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XIMENGITE, A NEW OCCURRENCE FROM APUAN ALPS (TUSCANY, ITALY)

Abstract - Ximengite is a very rare bismuth phosphate, formed through the alteration of Bi-bearing sulfides and sulfosalts. It was discovered in the tin mining district of the Ximeng County (Yunnan, China) in 1989. Recently this mineral species was also identified in the hydrothermal veins from Fornovolasco (Apuan Alps, Tuscany, Italy), in white earthy masses, associated with mimetite and bismutite, originated by the alteration of bismuth-bearing sulfides or sulfosalts.

Key words - Ximengite, bismuth phosphate, Fornovolasco, Apuan Alps.

Riassunto - Ximengite, nuovo ritrovamento sulle Alpi Apuane (Toscana, Italia). La ximengite è un rarissimo fosfato derivante dall'alterazione di solfuri e solfosali contenenti bismuto. Scoperto nel 1989 nel distretto minerario stannifero della Ximeng County (Yunnan, Cina), questa specie è stata recentemente identificata anche nelle vene idrotermali di Fornovolasco (Alpi Apuane, Toscana, Italia), in masserelle terrose bianche associate a mimetite e bismutite, derivanti dall'alterazione di solfuri o solfosali contenenti bismuto.

Parole chiave - Ximengite, fosfato di bismuto, Fornovolasco, Alpi Apuane.

INTRODUCTION

Three bismuth phosphates are known in nature, namely petitjeanite, $\text{Bi}_3\text{O}(\text{OH})(\text{PO}_4)_2$, smrkovecrite, $\text{Bi}_2\text{O}(\text{OH})(\text{PO}_4)$, and ximengite, $\text{Bi}(\text{PO}_4) \cdot 0.5\text{H}_2\text{O}$. These three mineral species are rare secondary products of alteration in Bi-bearing mineral assemblages. During the mineralogical studies carried on the magnetite-pyrite ore from Fornovolasco (Apuan Alps, Tuscany, Italy), ximengite was identified.

This mineral is very rare and was described by Shi (1989) from the Ximeng tin mining district, 420 km SW of Kunming, in the Chinese province of Yunnan. In this locality, ximengite is an alteration product of bismuthinite and it is associated with waylandite and «monazite», in a rock formed by cassiterite, «tourmaline», quartz, and K-feldspar. It forms veinlets or granular earthy aggregates, white or colorless; single grains are smaller than 0.1 mm. According to Shi (1989), the ideal formula of ximengite is anhydrous, $\text{Bi}(\text{PO}_4)$. In fact, TGA-DTA and infrared studies indicated that this mineral does not contain hydroxyl groups or structurally bound water. Comparison with X-ray powder data for the synthetic equivalent obtained by Mooney-Slater

(1962) indicates that ximengite is trigonal, space group $P3_121$, with a 6.9860, c 6.4753 Å.

Mooney-Slater (1962) reported the existence of three different modifications of the bismuth phosphate: two of them are stable at room temperature and are characterized by monoclinic (monazite-type structure) and trigonal symmetry, respectively. A third phase is stable only at high temperature (about 800°C). At room temperature, the synthesis of bismuth phosphate revealed that the product may be trigonal, monoclinic, or a mixture of the two phases, as a function of temperature and pH. Lower temperature and acidity favor the growth of the trigonal phase. Although Shi (1989) stated that ximengite is anhydrous, according to Mooney-Slater (1962) the trigonal bismuth phosphate may be hydrated. According to Romero *et al.* (1994), the molecular water hosted in the structural channels stabilizes the trigonal form and the dehydration induces the transformation to the monoclinic phase. The scrutiny of the crystal structure refined by these latter authors shows the presence of O...O distances lower than 3 Å, involving undersaturated oxygens, suggesting the existence of hydrogen bonds; consequently, the role of H_2O molecules may be important in stabilizing the crystal structure of ximengite that could not be anhydrous.

In addition to the type locality, ximengite was identified in the Variscan granitic pegmatites in Portugal, as an alteration product of Ag-Bi-Pb sulfosalts (Leal Gomes, 2010). On the web-site www.Mindat.org, ximengite is reported also from Eta-Etu (Kivu Province, Democratic Republic of Congo). Eta-Etu is the type locality of zaïrite, $\text{BiFe}^{3+}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$; in the type-description of this latter phosphate, Van Wambeke (1975) described the presence, in the same locality, of a probably new mineral species. Its qualitative chemical analysis showed only the presence of Bi and P; therefore, it could actually be ximengite.

The aim of this paper is the description of a new occurrence of this very rare mineral from the hydrothermal veins of Fornovolasco (Apuan Alps).

