RESPONSE OF PRE-EDGE DETAILS FROM Fe K-EDGE XANES SPECTRA TO THE LARGE CATION IN JAROSITES *

T. PEREIRA da SILVA & M.O. FIGUEIREDO

Cryst. Miner. Centre, IICT & INETI / LNEG, Geological Data Centre, Estrada da Portela, Alfragide, Apartado 7586, 2721-866 Amadora, Portugal
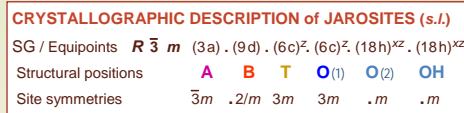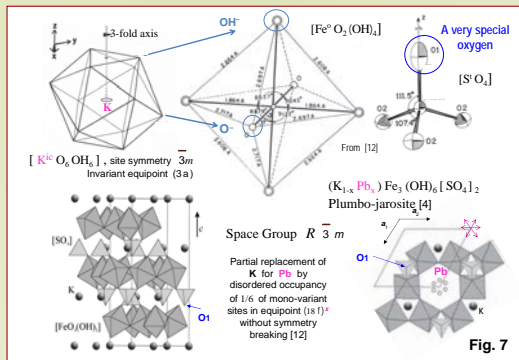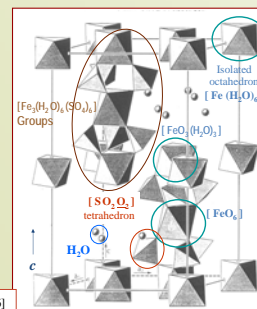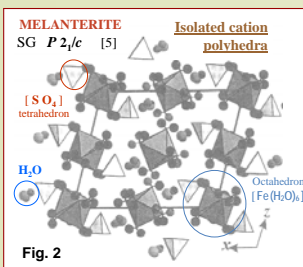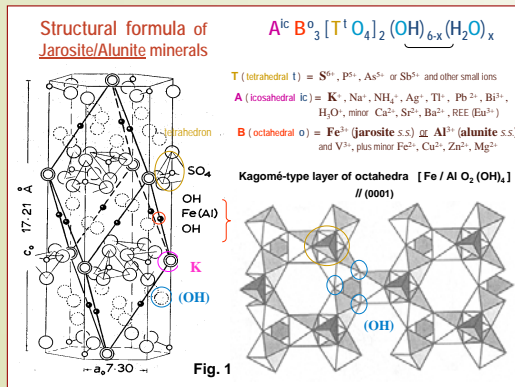
teresa.pena@ineti.pt

Introduction

"*Jarosites*" are environmentally important sulphate minerals, frequent in acid mine drainage (AMD), because they configure an ultimate sink of lead and other hazardous metals reducing their spread in soils and rivers.

With general formula $AB_3(OH)_6(SO_4)_2$, where $\underline{A}$ is mainly K^+, Na^+, plus minor Ag^+, Tl^+, Pb^{2+}, Bi^{3+}, and $\underline{B}$ is Fe^{3+} (jarosite *s.s.*) or Al^{3+} (alunite), the jarosites mineral group (*s.l.*) has trigonal symmetry [1] and display Kagomé-type layers of corner-sharing $\underline{B}$ octahedra, $[Fe/AlO_2(OH)_4]$. The large cation $\underline{A}$ stays in a pseudo-icosahedral site, coordinated by 6O-atoms from $[SO_4]$ tetrahedra and 6OH shared with $\underline{A}$ octahedral cations (fig.1), thus configuring unique magnetic properties to jarosite (*s.s.*). 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 a paradigmatic **Kagomé Heisenberg Anti-Ferromagnet**, KHAFM [2].

By analogy with what happens with the white line in sulphur K-edge XANES spectra of iron sulphates [3], it is then expectable that the **pre-edge details** of Fe K-edge XANES spectra will respond to the **different nature of the large cation**. Once doubts still subsist concerning the exact crystal structure of Pb-rich jarosite [4], 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) .

Table 1

[Fe° X₆]			[S¹O₄]		Studied sulphate minerals		
[Fe° O₆]	[Fe° O₅ (H₂O)]	[Fe° O₄ (OH) z]	[S¹O₄] isolated tetrahedr.	[S¹ O₂ O₂]	(H₂ O) isolated molecules		

The number of iron coordination polyhedra (octahedra, o) and sulphur coordination polyhedra (tetrahedra, t) in the unit cell of the mineral is indicated. Oxygen anions shared between Fe & S are underlined.

