

## SECONDARY IRON SULPHATES in AMD: a microchemical analysis on JAROSITE supporting the valorization of its geoenvironmental contribution

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### Introduction

Secondary iron sulphates formed in abandoned polymetallic sulphide-ore mines have a negative connotation within acid mine drainage (AMD) once usually these secondary hydroxylated and/or hydrated minerals concentrate a large span of toxic elements. However, this penalizing feature may occasionally turn out to be a very positive environmental contribution because sequestering toxic elements in stable minerals – e.g., *jarosite* – significantly reduces their spread in soils and rivers. The application of an energetic analysis to sustainability assessment provides an useful means of evaluating the degradation of mineral resources (fig. 1) and a recent *exergetic life cycle assessment* (ELCA) focused on jarosite [1] has emphasized the positive role of this mineral.

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

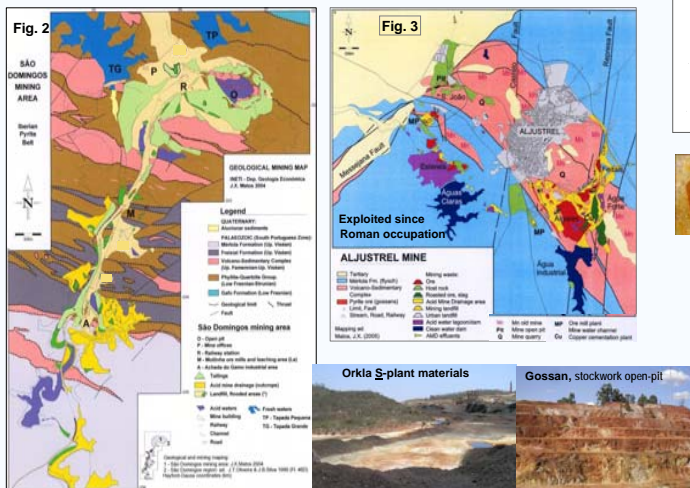
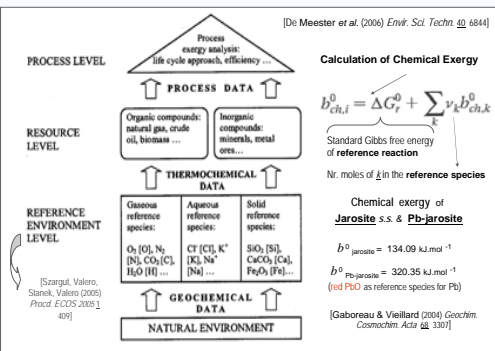


Fig. 1 – Scheme for calculating the chemical exergy of resources in a life cycle assessment of processes



### References

[1] M.O. FIGUEIREDO, T.P. SILVA & J. MIRÃO (2007) How does the uptake of lead along acid mine drainage processes affect the chemical exergy of jarosite in exergetic life cycle assessment (ELCA)? *IEEES-3.3<sup>rd</sup> Int. Energy, Exergy & Environ. Symp.*, Evora/ Portugal, Extend. Abstr. (4p.), CD-ROM, ISBN: 978-989-95091-1-5.

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[3] ----- (2005) Carta geológica e mineira da Mina de Aljustrel, esc. 1/5000, INETI.

[4] R. BALLOU, B. CANALS, M. ELHAJAL, C. LACROIX & A.S. WILLS (2003) Models for ordering in the jarosites Kagomé systems. *J. Magnetism & Magnet. Mat.* 262: 465.

### Problematic

*Jarosite s.s.* – ideally  $KFe_3(OH)_6(SO_4)_2$  – is a common secondary iron sulphate in AMD environments with high potassium content. This mineral is not only *environmentally important* because it may configure the *ultimate mineral sink* of *hazardous metals* (namely lead and thallium), beyond silver, but it is also economically relevant within various *hydrometallurgical routes*.

