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CRYSTAL-CHEMISTRY OF SECONDARY MINERALS OF THALLIUM-RICH PYRITE ORES FROM THE APUAN ALPS (TUSCANY, ITALY)

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INTRODUCTION

A mineralogical and crystal-chemical study of several secondary minerals formed throught the weathering of the pyrite ore deposits occurring in the southern sector of the Apuan Alps (Tuscany, Italy) was carried out. In the last decade, the discovery of the thallium-rich nature of these pyrite ores posed several concerns about their potential environmental impact (Biagioni *et al*., 2013; George *et al*., 2018). Indeed, pyrite oxidation can release acids, toxic and heavy metals with negative effects for environment and living organisms. In this framework, secondary minerals can play a key role in storing and releasing acidity and environmentally critical elements through dissolution during the wet season (*e.g*., Jerz & Rimstidt, 2003).

The occurrence of secondary minerals related to the oxidation of the pyrite ores from the Apuan Alps has been known since the second half of the 19th Century when D'Achiardi (1872) reported the occurrence of alum-(K), gypsum, halotrichite, and melanterite, as well as the doubtful identification of coquimbite and goslarite. More than one Century later, Orlandi & Dini (2004) described the occurrence of diadochite, an amorphous iron phosphate-sulfate from the Buca della Vena mine. Later, Biagioni (2009) critically re-examined the description reported by the latter authors and, taking into account the crystalline nature of this phases, attributed the name destinezite to these samples. More data on a few number of mineral species from Buca della Vena, *i.e*., copiapite, gypsum, and melanterite, was reported by Biagioni (2009). In the last decade the finding of some sulfate piles at the Fornovolasco mine allowed the description of some very common sulfates (*i.e*., copiapite, halotrichite, melanterite, römerite, and voltaite; Biagioni *et al*., 2008) as well as the discovery of the new mineral species volaschioite, $Fe^{3+}_4(SO_4)O_2(OH)_6{\cdot}2H_2O$ (Biagioni *et al.,* 2011). Finally, an updated list of the sulfates occurring in this locality was provided by Mauro (2016).

Among the several localities from the Apuan Alps where pyrite ores were exploited, only three of them have been investigated in this work, *i.e*., Fornovolasco, Buca della Vena, and Monte Arsiccio, owing to the presence of several well-crystallized secondary minerals. In these localities, twenty-five mineral species (Table 1) have been identified so far; eight of them, showing interesting crystal-chemical features, were studied using a multi-technique approach involving X-ray diffraction (both single-crystal and powder techniques), EDS and WDS chemical analyses, as well as several spectroscopic techniques, *i.e*., micro-Raman, Fourier-Transform Infrared (FTIR), Mössbauer, and X-ray Absorption Spectroscopy (XAS).

This works aims at providing a full set of mineralogical and crystal-chemical data of the secondary minerals sampled but also at improving our understanding on their role as scavengers of toxic and heavy metals from the environment.

FORNOVOLASCO

The re-examination of the sulfate piles from Fornovolasco allowed the investigation of a Mg-rich sulfate assemblage. This pile is mainly formed by epsomite and an intermediate member of the series halotrichite/pickeringite, associated with minor melanterite, magnesiocopiapite, and wilcoxite. Single-crystal X-ray diffraction studies were carried out on epsomite and wilcoxite only. Epsomite, ideally $Mg(H_2O)_6SO_4{\cdot}H_2O$, occurs as equant anhedral or prismatic to acicular colorless crystals, in some cases up to 3 cm long. Its origin is likely related to the interaction between H_2SO_4 and metadolostone hosting the pyrite ores. The sample from

Fornovolasco allowed the first high-quality refinement on natural material, confirming the structural features previously reported for synthetic analogues (Mauro *et al.*, 2019a).

Table 1- Mineral species identified in the studied localities.

Mineral species	BdV	For	MA	Mineral species	BdV	For	MA
Alum-(K)		×	×	**Khademite**			×
Alunogen		×	×	Krausite		×	×
Bohuslavite	×			Magnanelliite			×
Copiapite	×	×	×	Magnesiocopiapite		×	
Coquimbite		×	×	Magnesiovoltaite		×	
Destinezite	×		×	Melanterite	×	×	×
Epsomite		×	×	Pickeringite		×	
Fibroferrite		×		Rhomboclase		×	
Giacovazzoite			×	Römerite		×	×
Goldichite			×	Scordariite			×
Gypsum	×	×	×	**Voltaite**		×	×
Halotrichite		×	×	**Wilcoxite**		×	
Jarosite	×	×	×				

Mineral species discussed in this work are shown in bold.
Note: BdV = Buca della Vena; For = Fornovolasco; MA = Monte Arsiccio.

