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# INFLUENCE OF THE LARGE CATION UPON PRE-EDGE DETAILS OF Fe 1s XANES SPECTRA IN JAROSITE-TYPE SULPHATE MINERALS\*

M.O. FIGUEIREDO & T. PEREIRA da SILVA

Cryst. Miner. Centre, IICT & INETI/IGM, Geological Data Centre, Estrada da Portela, 2721-866 Alfragide and CENIMAT/I3N, Mater. Sci. Dpt., Fac. Sci. & Technology, New Univ. Lisbon, 2829-516 Caparica, Portugal



ondina.figueiredo@ineti.pt

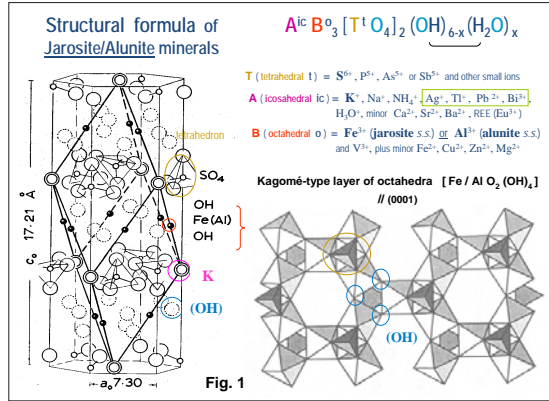
## Problematic

**Jarosite s.s.** – ideally  $KFe_3(OH)_6(SO_4)_2$  – is a secondary iron sulphate very common in acid mine drainage (AMD) environments with high potassium content.

This mineral is not only **environmentally important** because it may configure the **ultimate mineral sink of lead** and other **hazardous metals** (e.g. thallium), beyond silver, occurring frequently in the oxidized part of sulfide ore deposits, but it is also economically relevant within various **hydrometallurgical routes**.

Besides, the **2D Kagomé-pattern of iron octahedra** in the crystal structure (fig.1) awards unique magnetic properties to this mineral. 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 jarosite an important, paradigmatic **Kagomé Heisenberg Anti-Ferromagnet**, KHAFM [1]. Remarkably, jarosite is also the terrestrial analogue of Martian sulphates [2].

Once many doubts still subsist concerning the exact crystal structure of Pb-rich and other jarosites, a **comparative study on the electronic state of iron** in these important sulphates was undertaken by comparing and analysing the **pre-edge details of Fe 1s XANES spectra** from various jarosites and structurally affine iron sulphates (Table 1).



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

SG / Equipoints  $R\bar{3}m$  (3a). (9d). (6c)z. (6c)z. (18h)xz. (18h)xz

Structural positions **A B T O(1) O(2) OH**

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

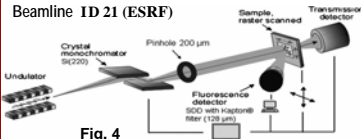
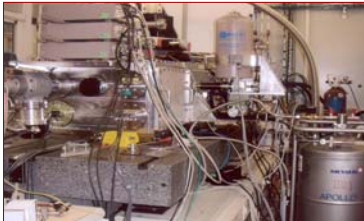


## Crystallography of Jarosites

The jarosite-alunite mineral group has the simplified **crystal chemical formula**  $A^{ic} B^o_3 (T^t O_4)_2 (OH)_6$  where **ic** stands for **pseudo-icosahedral** (coordination number CN = 12, with  $\underline{A} = K^+$ ,  $Na^+$ ,  $NH_4^+$ ,  $Ag^+$ ,  $Tl^+$ ,  $Pb^{2+}$ ,  $Bi^{3+}$  or even  $H_3O^+$ , and minor  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$  plus trivalent rare-earth ions, namely  $Eu^{3+}$ ), **o** for **octahedral** (CN=6, with  $\underline{B}$  standing for  $Fe^{3+}$  (jarosite s.s.) or for  $Al^{3+}$  (alunite s.s.) and also for  $V^{3+}$ , plus minor  $Fe^{2+}$  along with other divalent cations,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ), **t** for **tetrahedral** (CN = 4, with  $\underline{T} = S^{6+}$ ,  $P^{5+}$ ,  $As^{5+}$ ).

Octahedral **B** cations are coordinated by 4OH and 2O-anions from tetrahedral groups, while **A** cations are surrounded by 6OH shared with B-cation octahedra plus 6O-anions from the tetrahedral groups (including the non-shared oxygens).

**Jarosite crystal structure** (fig.1) was determined in 1937 [3]. It is **trigonal**, space group  $R\bar{3}m$ , and the unit cell (hexagonal description, with  $Z=3$  and  $c/a$  ratio ~2.5) contains **3 A** and **9 B** atoms occupying **invariant equipoints** and **6 T** plus **6O**-atoms filling **mono-variant sites** (positional free parameter  $z$  along the 3-fold axis) and **18O**-atoms plus **18OH** replaced by minor  $H_2O$  in **bi-variant sites** with  $\pm z$  free parameters. Na-jarosite and Pb-jarosite are isostructural and form solid solution with jarosite despite the different nature of the **A**-cation.



## Experimental

**X-ray absorption experiments** were carried out at the **ESRF using beam line ID-21** [6]. XANES spectra were collected in fluorescence yield (FY) mode with an energy-dispersive high-purity Ge-detector mounted perpendicular to the X-ray beam in the horizontal plane (fig.4) by irradiating a small area (~1µm²) of well crystallized mineral fragments.

