LETTER

Icosahedral coordination of phosphorus in the crystal structure of melliniite, a new phosphide mineral from the Northwest Africa 1054 acapulcoite

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ABSTRACT

Melliniite, ideally $(Ni,Fe)_4P$, is a new mineral from the Northwest Africa 1054 acapulcoite. It occurs as anhedral to subhedral grains up to 100 μm, associated with kamacite and nickelphosphide. Melliniite is opaque with a metallic luster and possesses a gray streak. It is brittle with an uneven fracture; the Vickers microhardness (VHN_{500}) is 447 kg/mm^2 (range 440–454) (calculated Mohs hardness of 8–8½). The calculated density is 7.88 g/cm^3 (on the basis of the empirical formula). In plane-polarized reflected light, melliniite is cream-yellowish. Between crossed polars it is isotropic, with no internal reflections. Reflectance percentages (R) for the four standard COM wavelengths are 60.5 (471.1 nm), 50.4 (548.3 nm), 52.5 (586.6 nm), and 55.9 (652.3 nm), respectively. Electron-microprobe analyses give the chemical formula $(Ni_{2.30}Fe_{1.64}Co_{0.01})_{\Sigma=3.95}P_{1.05}$ on the basis of total atoms = 5.

Melliniite is cubic, space group $P2_13$, with $a = 6.025(1)$ Å, $V = 218.71(6)$ Å^3, and $Z = 4$. The crystal structure has been solved and refined to $R = 2.72\%$ using single-crystal X-ray diffraction data. It shows the $AlAu_4$-type structure, which is an ordered form of the β-Mn structure. The metal atoms occupying the 12b site (M1) are effectively 14 coordinated whereas the metals at the 4a site (M2) are 12 coordinated by three P atoms and nine metals. The phosphorus atoms (4a site) coordinate 12 metal atoms in a somewhat distorted icosahedral arrangement. This new phosphide is the first phase with such a high coordination-number for phosphorus.

The new mineral is named after Marcello Mellini, Professor of Mineralogy, who strongly developed the study of meteorites in Italy. The new mineral and mineral name have been approved by the IMA Commission on New Minerals and Mineral Names (2005-027).

Keywords: Melliniite, chemical composition, meteorites, X-ray data, new mineral

INTRODUCTION

The recent discovery that meteoritic schreibersite, $(Fe,Ni)_3P$, can provide enough phosphorus essential for the biomolecular building blocks of life (Pasek et al. 2004), has drawn attention to the study of extraterrestrial iron nickel phosphides. These minerals are fundamental constituents of iron and stony-iron meteorites (Buchwald 1975; Geist et al. 2005; Heide and Wlotzka 1995) and could represent the potential reservoirs of light elements in the Earth's core. Besides schreibersite, four other natural phosphides are known: nickelphosphide $(Ni,Fe)_3P$ (Britvin et al. 1999; Skála and Drábek 2003), barringerite $(Fe,Ni)_2P$ (Buseck 1969), alla-bogdanite $(Fe,Ni)_2P$ (Britvin et al. 2002) and florenskyite FeTiP (Ivanov et al. 2000). Another P-bearing nickel-iron silicide mineral called perryite [simplified chemical formula: $(Ni,Fe)_8(Si,P)_3$ with 2.4–5.2 wt% of P] is known to occur as thin lamellae within metallic nickel-iron grains in the highly reduced stony meteorites (Okada et al. 1988). Among these minerals, however, schreibersite is the most common phase. Recent studies (Japel et al. 2002; Santillan et al. 2004) have pointed out that schreibersite is also stable at ultrahigh pressures and temperatures. The wide stability range of its tetragonal structure makes this mineral the most

likely phase by which phosphorus was originally incorporated in deep planetary interiors.

In the course of a study on acapulcoites, a group of primitive achondrites (Mittlefehldt 2003; Moggi-Cecchi et al. 2005; Patzer et al. 2004; Scott and Pinault 1999) a new nickel iron phosphide mineral was observed.

