of two or more strong reflections and with the resulting perceptible broadening of diffraction lines. The powder patterns of the Izok Lake and Vena material are identical within experimental error.

THE KOBELLITE HOMOLOGOUS SERIES

Definition and chemistry

The *kobellite homologous series* was proposed tentatively by Makovicky (1981), who recognized the close relationship of kobellite and giessenite. It was confirmed by Makovicky & Mumme in their determination of the structure of izoklakeite (1985). The detailed structural description of this series was given

by these authors, together with a detailed crystal-chemical discussion. Therefore, only the very basic structural features of *kobellite homologues* will be summarized here as the basis for the ensuing chemical interpretation. This interpretation and its mineralogical applications are presented in this paper only.

The *kobellite homologous series* represents perhaps the most complicated sulfosalt *homologous series* known to date, with respect to both structural and chemical aspects. Therefore, a short general introduction to the *homologous series* follows for readers wishing to become initiated to this problem.

Crystal structures of the phases belonging to a *homologous series* consist of layers or rods, or blocks built according to the same (usually fairly simple) crystal-chemical principle (*e.g.*, galena-like or SnS-like arrangement of anions and cations). These units

meet each other on boundaries along which the co-ordination states of ions (atoms) are profoundly different from those inside the units. This change of co-ordination implies a change in stoichiometry of the boundary layer (which is the interspace between units) compared to that valid inside the units. The boundary layers are of the same type for all members of a *homologous series*.

The dimensions of the units (*i.e.*, thickness of layers, diameters of rods and blocks) can vary by addition of layers of co-ordination polyhedra to (or subtraction of these from) the units at their surfaces. With such changes in the ratio of the relative volumes of units and of the boundary layers, regular changes of the overall chemical formula of the successively formed *homologues* (chemical compounds) take place. The order N of a *homologue* can be defined by the number of co-ordination polyhedra (polyhedral layers) across a suitably defined diameter of the building unit present in them.

Every *homologue* represents in principle a mineral species (or a synthetic compound) with its own crystal structure, cell parameters, and chemical formula.

However, isomorphic substitutions may take place in a *homologue*, either purely substitutional in character (*e.g.*, $\text{Ag} + \text{Bi} \rightleftharpoons 2\text{Pb}$), or involving the filling of interstitial vacancies (*e.g.*, $\text{Cu} + \text{Pb} \rightleftharpoons \text{vacancy} + \text{Bi}$). Thus *each homologue* can also represent a *solid-solution series*, which, under certain thermodynamic conditions, may be continuous over a range of compositions. Under other conditions it may exsolve into two or more separate phases, each with a limited (or practically no) compositional range, detailed structural arrangement (although based on the same general features for all of them), specific symmetry (identical to or a subgroup of the space group valid for the original phase with a continuous compositional range) and cell (or supercell) parameters. Then all these phases represent independent mineral-species.

The crystal structures of the *kobellite homologous series* consist of two types of rods, interested in a very nearly pseudotrigonal pattern (Fig. 2). The rods alternate both in the a and the b directions. The larger type of rod is based on a PbS-like archetype (Makovicky 1981) and has a general formula