Closely associated with epsomite, wilcoxite, $MgAl(SO_4)_2F(H_2O)_{11}\cdot6H_2O$, is a rare fluo-sulfate occurring at Fornovolasco as triclinic whitish individuals, up to 3 mm across. Its crystal-chemical study allowed a better understanding of its H-bond system, refining the data reported by previous studies (Mauro *et al.*, 2019a).

A pair of interesting sulfates is represented by alum-(K) and voltaite (Biagioni *et al.*, 2020a). Alum-(K), ideally $KAl(SO_4)_2(H_2O)_{12}$, occurs as colorless grains or, rarely, as mm-sized octahedra (Fig. 1a).

Fig. 1 - Selected images of some sulfate minerals from the Apuan Alps. a) Alum-(K), colorless octahedral crystals associated with römerite and halotrichite. Fornovolasco mine. b) Bohuslavite, lilac globular aggregates with colorless gypsum. Buca della Vena mine. c) Khademite, colorless tabular crystals associated with krausite, römerite, and coquimbite. Monte Arsiccio mine. d) Giacovazzoite, orange prismatic crystals associated with krausite and scordariite. Monte Arsiccio mine.

Crystal-chemical data suggested a more complex chemistry than the ideal one. Indeed, a higher unit-cell volume and a higher degree of structural disorder of the SO_4 tetrahedra, related to the size of the cations hosted at the K site, were observed. These data agreed with the chemical and spectroscopic (XAS, FTIR) data, showing a substitution of K^+ by Tl^+ and NH_4^+ at the K site. Voltaite, ideally $K_2Fe^{2+}_5Fe^{3+}_3Al(SO_4)_{12}(H_2O)_{18}$, occurs as dark green {100} crystals, with minor {111} and {110} forms, up to 1 mm in size. Backscattered electron images and X-ray maps of these samples showed a very complex crystal-chemistry, with a strong chemical zoning and an enrichment in Tl^+ and, in some cases, also in Mn. In addition, the occurrence of N was detected during the electron microprobe analyses but not quantified. Accordingly, the FTIR data revealed the occurrence of the bending mode related to the H–N–H bending mode of NH_4^+, with a band at 1428 cm^{-1}. It is worth noting to underline that an enrichment of K and Tl from the core to the rim was observed. Owing to this distribution of Tl, it is likely that a partial dissolution of Tl-bearing voltaite from Fornovolasco may be sufficient to release high amounts of this element in the hydrosphere.

BUCA DELLA VENA

During the study of several sample of diadochite from Buca della Vena, the new mineral species bohuslavite was identified (Mauro *et al.*, 2019b). This species, ideally $Fe^{3+}_4(PO_4)_3(SO_4)(OH)(H_2O)_{10}\cdot nH_2O$ ($5 < n < 14$), occurs as globular aggregates formed by thin tabular pseudohexagonal crystals, pink to lilac in color, up to 1 mm in size (Fig. 1b). The morphology of the crystals reflects the pseudohexagonal nature of the unit-cell parameters obtained by single-crystal X-ray diffraction. Bohuslavite is triclinic, space group $P\text{-}1$, with the following unit-cell parameters: $a = 13.376(3)$ Å, $b = 13.338(3)$ Å, $c = 10.863(4)$ Å, $\alpha = 92.80(2)°$, $\beta = 91.03(2)°$, $\gamma = 119.92(2)°$, $V = 1675.7(9)$ Å^3. Bohuslavite shows a novel crystal structure, characterized by {001} heteropolyhedral layers, with composition $[Fe_4(PO_4)_3O(OH)(H_2O)_{10}]$, and channels hosting H_2O groups. The layers are decorated, on both sides, by SO_4 groups. Additional H_2O groups are hosted in the interlayer. Owing to the low quality of the available crystals, the collection of data from independent techniques (X-ray diffraction, WDS analysis, thermogravimetry, Mössbauer, micro-Raman and FTIR spectroscopies) was mandatory in order to provide a full characterization of this new phase. The mineral and its name, honoring the Czech mineralogist Bohuslav Fojt (b. 1928), have been accepted by the Commission on New Minerals, Nomenclature, and Classification, of the International Mineralogical Association (IMA-CNMNC). Its origin is likely related to the interaction between sulfuric acid, released during pyrite oxidation, and phosphate minerals occurring in host rocks.

