



Experiment title: The influence of oxygen sharing on S and Fe K-edge XANES spectra from hydrated iron sulphate minerals

Experiment number:
EC 209

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Report:

Sulphates are quite common minerals. Amongst them, hydrated secondary iron sulphates may configure a serious environmental concern as alteration materials in acid mine drainage areas of polymetallic sulphide ores exploitations. These sulphates display a great variety of structural arrangements, always containing non-polymerized (isolated) tetrahedral sulphate ions $[S^t O_4]$ and metal cations in octahedral coordination by hydroxyls plus water molecules (beyond the oxygen atoms shared with sulphate anions). The sharing of oxygen anions with cation octahedra, $[M^o X_6]$ ($X = O, OH, H_2O$), may differ significantly (table below).

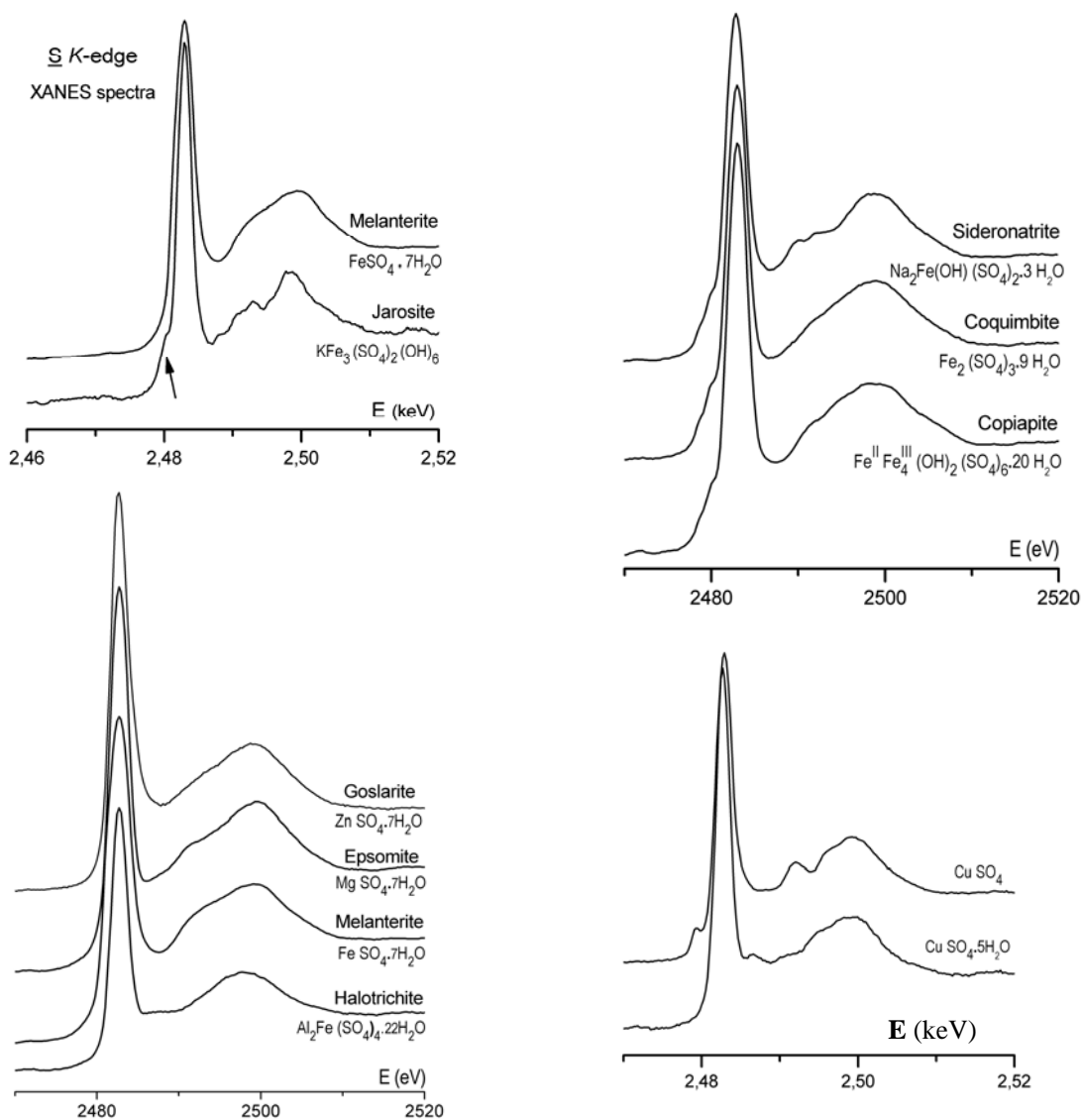
[M ^o X ₆]						[S ^t O ₄]				n (H ₂ O) isolated water molecules	Sulphate Minerals	
[M ^o (H ₂ O) ₆]/[Cu ^{sq} (H ₂ O) ₄]	[Fe ^o O(H ₂ O) ₅]	[Fe ^o O ₃ (H ₂ O) ₃]	[Fe ^o O ₃ (OH)(H ₂ O) ₂]	[Fe ^o O ₂ (OH) ₄]	[Fe ^o O ₆]/[Cu ^{sq} O ₄]	[S ^t O ₄] isolated tetrahedra	[S ^t O ₃ O]	[S ^t O ₂ O ₂]	[S ^t O ₂ O ₃]		Mineral name	Chemical formula
				3					2	0	JAROSITE	K Fe ₃ (OH) ₆ (SO ₄) ₂
				1					2	3*	SIDERONATRITE	Na ₂ Fe(OH)(SO ₄) ₂ · 3 H ₂ O
1			4						6	6	COIAPITE	Fe ^{II} Fe ^{III} ₄ (OH) ₂ (SO ₄) ₆ · 20 H ₂ O
1	2			1					6	6	COQUIMBITE	Fe ₂ (SO ₄) ₃ · 9 H ₂ O
2	1					3	1 [#]			5	HALOTRICHITE	Al ₂ Fe(SO ₄) ₄ · 22 H ₂ O
1						1				1	MELANTERITE EPSOMITE GOSLARITE	M S O ₄ · 7 H ₂ O M = Fe M = Mg M = Zn
1									1	1	CHALCANTHITE	Cu S O ₄ · 5 H ₂ O
				1					1	0	CHALCOCYANITE	Cu S O ₄

