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OCCURRENCE AND CRYSTAL STRUCTURE OF CALCIOPETERSITE FROM MONTE BENI (FIRENZUOLA, FLORENCE, TUSCANY, ITALY)

Abstract - The mixite group includes several hexagonal phosphates and arsenates, characterized by the general chemical formula $MCu_6(XO_4)_3(OH)_6 \cdot 3H_2O$. A phosphate belonging to this group has been identified on samples collected at the Fantoni quarry (Monte Beni, Firenzuola, Florence), as tufts of acicular crystals with hexagonal section, blue-green in color, associated with chrysocolla. Semi-quantitative chemical data point to a dominance of Ca over Y, indicating that these samples could be classified as calciopetersite. The crystal structure of this mineral has been solved and refined using intensity data collected through synchrotron radiation, due to the extremely small size of the single crystals. Calciopetersite is hexagonal, space group $P6_3/m$, cell parameters a 13.206(2), c 5.824(3) Å. Its crystal structure is analogous to those described for the arsenates belonging to the mixite group and it is composed by chains of $Cu^{[4+1]}O_5$ pyramids, infinite along [001], bonded to MO_9 polyhedra through edge-sharing. The structure is completed by PO_4 tetrahedra. Finally, the structural channels host H_2O molecules. The genesis of calciopetersite from Monte Beni is related to the superficial alteration of a copper mineralization hosted in the ophiolitic rocks.

Key words - Calciopetersite, mixite group, crystal structure, ophiolites, Monte Beni, Tuscany.

Riassunto - *Ritrovamento e struttura cristallina della calciopetersite di Monte Beni (Firenzuola, Firenze, Toscana, Italia).* Il gruppo della mixite comprende una serie di fosfati e arseniati esagonali, aventi formula generale $MCu_6(XO_4)_3(OH)_6 \cdot 3H_2O$. Un fosfato appartenente a questo gruppo è stato identificato in campioni provenienti dalla cava Fantoni (Monte Beni, Firenzuola, Firenze), sotto forma di aggregati raggiati di cristalli aciculari a sezione esagonale e colore verde-azzurro, in associazione a crisocolla. I dati chimici semi-quantitativi indicano una predominanza di Ca su Y, e quindi una attribuzione alla calciopetersite. La struttura cristallina di questo minerale è stata determinata e raffinata utilizzando dati di intensità raccolti con luce di sincrotrone, per ovviare alle minutissime dimensioni dei cristalli singoli. La calciopetersite cristallizza nel sistema esagonale, gruppo spaziale $P6_3/m$, con parametri di cella a 13.206(2), c 5.824(3) Å. La struttura di questa fase è analoga a quella descritta per gli arseniati appartenenti al gruppo della mixite ed è formata da catene di piramidi $Cu^{[4+1]}O_5$, infinite lungo [001], legate a poliedri MO_9 tramite condivisione di spigoli. La struttura è completata da tetraedri PO_4. Infine, all'interno dei canali strutturali, trovano posto molecole di H_2O. L'origine della calciopetersite di Monte Beni è legata a processi di alterazione superficiale di una mineralizzazione cuprifera incassata nelle rocce ofiolitiche.

Parole chiave - Calciopetersite, gruppo della mixite, struttura cristallina, ofioliti, Monte Beni, Toscana.

Introduction

The mixite group is formed by a series of hexagonal phosphates and arsenates, having the general chemical formula $MCu_6(XO_4)_3(OH)_6 \cdot 3H_2O$. M is represented by REE^{3+}, Y^{3+}, Al^{3+}, Bi^{3+}, Ca^{2+}, or Pb^{2+}; X can be As^{5+} or P^{5+}. Up to now, only two natural phosphates have been described: petersite-(Y) and calciopetersite. Petersite-(Y), ideally $YCu_6(PO_4)_3(OH)_6 \cdot 3H_2O$, was described by Peacor & Dunn (1982) and was found in very few localities world-wide; calciopetersite, ideally $CaCu_6(PO_4)_2(PO_3OH)(OH)_6 \cdot 3H_2O$, is rarer than the previous one and it was found only in three localities (Sejkora *et al.*, 2005; Kolitsch, 1997; Walenta, 2003). These two minerals are the P-analogues of agardite-(Y) and zálesíite, respectively. Whereas the crystal structure of some arsenates of the mixite group were determined and refined, the crystal structures of the P-dominant phases are still not experimentally determined.

Tuscan occurrences of the minerals of the mixite group are rather rare: mixite was reported by Bellé & Simonini (1997) and Orlandi (1999) from the Gioia quarry (Carrara), whereas Senesi & Sabelli (1999) described the occurrence of agardite-(Ce) in the Santa Caterina Valley (Campiglia Marittima), associated with arseniosiderite and scorodite.

