



	<b>Experiment title: Electronic state of sulphur in sulphides: an X-ray absorption study on S K-edge and 3d transition metal L-edge in sulphide minerals</b>	<b>Experiment number:</b> ME-821
<b>Beamline:</b> ID 21	<b>Date of experiment:</b> from: February 19, 2004 to: February 24, 2004	<b>Date of report:</b> 2004.10.13
<b>Shifts:</b> 15 #	<b>Local contact(s):</b> Dr. Barbara Fayard	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):		
* M.O. Figueiredo & * T.P. Silva, Cryst. Miner. Centre / IICT, Al. Afonso Henriques, 41-4º, 1000-123 Lisboa, and CENIMAT, Materials Science Dept., New Univ. Lisbon (UNL), 2829-516 Caparica, Portugal		
* J. Mirão, Geophysics Centre, Univ. of Évora, 7002-554 Évora, Portugal		

## Report:

Sulphur atoms present a variety of coordination environments by metal ions in natural sulphides, despite the crystal chemistry of these minerals being dominated by three main cubic crystal structure types: *pyrite*,  $\text{Fe}^0 [ \text{S}_2^{\text{t}} ]$ , *sphalerite*,  $\text{Zn}^{\text{t}} [ \text{S}^{\text{t}} ]$  and *galena*,  $\text{Pb}^{\text{o}} [ \text{S}^{\text{o}} ]$  (where  $\text{t}$  stands for tetrahedral and  $\text{o}$  for octahedral coordination). Thiospinels and complex sulphosalts are also common sulphur-rich minerals.

Pyrite-type minerals are disulphides containing anionic dimers  $[\text{S}_2]^-$ ; accordingly, the tetrahedron around each sulphur atom is formed by another sulphur plus three metal atoms. These are coordinated by six sulphur atoms each one from a distinct dimer.

Minerals with zinc blende (sphalerite) crystal structure typify the so-called “*tetrahedral structures*” where both constituting atomic species are tetrahedrally surrounded by the species of opposite sign and galena is the prototype of “*octahedral structures*” with the same reasoning applying to lead and sulphur, now in octahedral coordination. The coordination polyhedra (tetrahedra or octahedra) of sulphide anions ( $\text{S}^-$ ) and  $\text{M}^{2+}$  cations are both symmetry-constrained to geometrical regularity in these crystal structures.

The photon energy range available at beam line ID-21 allows to study both S *K*-edge and M *L*-edge on the irradiated point in a  $\text{M}_p\text{S}_q$  sulphide and, consequently, to *assess the conjugated influence of the nature of coordinating metal atoms and geometry of their arrangement over the electronic state of sulphur*.

A total of about 4400 scans allowed to obtain 79 good quality XANES spectra in fluorescence yield mode:  
**K-edge:** **S** (2.45-2.53 keV, 50 spectra); **Mn** (6.00-6.75 keV, 4 spectra); **Fe** (7.05-7.35 keV, 10 spectra);  
**L-edge:** **Nb** (2.36-2.395 keV, 3 sp.); **Ag** (3.33-3.39 keV, 4); **Cd** (3.5-3.6 keV, 1); **Sb** (4.11-4.19 keV, 7).

Figs. 1 to 3 illustrate S 1s absorption spectra collected from various minerals. Häüyne – an alumino-silicate of Na/Ca containing isolated sulphate groups – was also studied in a preliminary approach. Results of these experiments were presented at the *5<sup>th</sup> European Conference on Mineralogy & Spectroscopy (ECMS 2004)* held in Vienna last September [1-3].