Besides, the *2D Kagomé-pattern* of iron octahedra in the crystal structure (fig.4) awards unique magnetic properties to jarosite. The octahedral crystal field stabilizes *high spin-state ferric ions*, and this peculiar undistorted triangular motif, with fully occupied magnetic sites and weak interlayer coupling, renders this mineral a paradigmatic *Kagomé Heisenberg Anti-Ferromagnet* [4]. These characteristics are possibly related to the interaction with *microbial communities* in AMD eco-systems (fig.5), thus giving a positive contribution to the currently ongoing biogenically-driven processes [5] and enhancing the environmentally constructive role of secondary iron sulphates.

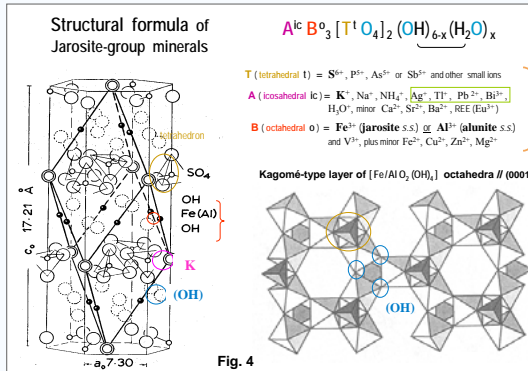
It is also worth remarking that jarosite is the *terrestrial mineral analogue* of *Martian sulphates* [6].

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[6] J.J. PAPIKE, J.M. KARNER & C.K. SHEARER (2006) Comparative planetary mineralogy: Implications of martian and terrestrial jarosite. A crystal chemical perspective. *Geochim. Cosmoch. Acta* 70: 1309.

[7] B. HENDRICKS (1937) The crystal structure of alunite & jarosite. *Am. Inst. Min. Met. Publ.* 22: 773.

[8] J. SZYMANSKI (1988) The crystal structure of beudantite  $Pb(Fe,Al)_3(O,SO_4)_2(OH)_4$ . *Can. Min.* 26: 923.

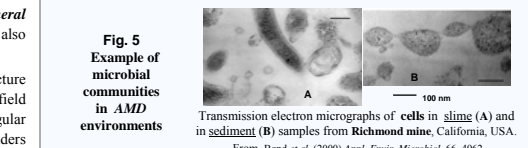
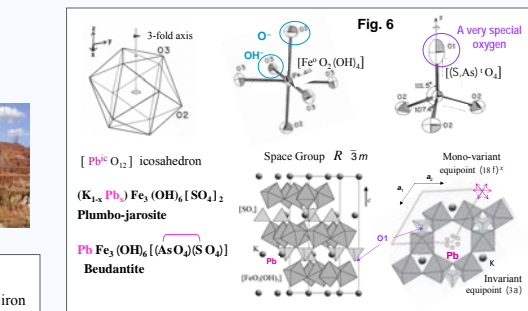


CRYSTALLOGRAPHIC DESCRIPTION OF JAROSITES (*s.l.*)

SG / equipoints  $R \bar{3} m$  (3a) · (9d) · (6c) $^2$  · (6c) $^2$  · (18h) $^{2x}$  · (18h) $^{2z}$

Structural positions A B T O (t) O (z) OH

Site symmetries  $\bar{3}m$  ·  $2/m$   $3m$   $3m$  ·  $m$  ·  $m$



Evidence of Pb-retention by jarosite in mine tailings

A compositional study on S. Domingos and Aljustrel mine tailings was recently started\* applying X-ray techniques (diffraction, XRD, and fluorescence spectrometry, XRF-WDS). First results have already provided a clear proof that jarosite retains lead: an  $\Delta$ - 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* (PbSO<sub>4</sub>) plus *hematite* ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), thus supporting previous structural considerations. Further work is in progress with the aim of illustrating the valorization of the geoenvironmental contribution from secondary iron-sulphates in AMD. Accordingly, a possible strategy for remediation could be foreseen, based on the addition of a potassium compound able of stabilizing waste materials to reduce AMD effects.