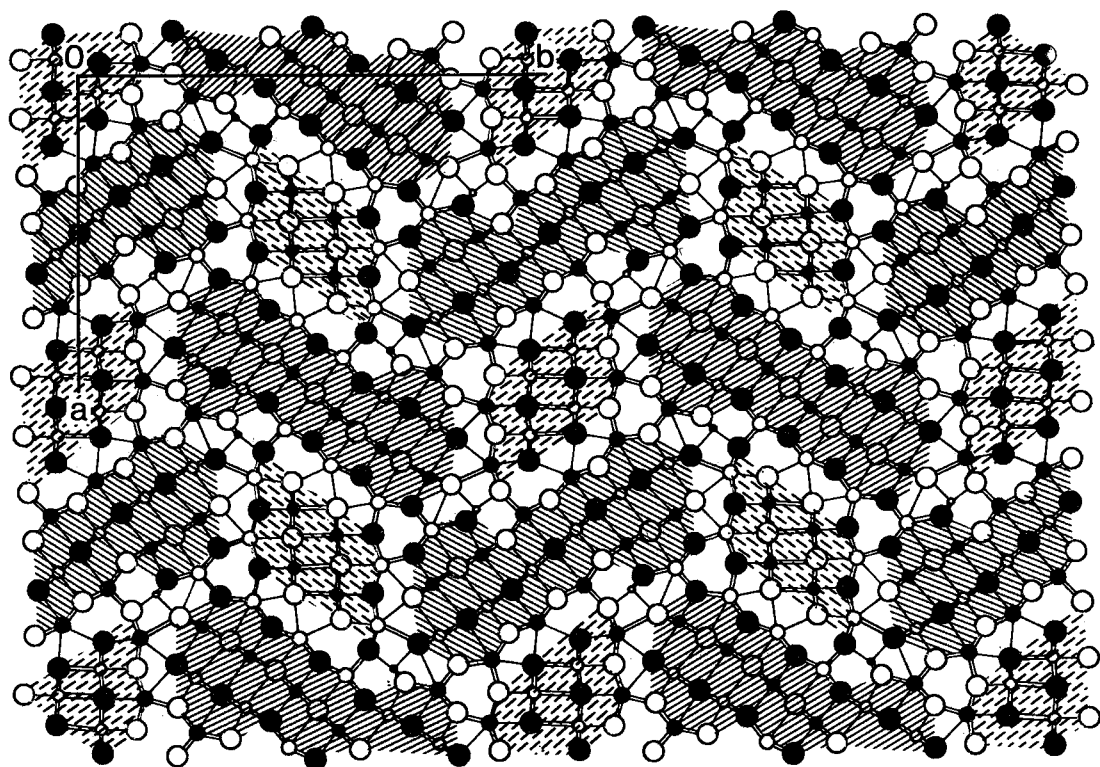


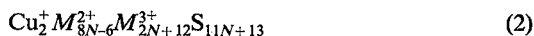
Fig. 2. The crystal structure of kobellite (Miehe 1971) projected along $[001]$. Circles in order of decreasing size represent S, Pb and the mixed (Pb,Bi,Sb) position, the mixed (Bi,Sb) and (Sb,Bi) positions, and (Cu,Fe). Empty circles represent atoms at $z = 0$, full circles, those at $z = \frac{1}{2}$. The PbS-based rods $\text{M}_{6(N+1)}\text{S}_{7N+9}$ are hatched, the SnS-based rods $\text{M}_{4N}\text{S}_{4(N+1)}$ are stippled.

$M_{6(N+1)}S_{7N+9}$. The smaller type of rod represents a 2-Å sheared PbS structure (*i.e.*, a SnS-like structure) and has a general formula $M_{4N}S_{4(N+1)}$. Two strings of tetrahedrally co-ordinated (Cu,Fe) atoms for each pair of rods are added in the interfaces of rods. For a 4-Å-repeat subunit of the structure and $Z = 2$, the total formula reads:

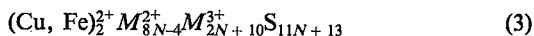


The order N of the *homologue* expresses the width of the smaller (*i.e.*, SnS-like) rods as a number of (Sb,Bi) co-ordination pyramids with common vertical edges, strung across the rod (Fig. 2). The co-ordination polyhedra in both types of rods are occupied by Pb^{2+} , Bi^{3+} and Sb^{3+} atoms. Bi^{3+} shows preference for the PbS-like rods, Sb^{3+} for the SnS-like rods. The distribution, however, is not sharp and has no bearing on the total chemical formula. The reader is referred to the paper by Makovicky & Mumme (1985) for further details.

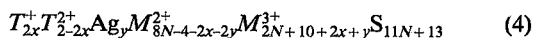
The proportion of divalent and trivalent metals in rods is influenced by the ratio of uni- and divalent metals occupying tetrahedral positions. This regularity explains the variability of the Pb/(Sb + Bi) ratio in natural specimens of kobellite observed, for example, by Mozgova & Bortnikov (1980). In the Pb-poor members the tetrahedrally co-ordinated position contains only Cu^+ cations:



For the Pb-rich members with divalent metals (Cu^{2+} , Fe^{2+}) and for potential (Cu^+ , Fe^{3+}), the formula reads:



Silver might substitute either for Cu^+ in tetrahedral positions or for Pb (primarily) according to the substitution scheme $2\text{Pb} \rightleftharpoons \text{Ag} + (\text{Bi, Sb})$. This leads to the formula:

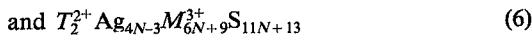


where $T^+ = \text{Ag}^+$, Cu^+ ; $T^{2+} = \text{Cu}^{2+}$, Fe^{2+} ;

$T^+ + T^{2+} = 2$; $x = \frac{T^+}{T^+ + T^{2+}}$, $0 \leq x \leq 1$; $M^{2+} = \text{Pb}$;

$\text{Ag}_y = \text{octahedral, substitutional Ag, with the empirical values } 0 \leq y \leq 2$, and $M^{3+} = \text{Sb, Bi}$.

The $2\text{Pb} \rightleftharpoons \text{Ag} + (\text{Bi, Sb})$ substitution points toward the hypothetical (and structurally not permissible) end-members:



If the tetrahedral positions are empty, the general formula is:



with the above substitution tending to the composition:



Calculation strategies and procedures

One of the implications of the model chemical composition derived from structural data is the possibility of checking the chemical data, especially the microprobe data on crystallographically poorly defined material. Firstly, it can be ascertained whether the mineral assumed to be a kobellite homologue belongs to this series or not. In the positive case, its identity and position in the series can be calculated. Finally, the data obtained by wet-chemical analyses can be checked for the presence of unsuspected admixtures.

The calculation of the formula of a kobellite homologue is carried out to 1) calculate the value of N , 2) to estimate the $T^+ : T^{2+}$ ratio for the tetrahedral sites, and 3) to elucidate the distribution of Ag among the four- and eight-co-ordinated sites.

