

Users' Meeting
February 5-7, 2008

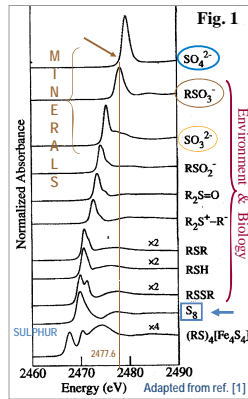
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Introduction

An extensive study of **sulphur speciation** using X-ray absorption spectroscopy was developed in the last years in view of the behaviour of this element as an *essential plant nutrient* and as a *serious environmental pollutant*. In soil colloids [1], possible **intermediate formal valences** were noticed between common stable sulphur oxidized states, S^{6+} & S^{4+} (fig. 1).

A search for the eventual occurrence of analogous electronic situations for sulphur in **well crystallized sulphate minerals** was undertaken by analysing the near-edge features of \underline{S} 1s X-ray absorption spectra (XANES). Following a preliminary study [2], the details observed at the shoulder of S^{6+} white line are further discussed on the basis of the sharing degree of oxygen anions between tetrahedral sulphur and octahedral metal ions.



Problematic

Sulphates are quite common minerals that display a great diversity of structural activities, containing *non-polymerized tetrahedral sulphate ions*, $[S^6O_4]^{2-}$. Metal ions usually have *octahedral environment*, being coordinated by hydroxyls plus water molecules beyond the oxygen atoms shared with sulphate ions.

The positional symmetry of S^{6+} ions is in general low and the degree of sharing the oxygen anions with cation octahedra $[M^X X_6]$ ($X=O, OH, H_2O$) varies from 0 to 4. This crystal chemical feature is crucial for the interpretation of details close to the white line in \underline{S} 1s X-ray absorption spectra.

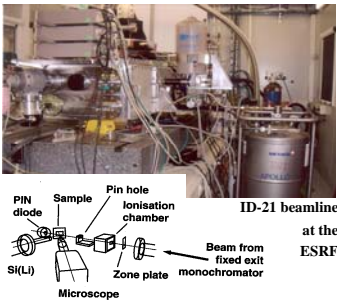
Table 1 – Structural constitution of studied sulphate minerals

Mineral name	Chemical formula	[M ^X X ₆]						[S ⁶⁺ O ₄]		Number of identical polyhedra configuring the coordination environment of metals & sulphur
		[Fe(OH) ₂]/[Cu ²⁺ (H ₂ O)]	[Fe ²⁺ (OH) ₂]	[Fe ³⁺ (OH)(H ₂ O)]	[Fe ³⁺ (OH) ₂]	[Fe ³⁺ (OH)]/[Cu ²⁺ (H ₂ O)]	[S ⁶⁺ O ₄]	[S ⁶⁺ O ₄]	n(H ₂ O) isolated water molecules	
JAROSITE	KFe ₃ (OH) ₆ (SO ₄) ₂		3				2	0	0	
SIDERONATRITE	Na ₂ Fe(OH)(SO ₄) ₂ · 3H ₂ O		1				3*	0	0	
COPIAPITE	Fe ²⁺ Fe ₂ (OH) ₂ (SO ₄) ₂ · 20H ₂ O	1	4				6	0	0	
COQUIMBITE	Fe ₂ (SO ₄) ₃ · 9H ₂ O	1	2		1		6	0	0	
HALOTRICHITE	Al ₂ Fe(SO ₄) ₄ · 22H ₂ O	2	1				3	1*	0	
MELANTRITE	M(SO ₄) ₂ · 7H ₂ O	1					1	1	0	
EPSOMITE	M(SO ₄) ₂ · 7H ₂ O						1	1	0	
GOSLARITE	M(SO ₄) ₂ · 7H ₂ O						1	1	0	
CHALCANTHITE	Cu(SO ₄) ₂ · 5H ₂ O	1					1	1	0	
CHALCOCYANITE	Cu(SO ₄) ₂	1					1	1	0	

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.

Crystal structure & bonding of O-atoms

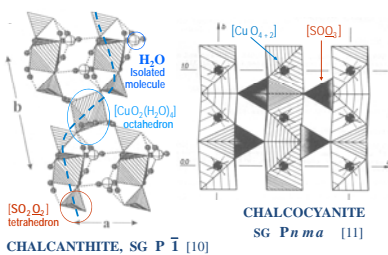
Studied sulfate minerals (Table 1) illustrate a variety of structural situations for $[SO_4]^{2-}$ tetrahedra and octahedral groups centered by Fe, Cu, Zn, Al, Mg. Corresponding crystal structures are reproduced with indication of space group symmetry (see figures); cation groupings are assigned to emphasize similarities and differences in atomic arrangements, likely to account for differences observed in \underline{S} K-edge XANES spectra