During a routine examination of mineral samples from the Fantoni quarry (Monte Beni, Firenzuola, Florence, Tuscany), a phosphate member of the mixite group was identified in two specimens collected by Mr. Tiberio Bardi. Using one of these two specimens, now kept in the mineralogical collection of the «Museo di Storia Naturale e del Territorio» of the Pisa University, under the catalogue number # 19444, a structural study was planned, in order to determine the true atomic arrangement of this phase.

Geological setting

The area of Monte Beni is characterized by outcrops of basalts, gabbros, and serpentinized ultramafites belonging to the Liguride units. These rocks were affected by oceanic metamorphism and by hydrothermal processes, with the appearance of a series of mineral phases typical of this geologic environment and described also in other localities from the Northern Apennines. D'Achiardi (1872/73) reported the occurrence of

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quartz, «diallage», talc, «labradorite», and chalcopyrite from Monte Beni, whereas Pedroni *et al.* (1996) cited the presence of pyrite, chalcopyrite, actinolite, epidote, diopside, rhodonite, and titanite. In 2002, an important rock fall occurred in the old Fantoni quarry and a mineralogical study was carried on these new materials, in which calciopetersite was found (Bardi *et al.*, in preparation).

MINERALOGICAL CHARACTERIZATION

Calciopetersite was identified in only two specimens found in the Fantoni quarry (Monte Beni, Florence, Tuscany). It occurs as divergent radiating sprays of acicular crystals, with a hexagonal cross-section 5 µm wide, up to 0.1 mm long, blue-green in color. Calciopetersite is associated with chrysocolla, in mammillary aggregates, on altered chalcopyrite. The identification was carried out by X-ray powder diffraction using a 114.6 mm Gandolfi camera with Ni-filtered Cu$K\alpha$ radiation and qualitative EDS chemical analysis with a Philips XL30 SEM, equipped with a EDAX DX4 system.
Notwithstanding the very small size of the crystals, X-ray powder diffraction revealed that the studied sample belongs to the mixite group. The observed reflections are [*d* in Å, visually estimated *I*, *hkl*]: 11.4, very

strong, 100; 4.32, medium, 210; 3.48, weak, 211; 3.17, weak, 310 and 130; 2.86, medium, 400; 2.625, weak, 230 and 320; 2.50, weak, 140; 2.419, medium, 212 and 122; 1.953, weak, 232 and 322. The indices of the reflections were attributed on the basis of the intensity calculated from the structural model of calciopetersite, using the software Powder Cell (Kraus & Nolze, 1996). Qualitative chemical EDS analysis showed the occurrence of Ca, Cu, Y, P, Si, and minor Nd as the only elements with $Z > 9$. Arsenic, detected in petersite-(Y) and calciopetersite from the type locality, was not observed. The occurrence of Si is probably related to a small coating of chrysocolla. Owing to the extensive substitution at the *M* and *X* sites, an unambiguous identification of the individual members of the mixite group is possible only through quantitative chemical analysis. However, due to the tiny dimensions and the difficulty in preparing a polished crystal of this mineral from Monte Beni, only semi-quantitative energy-dispersive microprobe could be carried out on unpolished crystal at a Stereoscan S360 Cambridge electron microscope with an Oxford Instruments INCA EDS analyzer, equipped with a Link Pentafet SATW detector, at the Dipartimento di Scienze Mineralogiche e Petrologiche of the University of Turin. The operating conditions were: 15 kV accelerating voltage, 1.5 nA beam current, 2.0 µm beam dimension and 100 s live-

Tab. 1 - Details on crystal data, data collection and structural refinement.

Crystal data	
Crystal size (mm^3)	$0.08 \times 0.005 \times 0.005$
Cell setting, space group	Hexagonal, $P6_3/m$
a, *c* (Å)	13.206(3), 5.824(2)
V (Å^3)	879.6(5)
Z	2
Data collection and refinement	
Radiation, wavelength (Å)	synchrotron, $\lambda = 1$ Å
Temperature (K)	293
Detector to sample distance	36 mm
Detector diameter (cm)	16.5
Number of frames	72
Rotation width per frame (°)	5
Maximum observed 2θ	37.68
Measured reflections	261
Unique reflections	261
Reflections $F_o > 4\sigma (F_o)$	261
Range of *h*, *k*, *l*	$0 \leq h \leq 12, \ -9 \leq k \leq 0, \ 0 \leq l \leq 5$
$R [F_o > 4\sigma (F_o)]$	0.0516
R (all data)	0.0516
wR (on F_o^2)	0.1288
Goof	1.184
Number of least squares parameters	43

time. Five analytical points were collected; in one of them, collected near the base of the studied crystal, no yittrium was detected. In the other four points, yittrium is always subordinated to calcium, with a quite constant ratio (Ca:Y ~ 60:40). On the basis of these data, it is possible to assign the studied sample to calciopetersite.