If the analytical results on all chemical elements are to be used, the general formula (1) leads to the equation:

$$N = \frac{8S - 13M}{11M - 10S} \quad (9)$$

where S is the molar fraction of sulfur (+ selenium) and M is the molar fraction of *all metals* reported, without regard to their position and role in the structure. Thus it includes the tetrahedrally co-ordinated metals. If the tetrahedral positions are empty, the formula changes to:

$$N = \frac{6S - 13M}{11M - 10S} \quad (10)$$

The sulfur concentrations usually represent the least reliable part of microprobe results for sulfides of heavy metals. Therefore, alternative formulae will be derived for the determination of *N* that omit S as a basis of consideration. They include valences of metals and, instead of being based on the ratio of total metal *versus* total anion contents, the value *N* is derived from the ratio of all divalent *versus* all trivalent metals in the large co-ordination polyhedra. The ratios of cations with different valences in the large co-ordination polyhedra are directly influenced by the ratios of uni- and divalent metals (as well as vacancies) in the tetrahedrally co-ordinated sites.

Therefore, the values of *N* have to be calculated separately from the formulae (2), (3) and (7) according to the situation in the tetrahedral sites. For univalent tetrahedral cations, formula (2) gives:

$$N_{T^+} = \frac{6M^{2+} + 3M^{3+}}{4M^{3+} - M^{2+}} \quad (11)$$

For divalent tetrahedral metals, formula (3) leads to:

$$N_{T^{2+}} = \frac{5M^{2+} + 2M^{3+}}{4M^{3+} - M^{2+}} \quad (12)$$

TABLE 4. EVALUATION OF PUBLISHED CHEMICAL ANALYSES OF DEFINITE AND PRESUMED KOBELLITE HOMOLOGUES WITH N=2

No	Original name	Locality	Atomic ratios for M=56 atoms (ideal S=70 atoms per unit cell)							Case A		Case B		T=Cu+Fe+IV _{Ag}		Charge balance for Cu=Cu ⁺				
			Cu	Fe	Ag	Pb	Sb	Bi	S	Sb Sb+BT	N _{Cu} ⁺	N _{Cu2+}	N _{Cu} ²⁺	N _{Cu2+}	N _{ideal}		x _{N=2}	Cu ²⁺	IV _{Ag}	
1	Kobellite	(H)Vena	2.70	1.12	0.92	20.76	11.34	19.13	75.15	0.372	2.14	1.63	2.35	1.80	2	0.43	1.16	0.18	0.72	-11.51
2	Kobellite	Vena	2.10	2.04	0.19	21.63	13.62	16.33	67.53	0.453	2.24	1.71	2.28	1.74	2	0.48	0.03	0.00	0.51	+4.42
3	Kobellite	Vena	2.39	1.76	0.16	22.05	12.04	17.61	69.50	0.406	2.29	1.76	2.33	1.79	2	0.39	0.77	0.00	0.58	+0.12
4	Tintinaite	Tintina	3.83	--	0.13	21.30	30.74	--	71.56	1.000	2.16	1.65	2.19	1.68	2	0.58	1.27	0.13	1.00	-4.34
5	Kobellite	Boliden	2.99	0.95	0.13	21.89	15.06	14.98	72.26	0.501	2.25	1.73	2.28	1.75	2	0.49	1.09	0.06	0.76	-5.60
6	Kobellite	Rosslund	2.27	1.36	0.40	20.55	17.72	13.70	72.06	0.564	2.07	1.58	2.15	1.64	2	0.76	0.72	0.36	0.66	-3.37
7	Kobellite	Transbaikal	2.30	1.58	0.72	19.77	12.12	19.51	65.56	0.384	2.00	1.52	2.15	1.64	2	0.42	0.62	0.12	0.61	+9.49
8	Kobellite	Darasun	2.39	1.56	--	22.32	9.94	19.79	72.75	0.334	--	--	2.31	1.77	2	0.51	0.73	--	0.64	-6.16
9	Kobellite	Ustarasay	2.33	1.41	--	22.09	12.58	15.10	66.73	0.422	--	--	2.26	1.73	2	0.51	0.42	--	0.85	+6.41
10	Kobellite	Korunka	2.77	2.14	0.25	23.16	12.58	15.10	66.73	0.454	2.54	1.95	2.61	2.02	2	0.49	0.72	0.36	0.66	-3.28
11	Kobellite	Transsylv.	3.13	2.13	--	22.93	18.92	8.89	69.53	0.680	--	--	2.50	2.02	2	0.51	0.42	--	0.85	+6.41
12	Kobellite	Raleigh	3.74	0.91	0.57	21.24	10.00	19.53	70.27	0.339	2.23	1.71	2.37	1.82	2	0.49	1.09	0.06	0.76	-5.60
13	Rezbanyite	Erzgebirge	1.96	2.21	0.25	21.00	10.56	20.02	68.40	0.345	2.15	1.64	2.20	1.68	2	0.61	0.00	0.00	0.47	+3.57
14	Rezbanyite	Erzgebirge	3.49	0.87	--	20.58	7.98	23.07	66.98	0.257	2.09	1.59	2.09	1.59	2	0.46	0.00	0.50	0.54	+5.98
15	Rezbanyite	Erzgebirge	4.81	0.11	--	20.08	17.44	13.54	63.69	0.563	--	--	2.06	1.56	2	0.46	0.00	0.50	0.54	+5.98
16	Group A	Val de Ribes	1.56	1.78	0.50	21.44	6.66	24.06	67.34	0.217	2.18	1.66	2.29	1.75	2	0.46	0.00	0.50	0.54	+5.98
17	Group A	Val de Ribes	4.76	0.10	0.28	20.14	24.48	6.24	66.12	0.797	2.07	1.58	2.13	1.63	2	0.46	0.00	0.50	0.54	+5.98
18	Synthetic Z		6.90	--	--	20.71	28.39	--	66.73	1.000	--	--	2.26	1.73	2	0.46	0.00	0.50	0.54	+5.98
19	Synthetic K		--	--	--	22.68	14.94	14.38	66.67	0.510	--	--	--	--	2	0.46	0.00	0.50	0.54	+5.98
20	Synthetic K _{Fe}		--	4.28	--	26.01	8.92	16.79	68.86	0.347	--	--	--	--	2	0.46	0.00	0.50	0.54	+5.98