OCCURRENCE AND METHODS

Sample

The sample containing melliniite was not found in situ, but originates from a thin section of a meteorite (acapulcoite) belonging to the Collection of Meteorites of the Museo di Scienze Planetarie della Provincia di Prato where it is labeled "Northwest Africa 1054" (Moggi-Cecchi et al. 2005). Acapulcoites are peculiar primitive achondrites with transitional characteristics from chondrites to more differentiated achondrites. Recently, with respect to their elemental distribution patterns, Patzer et al. (2004) distinguished four subtypes comprising primitive, typical, transitional and enriched acapulcoites. Differently from the other subtypes, the primitive acapulcoites, like Northwest Africa (NWA) 1054, did not experience sulfide melt loss and may contain relic and scattered intact chondrules consisting of olivine and orthopyroxene set in a matrix mainly composed of fine-grained orthopyroxene, olivine and plagioclase crystals.

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TABLE 1. Fractional coordinates and anisotropic displacement parameters of atoms for melliniite, space group $P2_13$, $a = 6.025(1)$ Å

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
M1	0.11684(9)	0.20686(9)	0.45493(9)	0.0295(3)	0.0289(3)	0.0286(3)	0.0001(2)	−0.0002(2)	0.0001(2)	0.0290(2)
M2	0.6803(1)	0.6803(1)	0.6803(1)	0.0261(2)	0.0261(2)	0.0261(2)	0.0004(2)	0.0004(2)	0.0004(2)	0.0261(2)
P	0.0622(2)	0.0622(2)	0.0622(2)	0.0242(3)	0.0242(3)	0.0242(3)	−0.0003(3)	−0.0003(3)	−0.0003(3)	0.0242(3)

Chunks of Fe-Ni metal alloys (mostly kamacite) and troilite are the most abundant non-silicate phases. Accessory phases are merrillite, magnesiochromite and nickelphosphide.

Melliniite occurs in the NWA 1054 acapulcoite, closely associated with kamacite (Fig. 1a) and nickelphosphide (Fig. 1b). We have named the new mineral melliniite in honor of Marcello Mellini, Full Professor of Mineralogy at the University of Siena, in recognition of his contributions to the development of the study of meteorites in Italy. Type material is housed in the Meteorite Collection of the Museo di Scienze Planetarie della Provincia di Prato, Prato, Italy, under catalog number MSP-2378. The new mineral and mineral name have been approved by the IMA Commission on New Minerals and Mineral Names (2005-027).

Physical and optical properties

Melliniite shows a gray streak. The mineral is opaque in transmitted light and exhibits a metallic luster. No cleavage is observed and the fracture is uneven. The calculated density (for $Z = 4$) from the empirical formula is 7.88 g/cm³. Unfortunately, the density could not be measured here because of the small grain size. Micro-indentation measurements carried out with a VHN load of 500 g give a mean value of 447 kg/mm² (range: 440–454) corresponding to a Mohs hardness of about 8–8½.

In plane-polarized incident light melliniite is cream-yellowish in color. Under crossed polars melliniite is isotropic. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means

TABLE 3. X-ray powder diffraction patterns for melliniite

	1		2				
I	d_{meas}	d_{calc}	I_{calc}	d_{calc}	h	k	l
2	3.48	3.4766	3.24	3.4785	1	1	1
15	**2.694**	**2.6930**	**13.05**	**2.6945**	**2**	**0**	**1**
5	2.457	2.4584	4.27	2.4597	2	1	1
100	**2.005**	**2.0072**	**100.00**	**2.0083**	**2**	**2**	**1**
60	1.906	1.9042	35.37	1.9053	3	0	1
			23.87	1.9053	3	1	0
20	1.816	1.8156	19.90	1.8166	3	1	1
5	1.609	1.6094	5.00	1.6102	3	1	2
10	**1.420**	**1.4193**	**5.78**	**1.4201**	**4**	**1**	**1**
10	**1.348**	**1.3465**	**2.23**	**1.3472**	**4**	**0**	**2**
			4.14	1.3472	4	2	0
5	1.203	1.2043	2.35	1.2050	4	3	0
15	**1.182**	**1.1810**	**8.35**	**1.1816**	**4**	**3**	**1**
			8.14	1.1816	4	1	3
5	1.160	1.1589	4.33	1.1595	5	1	1
15	1.119	1.1182	3.68	1.1188	4	3	2
			5.57	1.1188	4	2	3
			3.26	1.1188	5	0	2
			3.66	1.1188	5	2	0
2	1.098	1.0994	2.86	1.1000	5	1	2
5	1.017	1.0179	2.57	1.0184	5	3	1
			2.54	1.0184	5	1	3
2	1.003	1.0036	5.53	1.0042	4	4	2
5	0.976	0.9769	2.02	0.9774	6	1	1
			2.16	0.9774	5	2	3

