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Crystal-chemistry of the secondary minerals of the thallium-rich pyrite ores from the Apuan Alps (Tuscany, Italy)

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The mineralogy of secondary assemblages deriving from the alteration of pyrite ore deposits from the southern sector of the Apuan Alps (Tuscany, Italy) has been investigated. Twenty-five mineral species have been identified so far; among them, eight, showing interesting crystal-chemical features, were fully characterized using X-ray diffraction, chemical analyses, and spectroscopic techniques [1]. The structural description of some previously known minerals (epsomite, wilcoxite, coquimbite, khademite, alum-(K), and voltaite) allowed to improve our knowledge about H-bond systems in sulfates and to assess their role in hosting potentially toxic elements. Moreover, this study permitted the identification of two new mineral species, giacovazzoite, $K_5Fe_3^{3+}O(SO_4)_6(H_2O)_9 \cdot H_2O$, from the Monte Arsiccio mine, and bohusslavite, $Fe_4^{3+}(PO_4)_3(SO_4)(OH)(H_2O)_{10} \cdot nH_2O$ ($5 < n < 24$), from the Buca della Vena mine [2, 3].

Giacovazzoite (Figure 1) is the natural counterpart of the β -Maus' Salt. It is monoclinic, space group $P2_1/c$, with $a = 9.48$, $b = 18.44$, $c = 18.05$ Å, $\beta = 92.6^\circ$, $V = 3153.6$ Å³. Its crystal structure is characterized by a heteropolyhedral $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ cluster and by an interstitial complex with composition $[K_5(H_2O)_7]^{5+}$. The heteropolyhedral cluster is known in other minerals (metavoltine, scordariite, carlsonite) as well as in some synthetic compounds.

Bohusslavite (Figure 1) is triclinic pseudo-hexagonal, space group P-1, with unit-cell parameters $a = 13.38$, $b = 13.34$, $c = 10.86$ Å, $\alpha = 92.8$, $\beta = 91.0$, $\gamma = 119.9^\circ$, $V = 1675.7$ Å³. This mineral can be considered a new kind of microporous compound, with heteropolyhedral layers with composition $[Fe_4^{3+}(PO_4)_3O(OH)(H_2O)_{10}]$, decorated on both sides by SO_4 groups. Additional H_2O groups are hosted in channels running along c as well as in the interlayers.

This work stressed the complexity of sulfates, improving the knowledge of their systematics.

[1] C. Biagioni, D. Mauro, M. Pasero Minerals. 2020, 10, 1092.

[2] C. Biagioni, L. Bindi, D. Mauro, M. Pasero Phys Chem Miner. 2020, 47, 7.

[3] D. Mauro, C. Biagioni, E. Bonaccorsi, U. Hålenius, M. Pasero, H. Skogby, F. Zaccarini, J. Sejkora, J. Plášil, A.R. Kampf, J. Filip, P. Novotný, R. Škoda, T. Witzke Eur J Mineral, 2019, 31, 1033.

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