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Introduction

Cultural heritage when involving geological mining patrimony could carry a vast scientific knowledge, namely about iron sulphates formed in abandoned sulphide-ore mines. The variety of waste materials that resulted from the mining activity through the ages usually are dispersed along the mine, resulting in the occurrence of acidic drainage (AMD).

The geochemical behaviour of secondary iron sulphates, more or less hydrated, is strongly conditioned by their crystal structure, e.g. jarosite. The knowledge of these materials is particularly important in what concerns preservation strategies of mining heritage.

With the purpose of further exploring the positive geo-environmental contributions of secondary iron sulphates, a summary is presented on the crystal chemistry and on the geochemical tendencies of jarosites *s.l.*, copiapite and voltaite, susceptible of being developed to enhance their environmental role in the context of old mines in the Iberian Pyrite Belt (IPB), southern Portugal, e.g. São Domingos and Aljustrel (Figs. 1-3) [1,2].

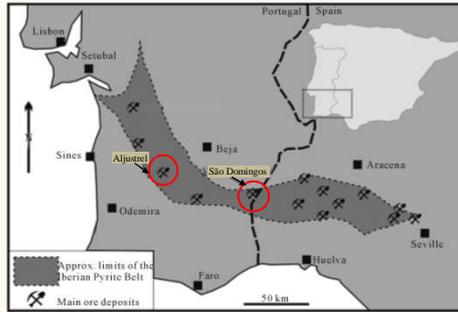


Fig. 1 - Location of the mining sites of São Domingos and Aljustrel in the IPB.

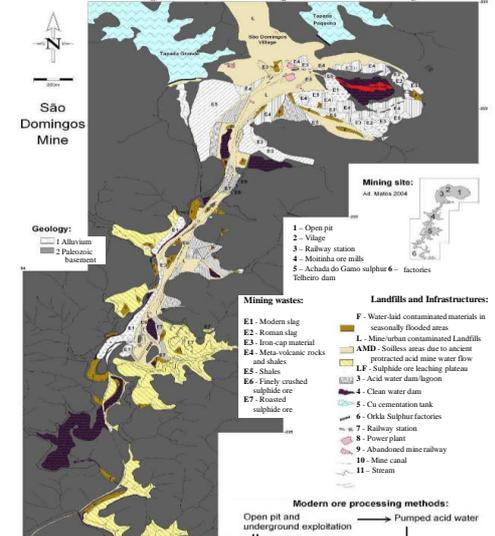


Fig. 2 - Simplified mining map of São Domingos mine (after [3,4]).

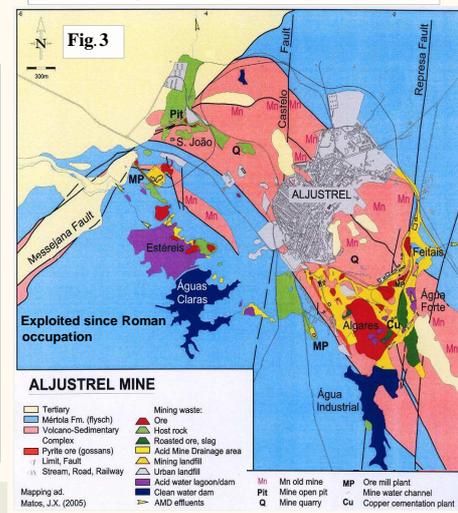


Fig. 3 - Geological map of the Aljustrel mine area.

Structural formula of Jarosite-group minerals



- T (tetrahedral t) = S^{6+} , P^{5+} , As^{5+} or Sb^{5+} and other small ions
- A (icosahedral ic) = K^+ , Na^+ , NH_4^+ , Ag^+ , Tl^+ , Pb^{2+} , Bi^{3+} , H_3O^+ , minor Ca^{2+} , Sr^{2+} , Ba^{2+} , REE (Eu³⁺)
- B (octahedral o) = Fe^{3+} (jarosite *s.s.*) or Al^{3+} (alunite *s.s.*) and V^{5+} , plus minor Fe^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+}