References: 1,4,5,6,12 Moëlo *et al.* (1984a); 2,3 De Haas (1985); 7,8,9 Mozgova & Bortnikov (1980); 10,11 Miehle (1971); 13,14,15 Kupčik *et al.* (1969); 16,17 Ayora & Phillips (1981); 18 Hoda & Chang (1975); 19,20 Chang *et al.* (1980).

TABLE 5. EVALUATION OF PUBLISHED CHEMICAL ANALYSES OF DEFINITE AND PRESUMED KOBELLITE HOMOLOGUES WITH N=4

No.	Original name	Location	Space group	Atomic ratios for M=96 atoms (ideal S=114 atoms per unit cell)							Case A		Case B		T=Cu+Fe+IV _{Ag}		Charge balance for Cu=Cu ⁺				
				Cu	Fe	Ag	Pb	Sb	Bi	S	Sb Sb+BT	N _{Cu} ⁺	N _{Cu2+}	N _{Cu} ²⁺	N _{Cu2+}	N _{ideal}		x _{N=4}	Cu ²⁺	IV _{Ag}	
1	Izoklakeite	Vena		2.85	1.18	1.63	50.54	22.07	17.69	115.71	0.555	3.90	3.06	4.43	3.50	4	0.54	0.67	0.00	0.71	-4.22
2	Izoklakeite	Izok Lake	Pnmm*	3.14	0.88	3.88	45.28	22.64	19.48	109.73	0.538	3.28	2.91	4.41	3.48	4	0.56	0.88	0.00	0.78	+7.64
3	Izoklakeite	Vena	Pnmm	2.94	0.72	1.16	51.29	20.37	19.52	112.06	0.510	3.95	3.11	4.32	3.41	4	0.77	0.20	0.34	0.82	+3.67
4	Izoklakeite	Vena		2.92	0.76	1.32	51.52	20.17	19.31	111.84	0.510	4.02	3.16	4.46	3.52	4	0.61	0.78	0.30	0.81	+3.60
5	Izoklakeite	Vena		3.18	0.75	1.32	50.35	20.11	20.28	114.16	0.498	3.81	2.99	4.21	3.32	4	0.78	0.13	0.07	0.81	-0.45
6	Sb-kobellite	Vena		3.24	5.20	--	51.53	17.80	18.23	115.12	0.494	--	--	4.51	3.56	4	0.78	0.13	0.07	0.81	-0.45
7	Phase VI	Transbaikal		5.26	1.39	2.90	45.46	20.13	20.86	106.46	0.491	3.34	2.61	4.18	3.30	4	0.78	0.13	0.07	0.81	+11.91
8	Sb-illianite	Darasun		3.62	--	--	51.73	18.71	21.57	111.28	0.464	--	--	3.94	3.10	4	0.78	0.13	0.07	0.81	+11.91
9	Izoklakeite	Vena		3.07	1.06	0.87	51.62	18.01	21.71	110.84	0.453	4.00	3.15	4.24	3.35	4	0.73	0.05	0.00	0.74	+6.78
10	Sb-illianite	Ustarasay		4.04	0.77	--	50.21	16.93	24.05	121.20	0.413	--	--	3.73	2.93	4	0.73	0.05	0.00	0.74	+6.78
11	Glessenite	Zerzveilla	Pnmm*	2.63	1.34	0.88	53.75	14.75	22.65	117.27	0.395	4.54	3.58	4.89	3.87	4	0.14	2.10	0.03	0.67	-8.66
12	Mineral A	Transbaikal		3.89	--	2.57	46.48	15.88	27.18	104.26	0.369	3.24	2.53	3.91	3.07	4	1.14	0.00	0.11	0.97	+20.08
13	Group B	Val de Ribes		4.73	1.73	2.06	45.21	11.42	30.84	109.23	0.270	3.21	2.51	3.74	2.93	4	0.79	0.43	0.29	0.90	+8.99
14	Glessenite	Stnata	P2 ₁ /n	4.37	--	--	51.62	7.83	32.18	116.20	0.196	--	--	3.96	3.12	4	1.04	0.00	--	1.00	-4.76
15	Glessenite	Björkåsen	P2 ₁ /n	3.10	0.36	0.29	53.00	5.73	33.53	114.86	0.146	4.19	3.30	4.29	3.38	4	0.79	0.43	0.29	0.90	-1.87
16	Synthetic Z ₁			--	--	--	46.00	23.00	23.00	115	0.500	--	--	--	--	4	3.67	T=0	--	0	0
17	Synthetic Z ₂			--	--	--	46.00	30.36	15.64	115	0.660	--	--	--	--	4	3.67	T=0	--	0	0

References: 1 De Haas (1985); 2 Harris *et al.* (1986); 3,4,5 this study; 6 Flink (1915); 7,8 Mozgova & Bortnikov (1980); 9 De Haas (1985); 10 Mozgova & Bortnikov (1980); 11 Armbruster *et al.* (1984); 12 Bortnikov *et al.* (1982); 13 Ayora & Phillips (1981); 14 Graeser & Harris (1986); 15 Makovicky & Karup-Møller (1986); 16,17 Chang *et al.* (1980). * Space group Pnmm2 is not excluded.