						Name	Chemical Formula [crist struct.]
		3		2	–	JAROSITE	K Fe^{iii}₃ (OH)₆ (SO₄)₂ [fig. 1]
	1		1		1	MELANTERITE	Fe^{ii} (SO₄) . 7 H₂O [fig. 2]
1	1	1	6		3	COQUIMBITE	Fe^{iii}₂ (SO₄)₃ . 9 H₂O [fig. 3]

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 the superscript **ic** stands for **pseudo-icosahedral** (coordination number CN=12, with 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 **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** for **tetrahedral** (CN=4, with $T = S^{6+}$, P^{5+}, As^{5+}). Octahedral $\underline{B}$ cations are coordinated by 4 OH and 2 O-anions from tetrahedral groups, while $\underline{A}$ cations are surrounded by 6 OH shared with $\underline{B}$-cation octahedra plus 6 O-atoms from the tetrahedral groups (including the non-shared oxygen anions).

Jarosite crystal structure (fig.1) was determined in 1937 [1]. It is **trigonal**, space group $R\,\overline{3}\,m$, and the unit cell (hexagonal description, with Z=3 and c/a ratio ~ 2.5) contains 3$\underline{A}$ and 9$\underline{B}$ atoms occupying **invariant equipoints** and 6$\underline{T}$ plus 6 O-atoms filling **mono-variant sites** (positional free parameter $\underline{z}$ along the 3-fold axis) and 18 O-atoms plus 18 hydroxyls (OH) replaced by minor H_2O in **bi-variant sites** with $\underline{x,z}$ free parameters. Na- and K-jarosite are isostructural minerals that form a complete solid solution [7,8]. Despite the different nature of the $\underline{A}$-cation, Pb-jarosite is also isostructural but only partial diadochic replacement of $\underline{K}$ for $\underline{Pb}$ is observed.

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Structural formula of Jarosite/Alunite minerals

$$A^{ic} B^o_3 [T^t O_4]_2 (OH)_{6-x} (H_2O)_x$$

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^{3+}, Bi^{3+}, H_3O^+, minor Ca^{2+}, Sr^{2+}, Ba^{2+}, REE (Eu^{3+})
B (octahedral o) = Fe^{3+} (**jarosite** *s.s.*) or Al^{3+} (**alunite** *s.s.*) and V^{3+}, plus minor Fe^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}

Kagomé-type layer of octahedra [Fe / Al O₂ (OH)₄] // (0001)

Fig. 1

MELANTERITE SG $P\,2_1/c$ [5] — *Isolated cation polyhedra*

[S O₄] tetrahedron ; H₂O ; Octahedron [Fe (H₂O)₆]

Fig. 2

Fig. 3 - COQUIMBITE SG $P\,\overline{3}1c$ [6]

[Fe₂(H₂O)₆(SO₄)₄] Groups ; Isolated octahedron [Fe (H₂O)₆] ; [FeO₂(H₂O)₄] ; [SO₂O₂] tetrahedron ; [FeO₆] ; H₂O

[Fe° O₂ (OH)₄] ; 3-fold axis ; OH⁻ ; O²⁻ ; K ; [K^{ic} O₆ OH₆], site symmetry $\overline{3}m$ Invariant equipoint (3a) ; From [12]

A very special oxygen ; [S¹ O₄]

$(K_{1-x} Pb_x)$ Fe₃ (OH)₆ [SO₄]₂ Plumbo-jarosite [4]

Space Group $R\,\overline{3}\,m$

Partial replacement of K for Pb by disordered occupancy of 1/6 of mono-variant sites in equipoint (18 t)^z without symmetry breaking [12]

[SO₄] ; [FeO₄/OH₆] ; O1 ; Pb

Fig. 7

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

SG / Equipoints	$R\,\overline{3}\,m$ (3a)	. (9d)	. (6c)^z	. (6c)^z	. (18h)^{xz}	. (18h)^{xz}
Structural positions	A	B	T	O(1)	O(2)	OH
Site symmetries	$\overline{3}m$	.2/m	3m	3m	.m	.m

Experimental

X-ray absorption experiments were carried out at the ESRF using **beam line** ID-21 [9]. 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 with an energy resolution of 0,3 eV at the iron edge was used for the energy scans (7050-7350 eV). Energy calibration was performed with a metallic iron foil.