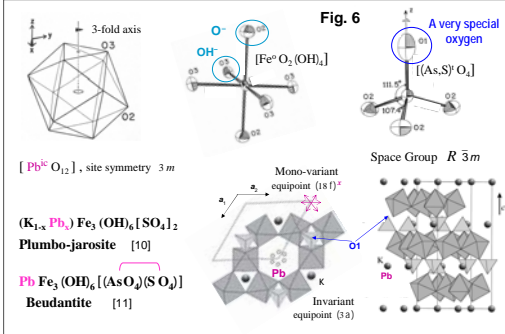
A fixed-exit Si(220) monochromator assuring an energy resolution of 0,3 eV was used for the energy scans (7050-7350 eV). Metallic iron was used for energy calibration.

Pre-edge details of XANES spectra were analysed using Fityk program [7] to deconvolute this spectral region into pseudo-Voigt components and assess iron electronic state.

Table 1

[Fe <sup>o</sup> X <sub>6</sub> ]	[S <sup>o</sup> O <sub>4</sub> ]	Studied sulphate minerals	Name	Chemical Formula [cryst. struct.]
[Fe <sup>o</sup> O <sub>6</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Fe <sup>o</sup> (H <sub>2</sub> O) <sub>6</sub> ]			
[Fe <sup>o</sup> O <sub>6</sub> (OH) <sub>2</sub> ]	[S <sup>o</sup> O <sub>4</sub> ]	The number of <u>icg</u> coordination polyhedra (octahedra, o) and sulphur coordination polyhedra (tetrahedra, t) in the unit cell of the mineral is indicated. Oxygen anions shared between <u>Fe</u> & <u>S</u> are underlined.	JAROSITE	$K Fe^{III}_3 (OH)_6 (SO_4)_2$ [fig. 1]
[Fe <sup>o</sup> O <sub>6</sub> (OH) <sub>2</sub> ]	[S <sup>o</sup> O <sub>4</sub> ]		MELANTERITE	$Fe^{II} (SO_4) \cdot 7 H_2O$ [fig. 2]
[Fe <sup>o</sup> O <sub>6</sub> (OH) <sub>2</sub> ]	[S <sup>o</sup> O <sub>4</sub> ]		COQUIMBITE	$Fe^{II}_2 (SO_4)_3 \cdot 9 H_2O$ [fig. 3]

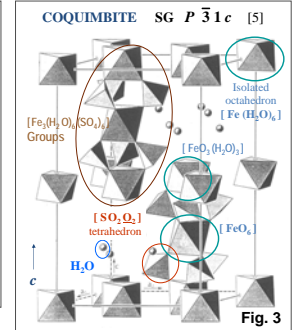
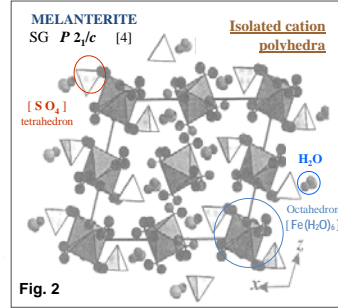
Plumbojarosite: accommodation of the lone pair of 5s<sup>2</sup> electrons from Pb<sup>2+</sup> ions without symmetry breaking



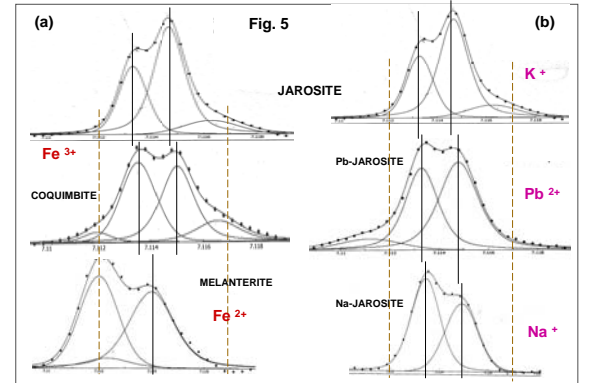
## Results and conclusions

The pre-edge features of **Fe 1s XANES spectra** collected from studied sulphate minerals are reproduced in fig.5. As expected [8], the average pre-peak centroid (fig.5a) clearly differentiates between ferrous and ferric states: 7112.5 vs 7114 eV, close to the published value of 1.4 eV for the energy difference [9]. The similitude of the main pre-edge contributions is remarkable despite the occurrence of three distinct Fe<sup>3+</sup> coordination environments in coquimbite comparatively to one unique situation in jarosite (Table 1).

Conversely, the size and speciation or electronic state of the large cation – in icosahedral coordination by 12 O-atoms from the sulphate tetrahedral groups – may explain the observed differences (fig.5b): (1) K<sup>+</sup> and Na<sup>+</sup> are closed shell, non-polarisable alkaline ions with different radius inducing a smaller c/a ratio for natrojarosite; (2) off-centering of Pb<sup>2+</sup> ions within the icosahedron (fig. 6) to accommodate the lone-pair of 5s<sup>2</sup> electrons through a statistical partial occupation of a non-invariant equipoint within the same space group symmetry.



## Pre-edge region of Fe K-edge XANES spectra



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