EXPERIMENTAL

Ximengite was identified in only one specimen found in the Fornovolasco mine (Apuan Alps). The identification was carried out by X-ray powder diffraction using a 114.6 mm Gandolfi camera with Ni-filtered $\text{CuK}\alpha$ radiation and qualitative EDS chemical analysis with a Phil-

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ips XL30 SEM, equipped with a EDAX DX4 system. The specimen was also used for the intensity data collection on a powder sample, using synchrotron radiation at the European Synchrotron Radiation Facility (ESRF) of Grenoble, France, using a wavelength $\lambda = 0.4135 \text{ \AA}$. Rietveld refinement was performed through the software TOPAS-Academic (Coelho, 2004); due to the coexistence of ximengite and bismutite in the studied sample, atomic coordinates of these two phases could not be refined, and the study involved only the refinement of profile and cell parameters.

XIMENGITE FROM FORNOVOLASCO (APUAN ALPS, TUSCANY)

Geological setting and mineralogical description

In the area of Fornovolasco, small magnetite-pyrite ore bodies were exploited since the 13th century up to the end of the 1970s. Veins and lenticular bodies of magnetite \pm pyrite \pm sphalerite \pm pyrrhotite \pm iron hydroxides are hosted at the contact between a metavolcanic-

metasedimentary sequence (*Scisti di Fornovolasco* Formation) and lenses of dolomitic marble of uncertain stratigraphic setting, known as «*Grezzone metallifero*» (Carmignani *et al.*, 1976; Tanelli, 1983; Ciarapica *et al.*, 1985; Pandeli *et al.*, 2004). Mineral assemblages were described by Biagioni *et al.* (2008) and Orlandi *et al.* (2008); Fornovolasco is the type-locality of volaschi-oite, an oxy-hydroxy iron sulfate (Biagioni *et al.*, 2011). The specimen containing ximengite is kept in the collection of the *Museo di Storia Naturale e del Territorio* of the Pisa University, under the catalog number 19359. This specimen was found in the quartz \pm K-feldspar \pm albite \pm carbonates veins, embedded in phyllites and tourmaline-rich schists, in the Ribasso Ing. Cortese tunnel (level 675 m). Ximengite occurs as earthy white millimeter-sized masses, associated with yellow prismatic crystals of mimetite, as alteration product of prismatic crystals of a bismuth-bearing sulfide or sulfosalt. In the same occurrence, beyerite $(\text{Ca,Pb})\text{Bi}_2(\text{CO}_3)_2\text{O}_2$, and bismutite $(\text{BiO}_2)\text{CO}_3$, were identified. Table 1 reports the X-ray powder diffraction lines of the ximengite from Fornovolasco collected with the Gandolfi camera.

Tab. 1 - X-ray powder diffraction pattern of ximengite from Fornovolasco.

Fornovolasco mine (this work)		Ximeng County, China (Shi, 1989)		JCPDS 15-766		
d_{hkl}	I_{hkl}	d_{hkl}	I_{hkl}	d_{hkl}	I_{hkl}	$h k l$
6.04	mw	6.052	73	6.06	65	1 0 0
4.44	m	4.4198	91	4.421	100	1 0 1
3.505	mw	3.4930	88	3.494	45	1 1 0
		3.0724	34	3.073	45	1 1 1
3.035	s	3.0244	100	3.025	95	2 0 0
2.858	m	2.8537	65	2.854	80	1 0 2
2.389	mw	2.3738	8	2.375	30	1 1 2
2.293	w	2.2850	6	2.286	12	2 1 0
2.190	w	2.2090	3	2.211	6	2 0 2
2.164	m	2.1573	47	2.156	60	2 1 1
2.043	w	2.0304	12	2.032	6	1 0 3
		2.0197	2	2.016	4	3 0 0
1.935	mw	1.9268	16	1.925	20	3 0 1
1.879	m	1.8683	45	1.867	50	2 1 2
		1.8368	10	1.837	6	1 1 3
1.762	mw	1.7572	10	1.7571	25	2 0 3
		1.7474	48	1.7452	16	2 2 0
1.715	w	1.7114	19	1.7115	20	3 0 2
1.682	vw	1.6752	10	1.6774	12	3 1 0
1.636	w	1.6216	13	1.6239	12	3 1 1
		1.5720	0	1.5693	6	2 1 3
1.571	w	1.5639	16	1.5644	12	1 0 4
		1.5387	3	1.5368	6	2 2 2
		1.5139	2	1.5118	6	4 0 0

Note: intensity were visually estimated. s: strong; m: medium; mw: medium-weak; w: weak; vw: very weak.

The qualitative EDS chemical analysis showed the presence of Bi, P, and minor As, as the only elements with $Z > 9$. Arsenic could partially replace phosphorus in tetrahedral coordination and it may be the reason for the cell parameters slightly greater than those of the ximengite from China. Due to the very limited amount of available material and its admixture with other phases (in particular bismutite), no data were collected concerning the water content of ximengite.