Notes: (1) X-ray powder-diffraction data obtained with a 114.6 mm Gandolfi camera with Ni-filtered Cu$K\alpha$; (2) d values calculated on the basis of $a = 6.025(1)$ Å, and with the atomic coordinates reported in Table 1. Intensities calculated using XPOW software version 2.0 (Downs et al. 1993).

of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6, and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages (R) for the four standard COM wavelengths are 60.5 (471.1 nm), 50.4 (548.3 nm), 52.5 (586.6 nm), and 55.9 (652.3 nm), respectively.

X-ray crystallography and crystal-structure determination

A small crystal fragment ($15 \times 20 \times 20$ μm), dug out from a polished thin section, was selected for the X-ray single-crystal diffraction study. Unit-cell parameters, determined by centering 25 high-θ (20–25°) reflections, on an automated diffractometer (Enraf Nonius CAD4), are $a = 6.025(1)$ Å, $V = 218.71(6)$ Å³, and $Z = 4$. To check the possible presence of diffuse scattering or weak superlattice peaks, the crystal was also mounted (exposure time of 150 s per frame; 40 mA × 40 kV) on a CCD-equipped diffractometer (Oxford Xcalibur 2), but no additional reflections were detected.

Intensity data were collected using Mo$K\alpha$ radiation monochromatized by a flat graphite crystal in ω scan mode up to 2θ ≤ 75°. Intensities were corrected for Lorentz-polarization effects and subsequently for absorption following the semi-empirical method of North et al. (1968). The merging R for the ψ-scan data set in the $m\bar{3}$ Laue group decreased from 8.65% before absorption correction to 5.24% after this correction. The analysis of the systematic absences ($h00$: $h = 2n$) together with the statistical tests on the distribution of |E| values, that do not indicate the presence of an inversion center (|E² – 1| = 0.636), leads us to the choice of the space group $P2_13$.

The position of the two metal atoms (M1 and M2) was determined from the three-dimensional Patterson synthesis (Sheldrick 1997a). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R factor of 14.12%. Three-dimensional difference Fourier synthesis yielded the position of the remaining phosphorus atom. The full-matrix least-squares program SHELXL-97 (Sheldrick 1997b), working on F^2, was used for the refinement of the structure. The introduction of anisotropic temperature factors for all the atoms led to $R = 2.72\%$ for 187 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 2.78\%$ for all 202 independent reflections. Because the X-ray scattering factors of Fe and Ni are similar, it was impossible to study cation ordering in detail using X-ray data. We choose to assign the scattering curve of Ni (i.e., the dominant cation) at the M1 and M2 sites. Neutral scattering curves for Ni and P were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1974). Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 0.94 and 1.14 e⁻/Å³, respectively. Fractional atomic coordinates and anisotropic-displacement parameters are shown in Table 1. Table 2[1] lists the observed and calculated structure factors. Table 3 reports the X-ray powder pattern of melliniite obtained with a 114.6 mm Gandolfi camera with Ni-filtered Cu$K\alpha$.

Chemical composition

A preliminary chemical analysis using energy dispersive spectrometry, performed on the same crystal fragment used for the structural study, did not indicate the presence of elements (Z > 9) other than Ni, Fe, and P and minor Co, Si, Mg, and S. The