Crystal structure of calciopetersite

Due to the very small size of the available crystals (~ 80 × 5 × 5 μm^3), intensity data were collected at the XRD1 beamline of the Elettra Laboratory (Basovizza, Trieste, Italy), using synchrotron radiation. Calciopetersite has cell parameters a 13.206(3), c 5.824(2) Å, space group $P6_3/m$. Crystal data and experimental details are reported in Table 1. The solution and refinement of the crystal structure were performed by means of the SHELX set of programs (Sheldrick, 2008). The coordinates of the heavier atoms were found by direct methods, using SHELX-97; through difference-Fourier maps, oxygen atoms and water molecules were located. The isotropic displacement parameters of the three water molecules sites were constrained to be equal and their occupancies were refined. Only the displacement parameters of the cations were refined anisotropically. The final refinement converged to R = 5.2% for all 261 observed reflections with $F_o > 4\sigma(F_o)$. It is important to stress that the better R value was obtained assuming a complete occupancy of the M site by yittrium, whereas the chemical data suggest only a partial occupancy, with Ca > Y. There are three possible explanations: i) crystals of the P-member of mixite from Monte Beni are inhomogeneous, with Y- and Ca-dominant individuals; ii) the content of the HREE (in particular Nd), which was not taken into account during the refinement, can increase the observed electron density in the M site, giving rise to a fictictious high Y occupancy; iii) the refinement is affected by the quality of the set of the intensity data, and in particular by the low resolution of the measured reflections. The first hypothesis is unlikely, because the examined crystals always showed Ca

in excess of Y, with the only exception of an analytical point near the base of a crystal, which did not show at all the presence of yttrium.

Atomic coordinates and equivalent or isotropic displacement parameters are reported in Table 2, whereas selected bond distances are shown in Table 3. Figure 1 shows the crystal structure of calciopetersite, as seen down **c**.

The framework arrangement is the same observed in other synthetic or natural phases belonging to the mixite group (Hess, 1983; Mereiter & Preisinger, 1986; Aruga & Nakai, 1985; Miletich *et al.*, 1997): it is formed by infinite chains of edge sharing $Cu^{[4+1]}O_5$ pyramids, aligned parallel to [001] and linked to MO_9 polyhedra by edge-sharing. The framework is completed by PO_4 tetrahedra. Hexagonal channels along **c** host variable amounts of H_2O molecules. As reported by Miletich *et al.* (1997), non framework H_2O molecules have a zeolitic behavior and probably various degrees of hydration are possible.

The M cations (in the studied specimen, M = Ca, Y) are nine-fold-coordinated; the coordination polyhedron can be described as a tricapped trigonal prism. Cu^{2+} cations are coordinated by 4+1 oxygens, in a square-pyramidal coordination distorted by the Jahn-Teller effect.

Bond-valence balance, calculated according to Brese & O'Keeffe (1991), is reported in Table 4. The sum of bond-valence of the M site, calculates assuming a Ca:Y ratio equal to 60:40, is in agreement with a mixed occupancy by Ca^{2+} and Y^{3+}. Focusing the attention on the framework oxygens and in particular on their coordination geometries and bond-valence sums, it is clear that only O1 and O2 sites host hydroxyl groups, whereas O3, O4, and O5 sites are occupied by O^{2-} anions. The scrutiny of the interpolyhedral O⋯O distances suggests that O1⋯O2 and O2⋯O3 could correspond to hydrogen bonds, with bond distances of 2.765(14) and 2.889(10) Å, respectively (Fig. 2). The difference of bond valence sums between O1 and O2 (1.35 and 1.09 *v.u.*, respectively) suggests that the former is only a donor (O1–H ⋯O2), whereas O2 is both a donor (to O3) and an acceptor (from O1). O3