For the empty tetrahedral positions, formula (7) gives:

$$N = \frac{7M^{2+} + 4M^{3+}}{4M^{3+} - M^{2+}} \quad (13)$$

In all these formulae M^{2+} and M^{3+} represent the molar proportions of only the *large cations* corrected for octahedral silver according to the scheme $2Pb \rightleftharpoons Ag + (Bi, Sb)$, but excluding the tetrahedrally co-ordinated cations. For the natural samples, a mixture of uni- and divalent metals can be expected. The N can be calculated as a weighted average of the two formulae for T^+ and T^{2+} . If $x = T^+ : (T^+ + T^{2+})$ and $1-x = T^{2+} : (T^+ + T^{2+})$, then

$$N_x = xN_{T^+} + (1-x)N_{T^{2+}} = x \frac{6M^{2+} + 3M^{3+}}{4M^{3+} - M^{2+}} + (1-x) \frac{5M^{2+} + 2M^{3+}}{4M^{3+} - M^{2+}} \quad (14)$$

The $Cu^{2+} : Cu^+$ ratio is not usually known, so that only bracketing values can be obtained for N . In the present work the values of N were bracketed by assuming Fe (if present) to be divalent and Cu to be alternatively mono- and divalent. These calculations were performed either for total Ag included in the sum of tetrahedral metals (Tables 4, 5, case A) or Ag entirely excluded from these sites (case B). Thus, the "extreme" values of N obtained cover all crystallochemically possible situations that do not require profound changes of the structural principles valid for the kobellite homologous series.

The bracketing values in most cases unambiguously indicate which integral value of N should be assigned to the homologue analyzed. Using this value, a model formula is calculated based on the integral N value, *i.e.*, on the expected sum of metal atoms in a unit cell. The distribution of Ag between the tetrahedral sites (^{IV}Ag) and octahedral sites (^{VI}Ag) can then be obtained by filling up the tetrahedral sites by $Cu + Fe + ^{IV}Ag$ to the ideal limit of 4 metal atoms in a unit cell. Using the molar ratios of large cations (*i.e.*, assuming that the phase represents an unmodified kobellite homologue), the x_N value [*i.e.*, the $T^+ : (T^+ + T^{2+})$ ratio compatible with the observed valences of large cations] for the tetrahedral sites is calculated according to the equation:

$$x_N = \frac{(4N - 2)M^{3+} - (N + 5)M^{2+}}{M^{2+} + M^{3+}} \quad (15)$$

In order not to restrict narrowly the choice of older published compositions to be considered, the theoretical x_N values were calculated in the present work

for the cases in which the sum of tetrahedrally co-ordinated cations is within 4 ± 1 in a cell. Thus the measured values of Cu and Fe were assumed to be potentially inaccurate to an extent. Above these limits, the phases were assumed not to belong to the unmodified kobellite homologous series. It should be remembered that x_N will absorb all analytical errors as well as the possible deviation of the assumed N value from the true one.

The assumption of a known value of N also enables us to calculate the amount of divalent Cu:

$$Cu^{2+} = (1 - x_N)(Cu_{total} + ^{IV}Ag) - x_N Fe \quad (16)$$

The amount of Cu^{2+} as well as the values of $x = (Cu + ^{IV}Ag) / \Sigma T$ based on the true ΣT were calculated for all cases with $\Sigma T = 4 \pm 0.3$ (Tables 4, 5).

Finally, charge balance was calculated for each composition (for the ideal sum of metals in unit cell) assuming Cu^+ . Correction of this value for Cu^{2+} can be easily found from the ideal Cu^{2+} values indicated.

Discussion of the results of the calculation

1. Estimation of the order number N

Tables 4 and 5 show that the calculation scheme allows an estimate of the order of the kobellite homologue even if the valency of Cu and the distribution of Ag between the tetrahedral and octahedral positions are not known. The calculation immediately suggests that the results with Cu predominantly univalent and some Ag in the tetrahedral positions yield estimates closest to the expected value of N . Only selected compositions from those published in various sources could be given in the two tables. The values of N for the synthetic analogues of kobellite and izoklakeite indicate that their composition is not known with sufficient accuracy, especially in the cases with unoccupied tetrahedral positions.