MONTE ARSICCIO

Since the end of the 2000s, the mineralogy of the Monte Arsiccio mine has been investigated, showing the occurrence of several rare mineral species. Recently, the mineralogical studies carried out on this locality allowed the finding of a complex sulfate assemblage in an old mining stope. The main phases are alum-(K), alunogen, halotrichite, melanterite, römerite, and voltaite. Accessory phases are copiapite, coquimbite, khademite, and several potassium-ferric iron sulfates, *i.e.*, giacovazzoite, goldichite, jarosite, krausite, magnanelliite, and scordariite. It is worth noting that among the K-Fe-bearing sulfates currently known to the scientific community, all them were identified in this locality, the only exception being yavapaiite, $KFe^{3+}(SO_4)_2$, that has not yet been found here. Moreover, three out of them are new for science: giacovazzoite, magnanelliite, and scordariite. Mineralogical studies performed on the sulfate assemblage occurring in this locality have allowed to identify eighteen sulfate species so far. In the framework of the present study, full sets of crystal-chemical data were collected on alum-(K), voltaite, coquimbite, khademite, and giacovazzoite. Our attention was focused on these phases for some reasons: *i*) to assess the occurrence of Tl in K-sulfates; *ii*) to clarify the occurrence and the role played by Al in the crystal-structure of coquimbite, *iii*) to report a full set of crystal-chemical and micro-Raman data on khademite; *iv*) to describe the new mineral species, giacovazzoite. Alum-(K) occurs as colorless crystalline granular masses or as crude colorless {111} crystals, up to 1 mm across, whereas voltaite has been observed as

{100} to {111} crystals, up to 2 cm in size. The crystal-chemical data collected on these K-bearing minerals revealed a chemistry close to the ideal one. Indeed, no other elements than K, Al, and S for alum-(K), K, Fe, Al, and S for voltaite were found above the detection limits.

World-class specimens of coquimbite, $AlFe_3(SO_4)_6(H_2O)_{12}\cdot6H_2O$, occur in this assemblage, as violet pseudohexagonal crystals, up to 3 cm in diameter, associated with römerite, halotrichite, krausite, khademite, and alum-(K) (Mauro *et al.*, 2020a). Its structural features fully agree with those reported by previous authors, confirming the occurrence of an Al-centered octahedron in its crystal structure. Curiously, coquimbite was previously reported as an Al-free, hydrated Fe sulfate. Based on the critical examination of literature and taking into account the new data collected on the Monte Arsiccio's specimen, coquimbite was officially redefined as an Al-Fe hydrated sulfate by the IMA-CNMNC (Mauro *et al.*, 2020a).

An uncommon sulfate species found at Monte Arsiccio is khademite, $Al(SO_4)F(H_2O)_5$. This finding represents the first Italian occurrence for this species. It occurs as tabular colorless to whitish crystals, up to 5 mm in size, associated with krausite, halotrichite, and coquimbite (Fig. 1c). The high quality of the available material allowed to improve the knowledge of the crystal-chemistry of khademite and of its Raman spectroscopic features, reporting the first spectrum collected on a well-characterized sample (Mauro *et al.*, 2020b).

A new addition to sulfate systematic is represented by giacovazzoite, $K_5[Fe^{3+}_3O(SO_4)_6(H_2O)_9]\cdot H_2O$ (Fig. 1d). This mineral has been identified as orange-brown prismatic crystals, up to 1 mm in size, associated with alum-(K), magnanelliite and scordariite. Its genesis could be related to the decomposition of Fe-bearing alum-(K), in agreement with previous works on synthetic materials (Mereiter & Völlenkle, 1978). Giacovazzoite is monoclinic, space group $P2_1/c$, with unit-cell parameters a = 9.4797(2), b = 18.4454(5), c = 18.0540(4) Å, β = 92.626(2)°, V = 3153.55(13) Å^3. The X-ray diffraction and chemical data indicated its identity with the synthetic β-Maus's salt; such an isotypic relationship was confirmed through crystal structure refinement. Its crystal structure can be described as a bipartite structure formed by a structural unit, represented by a $[Fe^{3+}_3O(SO_4)_6(H_2O)_3]^{5-}$ heteropolyhedral cluster, and by an interstitial complex, having composition $\{K_5(H_2O)_7\}^{5+}$, which balances the negative charge of the structural unit and link together the heteropolyhedral clusters. The mineral and its name, honoring the crystallographer Carmelo Giacovazzo (b. 1940), have been approved by the IMA-CNMNC (Biagioni *et al.*, 2020b).

CONCLUSIONS

The current study is the first contribution focused on the sulfate mineralogy of the pyrite ore deposits from the Apuan Alps. In this way, an improvement of our knowledge of the secondary assemblages deriving from pyrite oxidation was achieved, representing a further step in assessing the environmental significance of these assemblages. In addition, this research contributed to mineral systematics through the description of two new mineral species (bohuslavite and giacovazzoite), showing the wide variability of genetic conditions and the structural complexity of sulfate minerals.

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