M = metallic ion (Fe, Al, Mg, Zn). Cation coordination: o, octahedral; sq, square; t, tetrahedral.

* water molecules coordinating only sodium ions; # oxygen sharing with iron octahedron.

The aim of the experiment was to assess the influence of oxygen-sharing on the near-edge details of \underline{S} $1s$ absorption spectra, complementing data collected in a previous experiment for iron (EC 87). XANES spectra were collected in fluorescence yield (FY) and total electron yield (TEY) modes (\underline{Fe} K-edge, 7.05-7.35 keV; \underline{S} K-edge, 2.44 to 2.56 keV). Small mineral fragments were irradiated at various points and ten scans were performed per point. From a total of about 1400 registered scans, 110 good sum spectra were obtained. Distinct anion sharing degrees imply a lowering of the formal sulphur oxidation state, explaining details preceding the characteristic white line (figures below). A paper reporting and discussing the results so far obtained is already in press [1] and two communications were submitted and accepted for presentation [2,3].

A preliminary approach to the study of \underline{In} L_3 absorption edge (3.72-3.80 keV) in sulphides was attempted.



[1] M.O. FIGUEIREDO & T. P. SILVA. The electronic state of sulphur in mineral sulphates: effect of oxygen sharing on the white line of \underline{S} K-edge XANES spectrum. *European J. Mineralogy* (in press).

[2] M.O. FIGUEIREDO, T. PEREIRA da SILVA & J.P. VEIGA. Oxidation state and coordination of iron in red pre-soils: first results from a \underline{Fe} K-edge XANES study on regoliths from Santiago Island, Cape Verde. *EGU 2008, Europ. Geosciences Union Gen. Assembly, Session SSS14*, Vienna/Austria, April 13-18, 2008 (poster).

[3] M.O. FIGUEIREDO, T. PEREIRA da SILVA, J.P. VEIGA, C. LEAL GOMES & V. de ANDRADE. The blue colouring of beryls from Licungo, Mozambique: an X-ray absorption spectroscopy study at the iron K-edge. *ICAM 2008, 9th Internat. Congr. Applied Mineralogy*, Brisbane/Australia, 8-10 September, 2008 (poster).