Not many phases are so close chemically to the known kobellite homologues as to cause confusion. Bi-jamesonite $FePb_4(Sb, Bi)_6S_{14}$ is one of them, yielding the apparent value of N of 1.6. An assumed value of $N = 2$, *i.e.*, 52 large cations per formula unit, gives 5.2 Fe atoms, instead of 4 atoms expected from the general formula of the kobellite homologous series. Ideal, Cu-free cosalite yields an apparent value of N of 3.67, as does the synthetic, Cu-free analogue of jaskólskiite. Natural jaskólskiite, with an apparent N_{Cu^+} of 3.78, yields up to 4.3 Cu atoms per formula unit with 96 metal cations. Neyite (Drummond *et al.* 1969), with an apparent N_{Cu^+} of 3.88, yields up to 10 atoms Cu for 96 cations. Eclarite (Paar *et al.* 1983, Kupčik 1984) represents a 1:1 intergrowth of kobellite-like slabs ($N = 2$) with the slabs of doubly truncated kobellite derivative (their

N is also equal to 2 but their general formula is different from that of kobellite). It yields an apparent value of N of 2.3 if half-occupied tetrahedral positions are assumed in our calculations based on a purely kobellite-like structure, and 2.4 in the same calculations if the empirically obtained occupancy of those positions is assumed; 2.5 tetrahedral atoms per 52 large metal atoms follow from the ideal formula.

2. The tetrahedrally co-ordinated metal sites

For the correctly estimated N , the sum of tetrahedrally co-ordinated metals in a unit cell of natural specimens ought to be equal to 4. Many of the compositions in Tables 4 and 5 display sums close to 4, in cases with involvement of smaller amounts of tetrahedrally co-ordinated silver. Deviations from this value may be caused by (1) imprecise chemical data (impure material for wet-chemical analyses, insufficient corrections in microprobe analyses), (2) deviations of the examined material from the structural schemes derived for the kobellite homologous series, (3) true value of N different from the calculated or assumed one, and (4) cation substitutions not yet known in the kobellite homologues.

The first type of deviation is for example represented by Miehe's (1971, 1972) microprobe data, which were obtained for structurally analyzed materials and yet show an excess of tetrahedrally co-ordinated metals. Furthermore, it might be Flink's (1915) chemical analysis of "Sb-kobellite" from Vena that appears to represent izoklakeite contaminated by pyrrhotite and minor amounts of other phases. Among the substitutions not proven for this family may be the Cu-for-Bi substitution observed in the pavonite and cuprobismutite homologous series (summarized in Makovicky 1981) and the Fe-for-Pb substitution suggested by Moëlo *et al.* (1984a) for kobellite. No structural data are available on the first possibility, which is difficult to observe in the presence of so many atoms with high atomic number. No site seems to be readily available for the second substitution. In fizelyite (Makovicky & Mumme 1983, Moëlo *et al.* 1984b), Fe appears to coexist with Pb in sites the average size of which is too small for occupancy solely by Pb. The other example, the two parallel meneghinite and berthierite homologous series (Makovicky 1985), shows that such an exchange (Fe for Pb) requires a pronounced change in the co-ordination of the site involved. In the kobellite homologues, this would require a mutual shift of adjacent rods by 2 Å along the c axis, *i.e.*, a change in the co-ordination of a number of atoms along block interfaces. No such phenomenon has been observed as yet. Finally, no proof of metal vacancies other than in tetrahedral positions was found in the structures of kobellite and izoklakeite.

Therefore, we recommend adherence to the formulae and schemes based on current structural knowledge (Miehe 1971, 1972, Makovicky & Mumme 1985).

The valency of copper in kobellite was discussed by Miehe (1971, 1972), who assumed mixed (Cu^+ , Cu^{2+} , Fe^{2+}) tetrahedral sites in the structure of two kobellite samples studied. Moëlo *et al.* (1984a) assumed Cu^+ using data from syntheses and crystal-chemical analogies with other Cu-containing sulfosalts. Finally, Bente *et al.* (1984) proved the presence of Cu^{2+} and Fe^{2+} in synthetic kobellite (Cu,Fe) $\text{Pb}_6\text{Sb}_2\text{Bi}_4\text{S}_{16}$ by means of electron-spin resonance and Mössbauer studies.

Calculations based on the above derived formulae suggest that the majority of kobellite samples analyzed, including tintinaite, contain some divalent Cu that occurs alone or alongside Fe. The same is suggested by the charge-balance calculations, although the value of both indicators, heavily influenced by the accuracy of the analytical results, can at best be *semiquantitative*.

Only minor amounts of Cu^{2+} are common for izoklakeite from Vena, but its role appears substantial in the example from Izok Lake and dominant in the material from Lake Zervreila. A number of older compositions with no Fe found or determined give only Cu^+ (Table 5). The charge imbalance is quite erratic for the phases with $N = 4$, neither proving nor disproving the above (at best semiquantitative) results.

3. The role of Ag

Only minor amounts of Ag substitute for other metals in tintinaite and kobellite (Table 4). The highest amount, up to 1 atom in a unit cell, was found in kobellite from Hvena (Vena) (Moëlo *et al.* 1984a). Calculations (again to be considered semiquantitative) indicate minor (up to 0.5 atom per cell) amounts of Ag in the tetrahedral sites, the rest taking part in the $\text{Ag} + (\text{Bi,Sb}) \rightleftharpoons 2 \text{Pb}$ or more complicated schemes of substitution in the octahedral sites.

The Ag content of the homologues with $N = 4$ is usually higher, between one and four Ag atoms in a cell. Again, minor substitution in tetrahedral sites is indicated; the preponderance of Ag replaces the large cations. The high Ag contents in the homologues with $N = 4$ suggest that it concentrates in the octahedral sites that appear during homologous expansion from $N = 2$ to $N = 4$ (Makovicky & Mumme 1985).

