



	<b>Experiment title:</b> Characterizing the electronic state of sulphur in complex sulphides through the XANES study of S <i>K</i> -edge coupled with metal(s) <i>K</i> - and <i>L</i> -edges	<b>Experiment number:</b> ME 1091
<b>Beamline:</b> ID-21	<b>Date of experiment:</b> from: 9 March 2005 to: 14 March 2005	<b>Date of report:</b> 2005.08.30
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Marine Cotte	<i>Received at ESRF:</i>
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**Report:**

A preliminary approach to *the state of sulphur in complex sulphides* (ME-821, report dated October 13, 2004) – has provided interesting results that stimulated the undertaking of a detailed study involving also the characterization of combined metals. The present experiment took profit of the energy range available at beamline ID-21 that allows to study simultaneously **S & *TM K*-edges** – *TM* being a 3*d*-transition metal (**Mn, Fe**) – and ***HM L<sub>III</sub>*-edge**, where *HM* is a heavy metal (e.g., the chalcophile elements **Ag, In, Sb**).

*Sulphides* are economically valuable minerals that gained increased interest as prototypes for technologically important materials. The crystal chemistry of sulphide minerals is dominated by three main cubic crystal structure-types: *pyrite*,  $M^{\circ} [S_2^{\square}]$  (a disulphide, with anionic dimers  $[S_2]^{\square}$ ), *sphalerite*,  $M^{\square} [S^{\square}]$  and *galena*,  $M^{\circ} [S^{\circ}]$  (t stands for tetrahedral and o for octahedral coordination, and **M** is a metallic element). Minerals with zinc blende structure are called “*tetrahedral structures*” once both atomic species are tetrahedrally surrounded by the species of opposite sign, and galena is the prototype of “*octahedral structures*”.

*Sulphosalts* configure more elaborated atomic arrangements and their chemistry is sometimes very complex. Attention is being focused on the *supertetrahedron family of chalcogenides* – the *tetrahedrites* – as a fruitful source of microporous materials for innovative applications in nanotechnologies (Li, Lane, O’Keefe & Yaghi, *Science* 283, February 1999, 1145-1147). With simplified formula  $(M^{1+})_{10}(M^{2+})_2(M^{3+})_4[S_{13}]$  – where  $M^{1+}$  represents mainly **Cu** and **Ag**, divalent ions being **Cu, Zn, Fe, Hg, Cd, Pb** and trivalent ions most frequently **Sb, As, Bi** – the cubic arrangement of tetrahedrites derives from sphalerite structure by replacing a tetrahedral cluster of four cubic closest-packing positions by one single S-atom surrounded by heavy metal ions.

An approach to the crystal chemical bases for the implementation of a data bank on sulphur in minerals [1] is a first output of the experiments.

A total of about 3000 scans in FY mode allowed to obtain 128 high quality XANES spectra:  
***K*-edge:** **S** (2.45 – 2.54 keV, 59 spectra); **Ti** (4.93 – 5.13 keV, 3 spectra); **Mn** (6.5 – 6.7 keV, 18 spectra); **Fe** (7.05 – 7.35 keV, 20 spectra).  
***L*-edge:** **Ag** (3.28 – 3.48 keV, 4 spectra); **In** (3.67 – 3.87 keV, 9 spectra); **Sn** (3.85 – 4.05 keV, 2 spectra); **Sb** (4.08 – 4.26 keV, 6 spectra); **Nb** (2.34 – 2.40 keV, 5 spectra); **Ce** (5.68 – 5.84 keV, 2 spectra).