Kagomé-type layer of [Fe/AlO₂(OH)] octahedra // (0001)

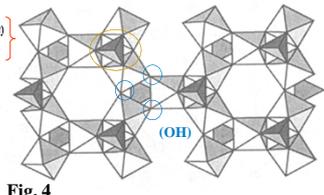


Fig. 4

Jarosite, copiapite and voltaite

Jarosites (*s.l.*) - with general formula $AB_2(OH)_4(SO_4)_2$ (Fig. 4), where **A** is mainly K^+ , Na^+ , plus minor Ag^+ , Tl^+ , NH_4^+ , Pb^{2+} , Bi^{3+} , and **B** is essentially Fe^{3+} (jarosite *s.s.*) or Al^{3+} (alunite) - have a trigonal crystal structure [5] and display Kagomé-type layers of corner-sharing **B** octahedra, [Fe/AlO₂(OH)]₄, that give rise to unique magnetic properties [6]; the large cation **A** stays in pseudo-icosahedral coordination by 6 O-atoms from [SO₄] tetrahedra and 6 hydroxyls shared with **A** octahedra [7].

Frequently found in the oxidized part of sulphide ore deposits, jarosite configures the ultimate sink of Ag and it transiently sequesters hazardous metals, Pb and Tl, reducing their environmental spread in rivers and soils.

Similarly, copiapite - $MFe_4(OH)_2(SO_4)_6 \cdot 20H_2O$, where **M** is a divalent metal (Fig. 5) - efficiently retains other toxic metals (namely, Cd). The crystal structures of these Fe-sulphates display a variety of cation coordinations, suitable to comply with diversified cations size and energetics (bonds).

Another notable iron sulphate is voltaite, $K_2Fe^{II}_2Fe^{III}_4(SO_4)_{12} \cdot 18H_2O$. This highly symmetric mineral has an unusually large cubic unit cell (Fig. 6) and displays an important capacity of retaining hazardous elements beyond metals (namely, As) and a unique potentiality to nest micro-organisms in its crystal surface due to the occurrence of large cavities in the structure.

Fig. 5 - COPIAPITE CRYSTAL STRUCTURE

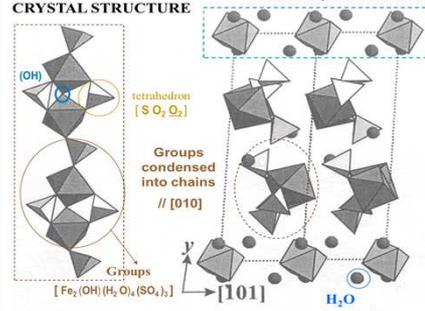


Fig. 5 - COPIAPITE CRYSTAL STRUCTURE

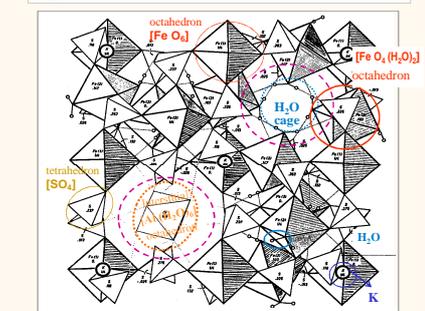


Fig. 6 - VOLTAITE CRYSTAL STRUCTURE

Table 1 - Secondary iron sulphates : comparative structural data

[Fe ^x X ₄]		[S ⁶⁺ O ₄]		Mineral		
[Fe ²⁺ O ₄]	[Fe ³⁺ O ₄]	[S ⁶⁺ O ₄]	[S ⁶⁺ O ₄]	Name	Chemical formula	Fe/(H ₂ O) ratio
1	1	1	1	MELANTERITE	Fe ^{II} (SO ₄) · 7 H ₂ O	0.14
2	1	1	4	RÖMÉRITE	Fe ^{II} Fe ^{III} ₂ (SO ₄) ₄ · 14 H ₂ O	0.21
1	2	1	6	COQUIBITE	Fe ^{II} ₂ (SO ₄) ₂ · 9 H ₂ O	0.22
1	2	1	3	COPIAPITE <i>s.s.</i>	Fe ^{II} Fe ^{III} ₂ (OH) ₂ (SO ₄) ₆ · 20H ₂ O	0.25
2	6	1	12	VOLTAITE	K ₂ Fe ^{II} ₂ Fe ^{III} ₄ (SO ₄) ₁₂ · 18H ₂ O	0.50
		3	2	JAROSITE	K Fe ^{III} ₃ (OH) ₆ (SO ₄) ₂	—