End members and nomenclature

With all the coupled substitutions involved, a large number of end members can be derived for the kobellite homologues with $N = 2$ and $N = 4$, respec-

TABLE 6. UNIT-CELL CONTENT OF THE HYPOTHETICAL END-MEMBERS OF THE KOBELLITE HOMOLOGOUS SERIES

		Bi end-members	Sb end-members
N=2	x=0	$\text{Fe}_4^{2+}\text{Pb}_{24}\text{Bi}_{28}\text{S}_{70}$	$\text{Fe}_4^{2+}\text{Pb}_{24}\text{Sb}_{28}\text{S}_{70}$
	x=0	$\text{Cu}_4^{2+}\text{Pb}_{24}\text{Bi}_{28}\text{S}_{70}$	$\text{Cu}_4^{2+}\text{Pb}_{24}\text{Sb}_{28}\text{S}_{70}$
	x=1	$\text{Cu}_4^{+}\text{Pb}_{20}\text{Bi}_{32}\text{S}_{70}$	$\text{Cu}_4^{+}\text{Pb}_{20}\text{Sb}_{32}\text{S}_{70}$
	T=0	$\text{Pb}_{16}\text{Bi}_{36}\text{S}_{70}$	$\text{Pb}_{16}\text{Sb}_{36}\text{S}_{70}$
N=4	x=0	$\text{Fe}_4^{2+}\text{Pb}_{56}\text{Bi}_{36}\text{S}_{114}$	$\text{Fe}_4^{2+}\text{Pb}_{56}\text{Sb}_{36}\text{S}_{114}$
	x=0	$\text{Cu}_4^{2+}\text{Pb}_{56}\text{Bi}_{36}\text{S}_{114}$	$\text{Cu}_4^{2+}\text{Pb}_{56}\text{Sb}_{36}\text{S}_{114}$
	x=1	$\text{Cu}_4^{+}\text{Pb}_{52}\text{Bi}_{40}\text{S}_{114}$	$\text{Cu}_4^{+}\text{Pb}_{52}\text{Sb}_{40}\text{S}_{114}$
	T=0	$\text{Pb}_{48}\text{Bi}_{44}\text{S}_{114}$	$\text{Pb}_{48}\text{Sb}_{44}\text{S}_{114}$
N=6	x=0	$\text{Fe}_4^{2+}\text{Pb}_{88}\text{Bi}_{44}\text{S}_{158}$	$\text{Fe}_4^{2+}\text{Pb}_{88}\text{Sb}_{44}\text{S}_{158}$
	x=0	$\text{Cu}_4^{2+}\text{Pb}_{88}\text{Bi}_{44}\text{S}_{158}$	$\text{Cu}_4^{2+}\text{Pb}_{88}\text{Sb}_{44}\text{S}_{158}$
	x=1	$\text{Cu}_4^{+}\text{Pb}_{84}\text{Bi}_{48}\text{S}_{158}$	$\text{Cu}_4^{+}\text{Pb}_{84}\text{Sb}_{48}\text{S}_{158}$
	T=0	$\text{Pb}_{80}\text{Bi}_{52}\text{S}_{158}$	$\text{Pb}_{80}\text{Sb}_{52}\text{S}_{158}$

tively. They represent the (partly hypothetical) Sb and Bi end-members with Cu^+ , Cu^{2+} , Fe^{2+} or vacancies in the tetrahedral positions, with or without Ag substitution in both the tetrahedral and octahedral positions. It does not seem structurally justified at present to indicate end members fully substituted by Ag. Therefore, 1 and 4 Ag atoms *per* cell still may represent "justifiable" indicators of substitutional trends for $N = 2$ and $N = 4$, respectively. End members for the still hypothetical homologue with $N = 6$ are given as well (Table 6).

Natural occurrences (Tables 4, 5) suggest full occupancy of the tetrahedrally co-ordinated positions with Cu dominant over Fe. The uncertainty connected with the estimation of the valency of Cu reduces further the use of the recognized and hypothetical chemical end-members determined above. Therefore, according to their Sb/(Sb + Bi) ratio, the known natural kobellite homologues with $N = 2$ are tintinaite and kobellite, and those with $N = 4$ are izoklakeite and giessenite. This situation is accentuated by differences in the crystallographic symmetry between these members.

Izoklakeite is orthorhombic, $Pnmm$, whereas giessenite is monoclinic $P2_1/n$ (Makovicky 1981, Makovicky & Karup-Møller 1986). However, in the latter case, the X-ray reflections that violate the extinction rules for $Pnmm$ are all weak, and the changes in the geometry of the reciprocal lattice and symmetry from orthorhombic are relatively minor. Giessenite might be orthorhombic at elevated temperatures. The presence of the potential high-to-low phase transformation in the crystals from Björkasen, Norway is suggested by intimate twinning (Makovicky & Karup-Møller 1986). At lower temperature giessenite and izoklakeite ought to be sepa-

rated by a miscibility gap; however, the results of a recalculation of chemical compositions with N close to 4 (Table 5) suggest that its width, in the otherwise continuous series that stretches from giessenite with Sb/(Sb + Bi) of 0.146 to izoklakeite with that ratio equal 0.555, is minimal. If Armbruster *et al.* (1984) have not overlooked the weak violations of the $Pnmm$ symmetry, the gap between izoklakeite and giessenite lies somewhere between the values 0.395 and 0.196. The presence of two phases with the Sb/(Sb + Bi) values 0.369 and 0.270 (Table 5, anal. 12, 13), both with unknown symmetry, reduces further the width of the potential gap. The unit-cell parameter a decreases systematically from the giessenite sample richest in Bi to the izoklakeite sample richest in Sb. Uncertainty in the published b parameters is too large to allow a similar generalization for this repeat distance.