\* Material sampled under EU project *ProMine Nano particle products from new mineral resources in Europe* (FP7-NMP-2008-LARGE-2, 228595)

Table 1 – MORPHOTROPIC DOMAIN of JAROSITE STRUCTURE TYPE

The Periodic Table of the Elements

Classification of Chemical Elements (excluding Rare Earths)

Group	I	II	III	IV	V	VI	VII	0										
Period	1	2	3	4	5	6	7	8										
2	Li	Be	Transition Metals						He									
3	Na	Mg	Transition Metals						Ar									
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	**	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	(At)	Rn
7	Fr	Ra	**	Rf	Db	Sg	Bh	Ht	Rf	Db	Sg	Bh	Ht	Rf	Db	Sg	Bh	Ht

The lone-pair of Tl<sup>+</sup>, Pb<sup>2+</sup>, Bi<sup>3+</sup>

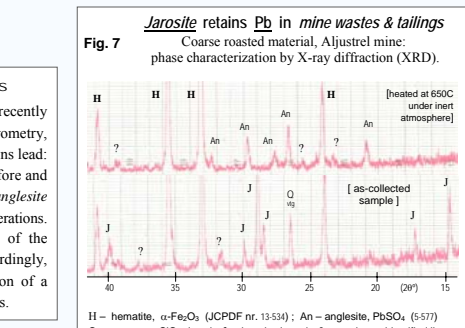
5s electrons [Xe] 4f<sup>14</sup> 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>4</sup> Electron distribution

Crystallography of Jarosites

Jarosite crystal structure (fig.4) was determined in 1937 [7]. It is *trigonal*, space group  $R \bar{3} m$ ; the hexagonal unit cell has  $Z=3$  and  $c/a$  ratio ~2.5 and contains 3  $\Delta$  and 9  $B$  atoms occupying *invariant equipoints* (3a) and (9d), and 6  $T$  plus 6  $O$ -atoms filling *non-variant sites* (6c) $^2$  (positional free parameter  $z$  along the 3-fold axis) and 18  $O$ -atoms plus 18  $OH$  replaced by minor H<sub>2</sub>O in *bi-variant sites* (18h) with  $z_x, z_y$  free parameters.

The jarosite-alunite mineral group has the simplified *crystal chemical formula*  $A^{\text{ic}} B^{\text{t}} O_3 (T^{\text{tet}} O_4)_2 (OH)_6 (H_2O)_x$  where  $ic$  stands for *pseudo-icosahedral* (coordination number CN = 12, with  $\Delta = K^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $Ag^+$ ,  $Tl^+$ ,  $Pb^{2+}$ ,  $Bi^{3+}$  or  $H_3O^+$ , and minor  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$  plus trivalent rare-earth ions, namely  $Eu^{3+}$ ),  $o$  stands for *octahedral*, CN=6, with  $B$  standing for  $Fe^{3+}$  (jarosite *s.s.*) or  $Al^{3+}$  (alunite *s.s.*) and also for  $V^{3+}$ , plus minor  $Fe^{2+}$  (along with other divalent cations,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ),  $t$  stands for *tetrahedral* (CN = 4, with  $T = S^{6+}$ ,  $P^{5+}$ ,  $As^{5+}$ ) [see Table 1].  $B$  cations are coordinated by 4  $OH$  and 2  $O$ -anions from tetrahedral groups, while  $\Delta$  cations are surrounded by 6  $OH/H_2O$  shared with  $B$ -octahedra plus 6  $O$ -atoms from tetrahedral groups, including the non-shared oxygens, structural position  $O_t$ , equipoint (6c) $^2$  (fig.6). Despite the different nature of  $\Delta$ -cation, both Na- and Pb-jarosite are isostructural and form solid solutions with jarosite *s.s.*

Whenever a metallic ion partially replaces the spherical alkaline ion  $K^+$  within the large icosahedral cage - invariant equipoint (3a) - a disordered partial occupancy of mono-variant equipoint (18f) may account for the accommodation of non-bonded electrons [see Table 1] without breaking the space group symmetry (fig.6). This has already been recognized for the lone pair of 6s<sup>2</sup> electrons of Pb<sup>2+</sup> ions in the crystal structure of beudantite [8].



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