Tab. 2 - Atomic coordinates and equivalent or isotropic displacement parameters.						
Site	**Occupancy**	**Wyckoff multiplicity**	x	y	z	$U_{eq/iso}$
M	Y	2c	1/3	2/3	3/4	0.0170(14)
Cu	Cu	12i	0.5869(1)	0.9031(1)	0.9969(2)	0.0229(13)
X	P	6h	0.6568(4)	0.1501(4)	1/4	0.0158(16)
O1	O	6h	0.5559(9)	0.8026(9)	1/4	0.0301(31)
O2	O	6h	0.6351(8)	0.0119(9)	3/4	0.0198(29)
O3	O	12i	0.3868(6)	0.8204(6)	0.5331(12)	0.0195(22)
O4	O	6h	0.5816(9)	0.7943(8)	3/4	0.0202(28)
O5	O	6h	0.3889(8)	0.9849(9)	3/4	0.0216(29)
W1	$(H_2O)_{0.28}$	6h	0.111(8)	0.957(9)	3/4	0.16(5)
W2	$(H_2O)_{0.29}$	6h	0.149(8)	0.101(8)	3/4	0.16(3)
W3	$(H_2O)_{0.08}$	2b	0	0	0	0.16(3)

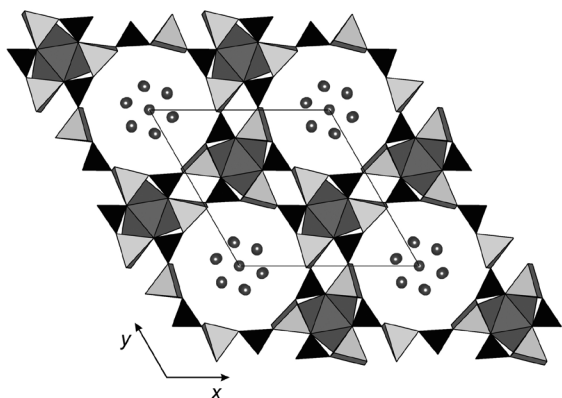| Tab. 3 - Selected atomic bond distances (in Å) for calciopetersite.					
M	- O3 (x 6)	2.430(7)	Cu	- O1	1.886(7)
	- O1 (x 3)	2.567(11)		- O2	1.903(7)
				- O5	1.997(7)
P	- O3 (x 2)	1.518(7)		- O4	2.009(7)
	- O5	1.570(12)		- O3	2.306(7)
	- O4	1.575(11)			

Fig. 1 - Crystal structure of calciopetersite, as seen down **c**. Grey: MO_9 polyhedra; Circles: H_2O molecules; light grey: CuO_5 pyramids; black: PO_4 tetrahedra.

has only a small deficiency in the bond valence sum, and it acts only as a hydrogen-bond acceptor. Due to the presence of a mirror plane, the O2–H:::O3/O3' is a bifurcated hydrogen bond; a simple O2–H···O3 bond would violate the required *m* symmetry. According to Miletich *et al.* (1997), the symmetry-breaking O2–H···O3 bonding could be possible in order to explain the substitution $(XO_4)^{3-}$ with $(XO_3OH)^{2-}$, required to balance the substitution $M^{3+} \rightarrow M^{2+}$, occurring also in calciopetersite. In fact, assuming the Ca:Y equal to 60:40, the balanced chemical formula of the sample from Monte Beni should be $(Ca_{0.60}Y_{0.40})$ $Cu_6[PO_3(OH_{0.60}O_{0.40})](OH)_6 \cdot nH_2O$. Consequently, in each phosphate tetrahedron, one O3 should be occupied by oxygen and the other should have a mixed occupancy by hydroxyl and oxygen. If a symmetrical hydrogen bond scheme is assumed (scheme 1 in Figure 2), O1 and O2 sites would be occupied by hydroxyl, with a good valence sum (1.15 and 0.97 *v.u.*, respectively), but O3 would be occupied by oxygen. On the contrary, if O2 is both acceptor and donor of hydrogen bonds, a second hydrogen bond scheme could be hypothesized (scheme 2 in Figure 2). In this case, the valence sum of O2 (1.29 *v.u.*) is a little higher than the expected values, whereas O3 has a valence sum of 1.90 and 1.58 *v.u.* Assuming the crystal-chemical formula proposed above, values of 2 and 1.40 *v.u.* could be expected, in agreement with the occupancy

by O^{2-} and $(OH^-_{0.6}O^{2-}_{0.4})$, respectively. Therefore, this second scheme seems to be preferable in order to take into account the occurrence of a mixed (OH, O) site in calciopetersite. This distribution should lower the symmetry from $P6_3/m$ to $P6_3$; however, a refinement in the $P6_3$ space group did not improve the *R* value, probably as a result of the disordered distribution, along **c**, of the hydrogen bonds.