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[1]Deposit item AM-06-009, Table 2. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.
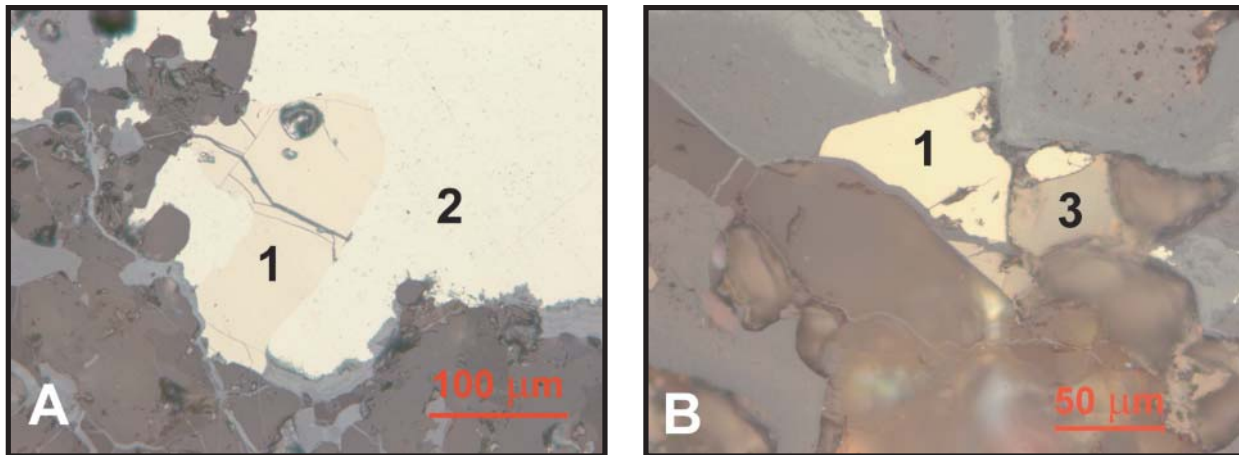
FIGURE 1. Reflected-light micrographs displaying melliniite. (**a**) An anhedral fragment of the new phosphide (1) associated with kamacite (2). (**b**) Association of melliniite (1) and nickelphosphide (3). The image was obtained using a Zeiss Axioplan 2 microscope with AxioCam-HR Digital Image Acquisition apparatus. Scale bars are indicated.

TABLE 4. Electron microprobe analyses for melliniite

Element	wt%	Range
Fe	34.9	33.9–36.6
Co	0.22	0.08–0.24
Ni	51.4	47.0–51.5
Si	0.01	0.00–0.04
Mg	0.03	0.00–0.07
P	12.4	11.6–12.4
S	0.02	0.01–0.05
Total	98.98	

Notes: Means and ranges in wt% of elements; n = 15.

chemical composition was then determined using wavelength dispersive analysis (WDS) by means of a Jeol JXA-8600 electron microprobe. Major and minor elements were determined at 15 kV accelerating voltage and 10 nA beam current, with a 15 s counting time. For the WDS analyses the $K\alpha$ lines for all the elements were used. The estimated analytical precision is: ±0.90 for Fe and Ni, ±0.55 for P, ±0.03 for Co, and ±0.01 for Si, Mg and S. The standards employed were: pure elements for Fe, Co, Ni, Si, and Mg, apatite for P, and marcasite for S. The melliniite fragment was found to be homogeneous within analytical error. The average chemical composition (15 analyses on different spots), together with ranges of wt% of elements, is reported in Table 4. On the basis of 5 atoms, the formula of melliniite is $(Ni_{2.30}Fe_{1.64}Co_{0.01})_{\Sigma=3.95}P_{1.05}$, ideally $(Ni,Fe)_4P$.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure of the new iron nickel phosphide shows the $AlAu_4$-type structure, which is an ordered form of the β-Mn structure (a polymorph of manganese). Phosphorus occupies a $4a$ site and the metal atoms (i.e., Ni and Fe) a second $4a$ and a $12b$ site. This corresponds to four formula units of $(Ni_{2.30}Fe_{1.64}Co_{0.01})_{\Sigma=3.95}P_{1.05}$ per unit cell. Within experimental uncertainties, all sites are fully occupied. The crystallographic features for the new phase are really unique for phosphorus-bearing compounds. The metal atoms occupying the $12b$ site (M1) are effectively 14 coordinated whereas the metals at the $4a$ site (M2) are 12 coordinated by three P atoms and nine metals (Table 5). The
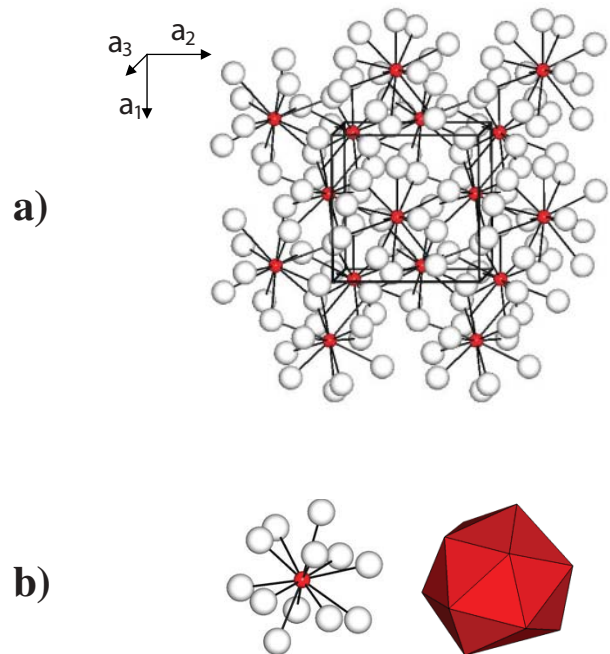