Rietveld analysis

The collected powder pattern showed the coexistence of ximengite and bismutite, with an estimated ratio 1:1 in the studied specimen. Trials were made to refine powder data with the ximengite and bismutite structural models given by Romero *et al.* (1994) and Grice (2002) respectively. The Rietveld refinement allowed to exclude the presence of the monoclinic dimorph of ximengite that, in some synthetic preparations, was observed together with the trigonal phase. For ximengite and bismutite, a Pawley refinement (Pawley, 1981) was initially performed, to get starting values for background, cell parameters, asymmetry, and peak shapes. A zero shift was refined, and the background was modeled with a 4-terms Chebyshev function. As written above, due to the coexistence of two different phases, atomic coordinates of ximengite and bismutite could not be refined, and the study involved only the refinement of profile and cell parameters. The refined cell parameters of ximengite are a 7.0197(6), c 6.4919(7)

Å, space group $P3_121$; these parameters are slightly greater than those of ximengite from the type locality, probably as a consequence of the substitution $P^{5+} \rightarrow As^{5+}$, suggested by the EDS chemical analysis. The cell constants of bismutite are a 3.8809(6), b 3.8954(6), c 13.800(1) Å, space group $Imm2$; also in this case, the cell parameters are slightly larger than those reported in literature (Grice, 2002). Figure 1 shows the results of observed (dotted lines), calculated (full line), and difference X-ray profiles for the studied sample.

DISCUSSION

The described occurrence of ximengite, bismutite, and beyerite in the hydrothermal veins from Fornovolasco is the first reported occurrence of bismuth secondary minerals in the Apuan Alps. Mooney-Slater (1962) observed that the trigonal bismuth phosphate was stable in low-temperature and low pH conditions; the occurrence of ximengite in the hydrothermal veins from Fornovolasco is in agreement with these environmental conditions and it is related to the alteration of Bi-bearing sulfides and/or sulfosalts. As stated in Orlandi *et al.* (2010), these mineral species are rather rare in the ores from the metamorphic complex of Apuan Alps; up to now, only seven bismuth minerals were reported from this area. In the vein systems from the Ribasso Ing. Cortese tunnel (Fornovolasco mine), some acicular Pb-Sb-(Bi) sulfosalts were identified; in particular,

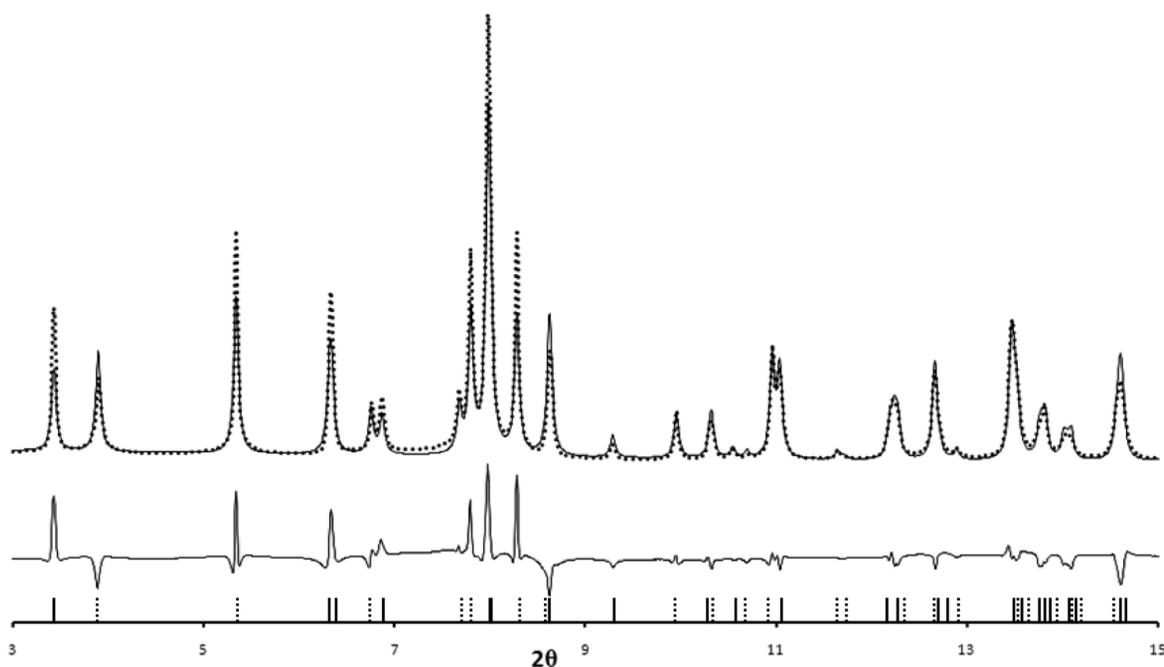


Fig. 1 - Observed (dotted line), calculated (full line), and difference X-ray profiles for the studied sample. In the 2θ axis, full lines indicate the position of the reflections of bismutite, whereas the dotted ones are related to ximengite.

the occurrence of jaskólskiite, $\text{Cu}_x\text{Pb}_{2+x}(\text{Sb,Bi})_{2-x}\text{S}_5$, has been reported (Biagioni *et al.*, 2008). Ximengite and bismutite usually occurs as pseudomorphs after acicular striated crystals, included in the quartz veins; the primary pseudomorphosed phase is still unknown and a more detailed study upon this sulfosalt assemblage is necessary to ascertain the actual nature of this phase.

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