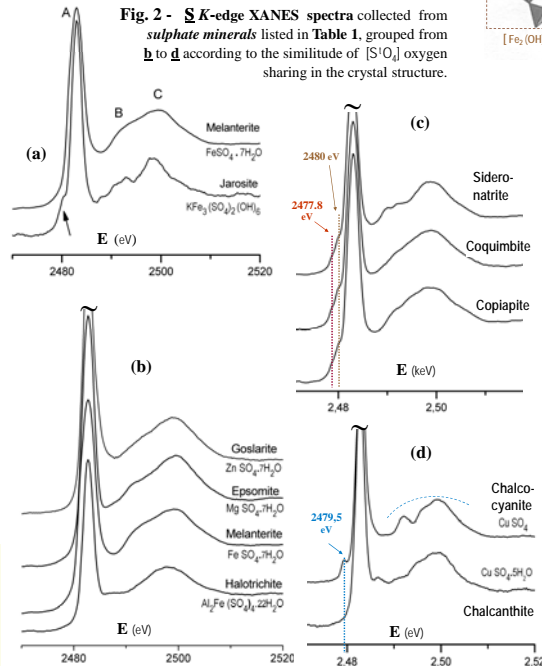
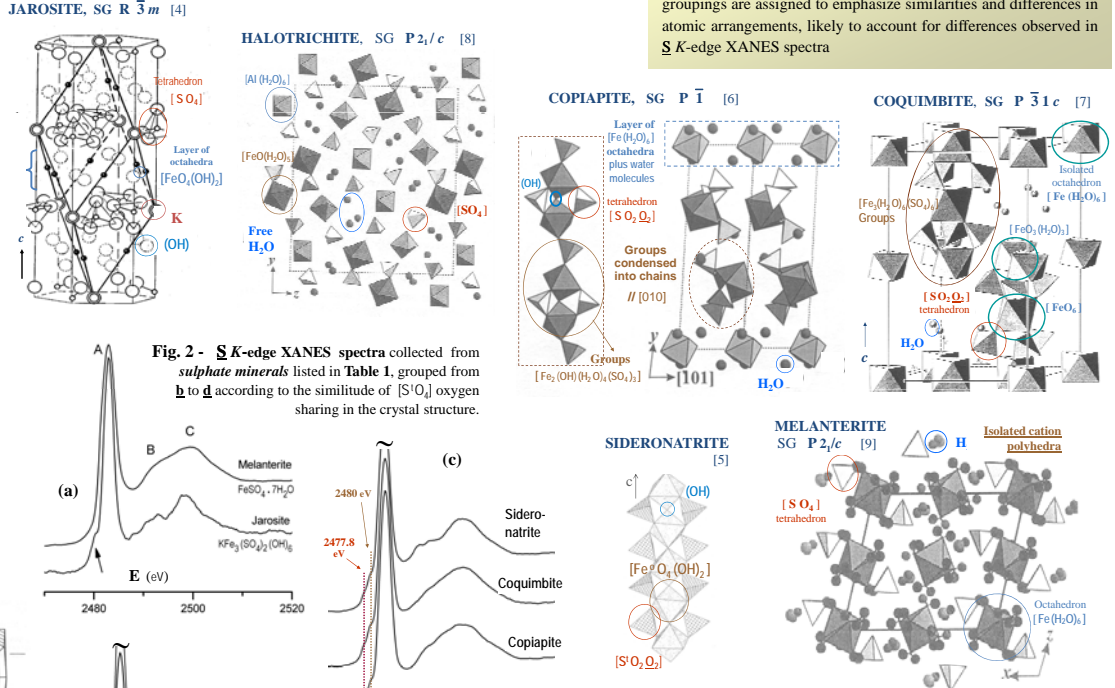
Experimental

X-ray absorption experiments were carried out at the ESRF using beam line ID-21 [3] by irradiating a small area (~1μm²) of well crystallized mineral fragments.

The fluorescence yield was collected with an energy-dispersive high-purity Ge-detector placed perpendicular to the X-ray beam (in the horizontal plane) and the transmission signal by a photodiode. The fixed-exit Si(111) monochromator used for energy scan assures an energy resolution of 0.2 eV at the \underline{S} K-edge.



CRYSTAL STRUCTURES of MODEL MINERALS



References

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Results

\underline{S} 1s XANES spectra collected from studied sulfate minerals (Table 1) are reproduced in fig. 2. It is remarkable that only minerals containing exclusively isolated $[SO_4]^{2-}$ tetrahedra display the characteristic white line of S^{6+} ions (2482 eV) free from any details (Fig. 2a), followed by not much diversified post-edge features (Fig. 2b).

Whenever O-sharing occurs, pre-edge details were noticed in Fe, Zn, Al, Mg sulfates at 2477.8 & 2480 eV (Fig. 2c) – energies close to the values quoted for the white line respectively in sulphone (\underline{S} with formal oxidation state 5+) and sulphonic acid [12].

XANES spectra collected from Cu-sulfates (Fig. 2d) show quite distinct trends for the \underline{S} 1s absorption edge: a pre-edge detail at 2479.5 eV occurs only for the anhydrous mineral, despite both minerals display O-sharing between sulphate tetrahedra and cation coordination polyhedra.

Further experiments are foreseen to extend this analysis to a larger set of mineral sulphates, along with theoretical spectra simulation using the FEFF code [13] in order to interpret spectra features B&C (Fig. 2a).

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