FIGURE 2. The crystal structure of melliniite. The P atoms are represented in red whereas the metal atoms (Ni,Fe) in white (**a**). The unit cell and the orientation of the structure are indicated. Portion of the structure of melliniite showing the twelve-coordination of phosphorus (**b**). A distorted icosahedral arrangement is clearly observable.

phosphorus atoms ($4a$ site) coordinate 12 metal atoms with bond distances ranging from 2.247 to 2.605 Å in a somewhat distorted icosahedral arrangement (Fig. 2). Our results show that the new phosphide reported here is the first phase with so high a coordination-number for phosphorus. In the crystal structure of the mineral perryite (Okada et al. 1991), there is a twelve-coordinated structural position named Si(P)1 but the dominant cation at that site is silicon. Generally phosphorus has 9 metal neighbors mostly in a tricapped triangular prismatic coordination

TABLE 5. Selected bond distances (Å) for melliniite

Atoms	Distances (Å)	Atoms	Distances (Å)
M1–P	2.399(2)	M2–3 P	2.247(1)
M2	2.500(1)	3 M1	2.500(1)
2 M1	2.496(1)	3 M1	2.520(1)
P	2.543(1)	3 M1	2.531(1)
2 M1	2.509(1)		
M2	2.520(1)	P–3 M2	2.247(1)
M2	2.531(1)	3 M1	2.399(2)
2 M1	2.584(1)	3 M1	2.543(1)
P	2.605(1)	3 M1	2.605(1)
2 M1	3.105(1)		

as in allabogdanite, $(Fe,Ni)_2P$ (Britvin et al. 2002). Rarely it can occur as ten-coordinated as, for instance, in the synthetic Co_2P (Rundqvist 1962), but higher coordination-numbers for P atoms are unknown in nature. On the contrary, a similar coordination to that found here for phosphorus was observed for Si and Ge in the recently synthesized compounds Mn_3IrSi (Eriksson et al. 2004b) and Mn_3IrGe (Eriksson et al. 2004a).

The new mineral melliniite represents the first report of a natural nickel iron phosphide with a metal/phosphorus ratio of 4:1. Hornbogen (1961), studying the products deriving from the precipitation of phosphorus from alpha iron, reported a compound with chemical composition Fe_4P; the crystal structure of such Fe_4P compound, however, is quite different from that of melliniite. It consists of a face-centered lattice of iron atoms with phosphorus at the (½, ½, ½) position. The whole lattice is orthorhombically distorted because not all the cube centers are filled with phosphorus atoms.

The calculated density for the new phase is 7.88 g/cm^3 (on the basis of the empirical formula). This value exceeds by 4% that calculated for nickelphosphide (7.61 g/cm^3), the densest iron nickel phosphide previously known. The higher density is more related to the metal/phosphorus ratio than to the higher coordination of the phosphorus atoms.

Although the scarcity and the size of materials precludes additional investigations (e.g., shock wave studies, laser heating in diamond anvil cells), we would like to speculate about the implications of this new phase as potential candidate by which phosphorus was originally incorporated in deep planetary interiors. The new phosphide shows a cubic symmetry, the highest coordination-number for P atoms yet discovered, and the highest density value for a Fe-Ni-P compound. It is well known that a higher symmetry and atom-coordination are characteristic of a high-pressure environment, therefore this new iron nickel phosphide could play a role for Earth's core mineralogy.

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