Jarosite retains Pb in mine wastes & tailings

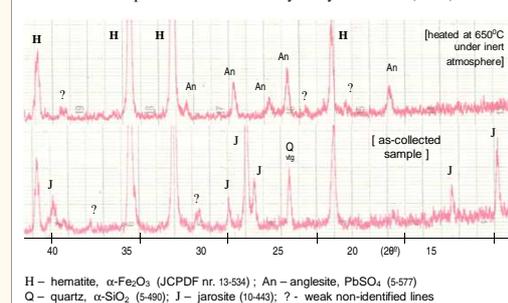


Fig. 7 - Jarosite retains Pb in mine wastes & tailings

References

- [1] J.X. Matos (2004) Carta geológico-mineira de S. Domingos, escala 1/5000, IGM.
- [2] J.X. Matos (2005) Carta geológica e mineira da Mina de Aljustrel, escala 1/5000, INETL.
- [3] J.X. Matos, Z. Pereira, M.J. Batista, D. De Oliveira (2012) São Domingos mining site - Iberian Pyrite Belt, in: Book of Abstracts of 9th Int. Symp. Environm. Geochem., 7-12.
- [4] A. Mateus, A. Pinto, L.C. Alves, J.X. Matos, J. Figueiras, N. Neng (2011) Roman and modern slag at S. Domingos mine (IPB, Portugal): compositional features and implications for their long-term stability and potential re-use. *Int. J. Environ. and Waste Management*, **8**, 133-159.
- [5] B. Hendricks (1937) The crystal structure of alunite and jarosite. *Amer. Inst. Min. Metallurg. Engr. Technical Publ.*, **22**, 773-784.
- [6] A.S. Wills, A. Harrison, C. Ritter, R.I. Smith (2000) Magnetic properties of pure and diamagnetically doped jarosites: model kagomé antiferromagnets with variable coverage of the magnetic lattice. *Phys. Rev. B*, **61**, 6156-6169.
- [7] S. Menchetti, C. Sabelli (1976) Crystal chemistry of alunite series: crystal structure refinement of alunite and synthetic jarosite. *Neues Jahrb. Miner. Monatsch. Heft*, **9**, 406-417.
- [8] M.O. Figueiredo, T. P. Silva, J. Mirão (2006) Mineralogy of the secondary iron sulphates: an environmental approach related to the abandoned mine of São Domingos (in Portuguese), in: *Abst. Book of VII Congr. Nac. Geologia*, 475-478.

Acknowledgments

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Results and Discussion

Iron-sulphate minerals contain a variety of cation polyhedra (Table 1) and an important factor is the remarkable chemical amplitude of the morphotropic domain covered by some of these sulphates (e.g., jarosite/alunite group) that stems from the atomic arrangement of their crystal structures.

The microchemical study by X-ray diffraction (XRD) and X-ray fluorescence spectrometry (XRF) performed on materials collected in São Domingos and Aljustrel mine tailings showed preferential retention of lead in jarosite-rich wastes [8]. Indeed, an As- and Pb-rich coarse roasted material - mineralogically characterized before and after heating at 650° C (Fig. 7) - showed the transformation of Pb-jarosite into anglesite (PbSO₄) plus hematite (α-Fe₂O₃).

Despite the negative connotation usually associated to the secondary iron sulphates formed by acid mine drainage (AMD) in abandoned mines of polymetallic sulphide ores, some minerals could have a positive behaviour.

Indeed, because these newly formed nanoparticulate minerals are intensively surface-active, they may retain heavy metals and other toxic elements, either by adsorption or through a diadochic replacement of basic chemical constituents.