Pre-edge details of XANES spectra were analysed using Fityk program [10] to deconvolute this spectral region into pseudo-Voigt components in order to assess iron electronic state.
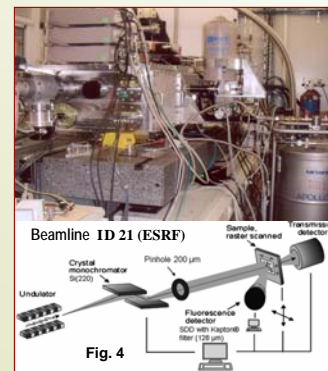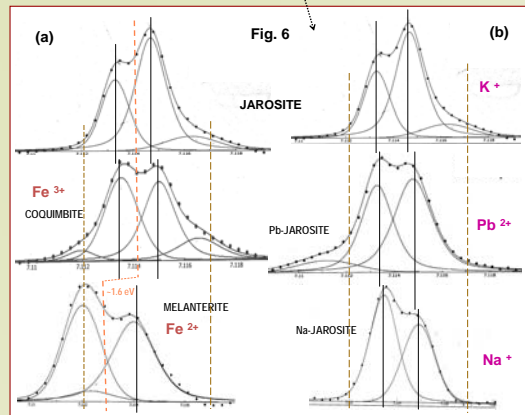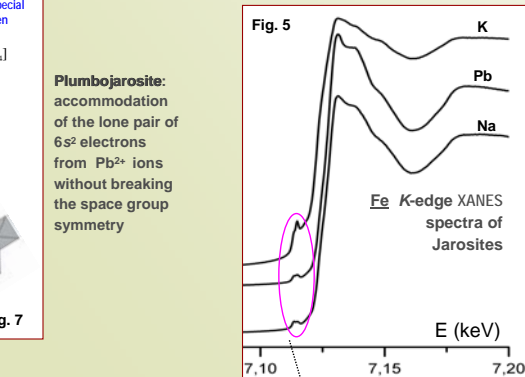

Beamline ID 21 (ESRF)

Fig. 4

Plumbojarosite: accommodation of the lone pair of 6s² electrons from Pb²⁺ ions without breaking the space group symmetry

Fe K-edge XANES spectra of Jarosites

K ; Pb ; Na

E (keV)

7,10   7,15   7,20

Fig. 5

Results and conclusions

The Fe 1s XANES **spectra** collected from studied jarosites are reproduced in fig.5 (pre-edge region is assigned). When comparing with pre-edge features from other sulphate minerals (fig.6), the pre-peak centroid clearly differentiates between ferrous (melanterite) and ferric (jarosite,coquimbite) states: 7112.5 vs. 7114.1 eV (fig. 6a), close to the published value of 1.4 eV for the energy difference [11]. The **similitude of the two main pre-edge contributions** is remarkable despite the existence of three Fe^{3+} coordination environments in coquimbite [6] comparatively to one unique situation in jarosite crystal structure (Table 1, fig. 7).

However, the **relative intensity** of these two components appears quite identical for Pb- and reversed for K- and Na-jarosite (fig.6b). A possible explanation for such reversing is given by the Fe-O distances calculated with IFEFFIT program [13]: shorter and distinct Fe-OH (1.980 for K- vs 1.998 Å for Na-jarosite) and identical Fe-O(2) for both (2.050 Å).

On the other hand, the **size** and the **speciation** (**electronic state**) of the **large cation**, staying in **icosahedral coordination** by 6 O-atoms from the sulphate tetrahedral groups plus 6 OH-anions from the iron octahedra (fig. 7), may contribute to the observed differences: K^+ and Na^+ are closed shell, non-polarisable alkaline ions which radii induce a smaller c/a ratio for Na-jarosite [14]; conversely, a partial statistical occupancy of a mono-variant site within the same space group would be required in order to accommodate the lone-pair of 6s² electrons from Pb²⁺ ions without breaking the space group symmetry.

Fig. 6 – Resolved pre-edge features of Fe 1s XANES spectra

(a) Fe³⁺ ; Fe²⁺ ; JAROSITE ; COQUIMBITE ; MELANTERITE ; ~1.6 eV
(b) K⁺ ; Pb²⁺ ; Na⁺ ; JAROSITE ; Pb-JAROSITE ; Na-JAROSITE

INETI ; INSTITUTO NACIONAL de ENGENHARIA, TECNOLOGIA e INOVAÇÃO ; LNEG Laboratório Nacional de Energia e Geologia ; IICT