The difference-Fourier maps showed the presence of maxima inside the tunnels; two maxima are located at (*x*,*y*,3/4), whereas the third is placed at the origin. These maxima were attributed to H_2O molecules. Hess (1983) found electron-density maxima on rings of approximately 2.7 Å in radius, whereas Aruga & Nakai (1985) located one H_2O site close to the origin; Mereiter & Preisinger (1986) described a maximum at $z = ¼$, and Miletich *et al.* (1997) reported five maxima, in a ring-like distribution, with some H_2O molecules at interatomic distances to framework-oxygen suitable for hydrogen bonding. In calciopetersite from Monte Beni, some hydrogen-bond distances between H_2O molecules were observed, whereas only very weak hydrogen bonds are possible with framework oxygens (W1···O4 = 3.06(9) Å; W2···O2 = 3.27(9) Å). In addition, the crystal structure refinement points to a low H_2O content, *i.e.* 0.65 H_2O *pfu*. Unfortunately, a direct determination of H_2O content in the studied sample was not possible. According to Miletich *et al.* (1997), the configuration of H_2O molecules within the channel is only related to the hydrogen bonds and the influence of these H_2O molecules onto the framework itself is probably small: these authors demonstrated experimentally that bond valences as well as the coordination geometries of the framework-oxygen atoms are very similar for the fully and partially hydrated structure of synthetic mixite. Consequently, H_2O content may be not so important for the stabilization of the crystal structure of this group of compounds.

DISCUSSION

After agardite-(Ce) and mixite, calciopetersite is the third mineral of the mixite group to be reported from Tuscany and the first phosphate of this group. The determination and refinement of its crystal structure confirm the identity with the As-members of this group. The origin of calciopetersite at Monte Beni is probably related to the leaching of chalcopyrite in an oxidizing and hydrous environment at a low temperature, during

Tab. 4 - Bond-valence balance (in valence unit) for intra-framework X-O bonds of calciopetersite, calculated according to Brese & O'Keeffe (1991).

	O1	O2	O3	O4	O5	Σν (X-O)
M	0.21[a]		0.30[b]			2.43
Cu	1.14[d]	1.09[d]	0.18	0.82[d]	0.85[d]	2.13
P			1.26[c]	1.08	1.10	4.70
Σν (O-X)	1.35	1.09	1.74	1.90	1.95	
Σν (O-X)*	1.15[1,2]	0.97[1] 1.29[2]	1.90[1] 1.90[2] 1.58[2]			

[a] (3 X →); [b] (6 X →); [c] (2 X →); [d] (0.5 X →).

* bond valence sum after correction for O···O bonds, according to Ferraris & Ivaldi (1988).

Note: the apexes 1 and 2 indicate the resulting bond-valence sums according to the hydrogen bond scheme 1 and 2 of Figure 2.
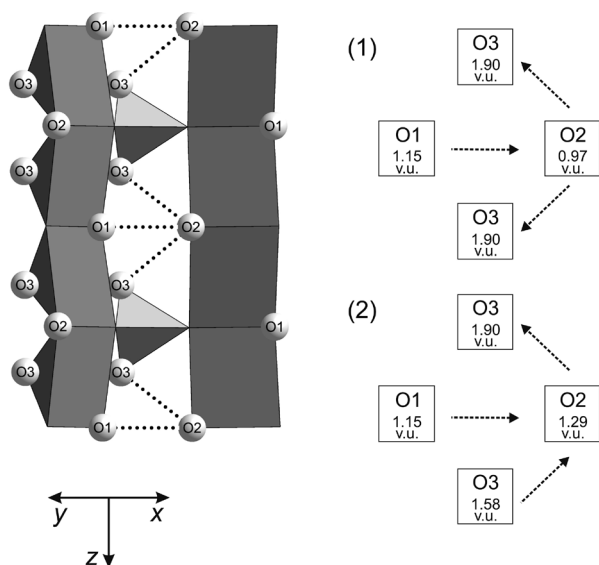

Fig. 2 - Hydrogen bonds in calciopetersite; two possible hydrogen-bond schemes are suggested.

weathering processes, in agreement with the genetic conditions of calciopetersite from the type locality (Sejkora *et al.*, 2005). The individual elements forming this phosphate were derived from chalcopyrite (Cu) and probably from «apatite» (Ca, P, Y, REE); this latter mineral has been identified in cumulitic layers, as white prismatic crystals, up to 5 mm, associated with magnetite and zircon, in a mineral assemblage similar to that described by Marinai & Nannoni (2003) in the Variante Quarry (Poggio Corbolone, Livorno). A similar genesis was suggested by Peacor & Dunn (1982) for petersite-(Y) from the type locality: the Cu derived from the alteration of chalcopyrite, whereas the source of P and REE was sought in «allanite» and «apatite», both identified in that locality.

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