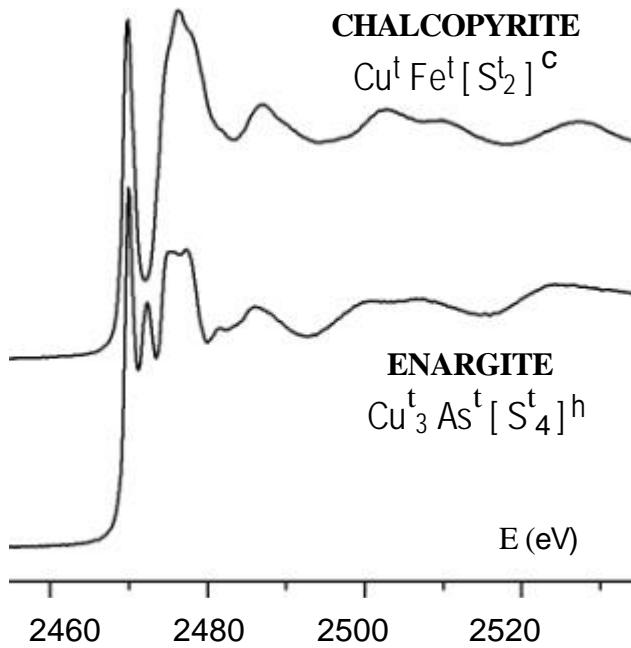


Fig. 1

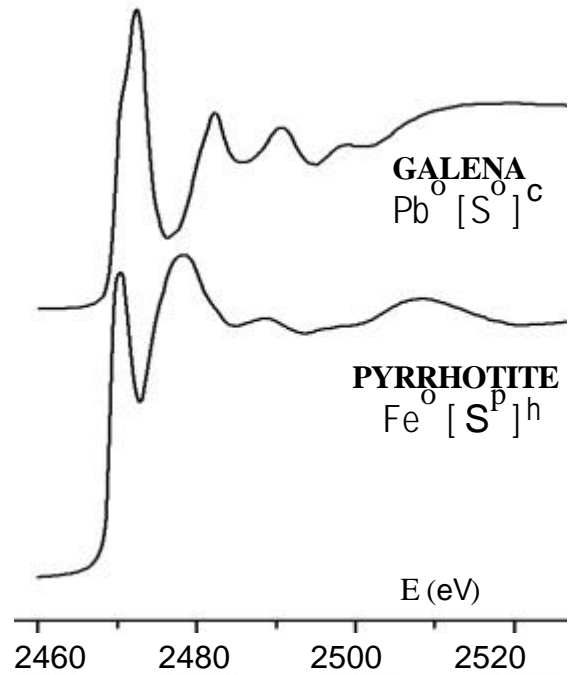


Fig. 2

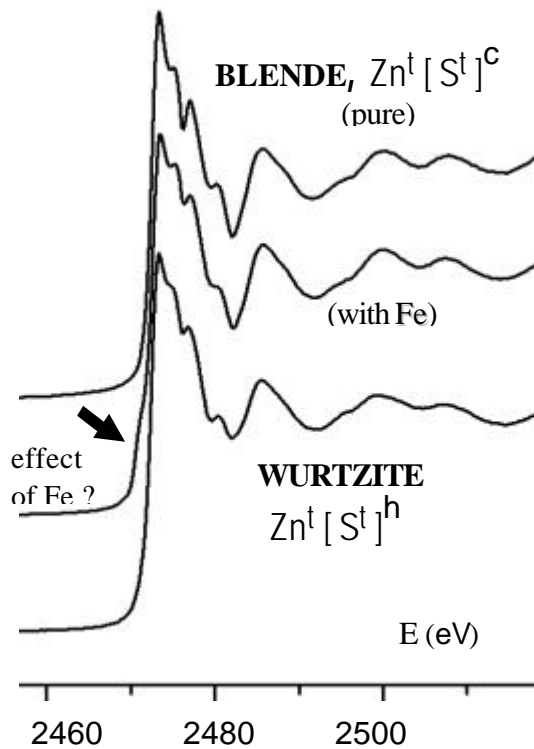


Fig. 3

[1] M.O. FIGUEIREDO & J. SUSINI (2004) Crystal chemical bases for a data bank on S K-edge XANES spectra in sulphide and sulphosalt minerals. *ECMS 2004*, Vienna/Austria, 4-8 September (Poster P-13); *Mitteilungen Österreich Mineralogische Gesellschaft* 149 31 (Abstract).

[2] J.A. FERREIRA & M.O. FIGUEIREDO (2004) Electronic state of sulphur in tetrahedrite-tennantite series: a micro-XANES study. *ECMS 2004* (Poster P-14); *Mitt. Öst. Min. Gesellschaft* 149 30 (Abstr.).

[3] M.O. FIGUEIREDO, T.P. SILVA, L.C. SILVA, J. MIRÃO & M.H. MENDES (2004) An X-ray absorption spectroscopy study at sulphur K-edge of Häuyne from St. Antão island (Cape Verde). *ECMS 2004* (Poster P-12); *Mitt. Öst. Min. Gesellschaft* 149 32 (Abstract).