Similar regularity was noted for homologues with $N = 2$, for which the unit-cell parameter a decreases systematically from the kobellite sample richest in Bi to the tintinaite sample richest in Sb, whereas the b and c axes remain unchanged (Harris *et al.* 1968, Miehe 1972). This group also shows slight differences in symmetry similar to those for $N = 4$. Tintinaite is orthorhombic (Harris *et al.* 1968). According to Miehe (1971), the $Pnmm$ symmetry of kobellite is disturbed to $P2_1/n$ for Bi-rich kobellite. The variation of the Sb/(Sb + Bi) ratio in natural homologues with $N = 2$ is between 1 and 0.2 (Table 4), considerably higher than in the case of homologues with $N = 4$.

Thus, the complications in symmetry of both the homologues with $N = 2$ and $N = 4$ imply that each of them can potentially be divided into two species, which represent an Sb-rich orthorhombic and a Bi-rich monoclinic solid-solution. The problem of the boundary between these solid solutions will not be solved until sufficient single-crystal data are accumulated for phases with different Sb/(Sb + Bi) values in order to locate the definite change in symmetry from $P2_1/n$ to $Pnmm$.

MINERAL-SYNTHESIS STUDIES AND THEIR APPLICATION

During experimental studies in the system $\text{PbS-FeS-Sb}_2\text{S}_3\text{-Bi}_2\text{S}_3$, Chang *et al.* (1980) produced several phases designated Y_1 , Y_2 and Y_{Fe} , with a composition similar to that of izoklakeite. At 500°C they formed a single-phase solid-solution plane between $\text{Pb}_2\text{SbBiS}_5$ - $\text{Pb}_2\text{Sb}_{1.52}\text{Bi}_{0.48}\text{S}_5$ and $\text{Pb}_{1.88}\text{Fe}_{0.32}\text{Sb}_{1.25}\text{Bi}_{0.63}\text{S}_5$. The X-ray powder-diffraction patterns suggest that these phases are the synthetic equivalent of jaskólskiite $\text{Pb}_{2+x}\text{Cu}_x(\text{Sb,Bi})_{2-x}\text{S}_5$. At $407 \pm 8^\circ\text{C}$ the Y phases transform into phase Z , which is a solid solution ranging from $\text{Pb}_2\text{SbBiS}_5$ to $\text{Pb}_2\text{Sb}_{1.32}\text{Bi}_{0.68}\text{S}_5$ (the Fe part of the system was not studied at lower temper-

ature). Recalculation of these compositions based on 92 cations gives $Pb_{46}Sb_{23}Bi_{23}S_{115}$ and $Pb_{46}Sb_{30}Bi_{16}S_{115}$, with a chemical N of 3.7 (Table 5). These formulae are fairly close to $Pb_{48}(Sb,Bi)_{44}S_{114}$, which is the theoretical $N = 4$ homologue of kobellite with empty tetrahedral positions. The X-ray powder-diffraction pattern of phase Z is, with the exception of a few lines of lower intensity, very close to that of izoklakeite. Further single-crystal investigations on phase Z could give the definite answer to the problem of identity of phase Z and izoklakeite.

In the Vena deposit, izoklakeite is associated with jaskólskiite, a mineral that seems to have formed earlier than izoklakeite, but there are no signs of a transformation analogous to that described by Chang *et al.* (1980) from the experimental studies.

The same authors obtained, at 500°C (and 450°C), synthetic phases K (idealized formula $3PbS \cdot Sb_2S_3 \cdot Bi_2S_3$) and K_{Fe} ($6PbS \cdot FeS \cdot Sb_2S_3 \cdot 2Bi_2S_3$); they observed complete miscibility at 500°C between the two phases, and they interpreted their powder pattern to be that of kobellite. Thus the phases ought to represent, respectively, kobellite with empty tetrahedral positions and kobellite with these positions occupied by divalent metals. When their microprobe results are evaluated (Table 4), the phase K_{Fe} yields a still acceptable value N of 2.36 (*i.e.*, 2), but the phase K indicates an N equal to 2.92, incompatible with the structural principles of the kobellite homologous series established by Makovicky & Mumme (1985). There are several significant discrepancies between the powder patterns of K and K_{Fe} , K_{Fe} being closer to natural kobellite. Therefore, single-crystal investigations of phase K are desirable.

The synthetic phase Z prepared by Hoda & Chang (1975) was found by Moëlo *et al.* (1984a) to correspond to tintinaite. The calculations of N based on large cations (Table 4) confirm their suggestion, but the Cu content indicated by Hoda & Chang (1975) is too high.

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