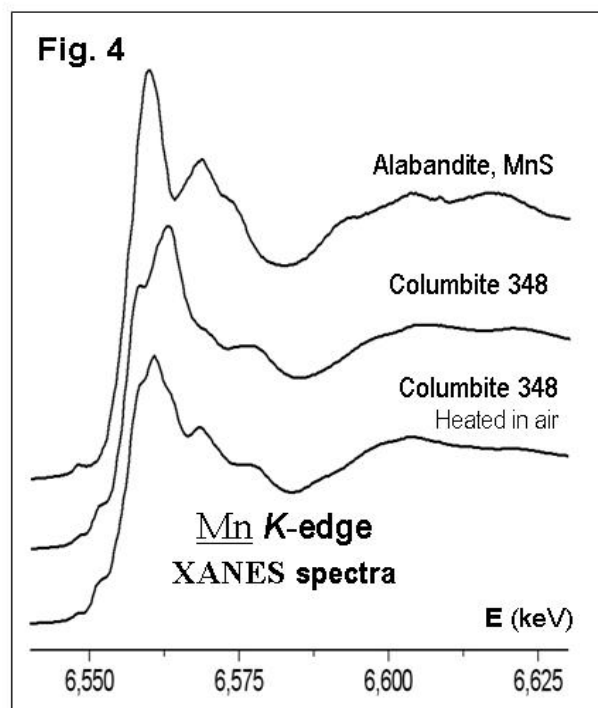
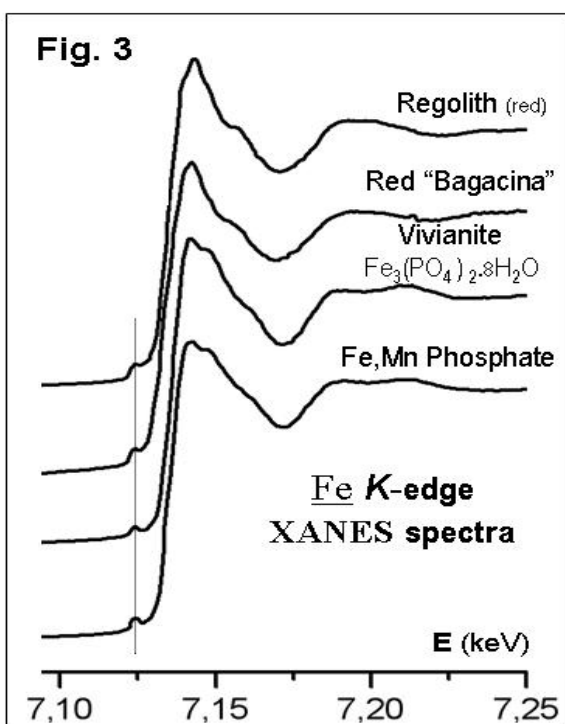
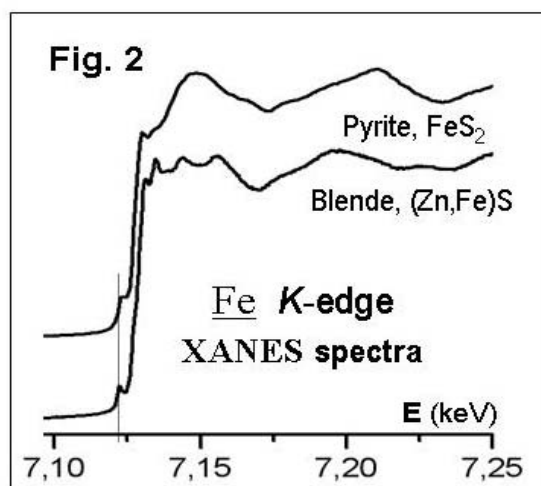
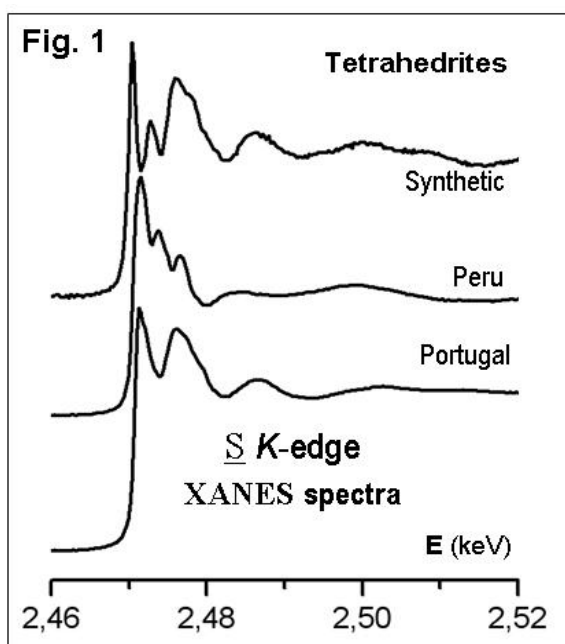
Whenever the element to study was present in a low concentration and occasionally dispersed, elemental mappings were performed to select the area to irradiate in the sample for XANES spectra collection.

Fig. 1 reproduces  $S$  1s absorption data from tetrahedrites, both natural and synthetic. These spectra are characterized by a strong white line followed by details that vary considerably depending on the population of metal ions and the degree of cationic ordering. Theoretical modelling of spectra is in progress using the FEEF code based on a multiple scattering approach.

$K$ -edge absorption spectra obtained for transition metals are illustrated in figs. 2 & 3, for  $Fe$  in sulphides and in various oxide minerals, and by fig. 4 for  $Mn$  in a diversity of model minerals, all with well-known crystal structure. These results stimulate further studies to correlate  $Fe$  state with colouring in iron-carrying materials.

$L_{III}$ -edge XANES spectra of  $Ag$ ,  $Sn$  and  $Sb$  were collected from tetrahedrites; they are still under study.

Preliminary appraisals of  $In$  and  $Ce$   $L$ -edge spectra in thin films designed for technological applications and in one model compound for each metal were also conducted with the purpose of designing further experiments.



[1] M.O. FIGUEIREDO & J. SUSINI (2005) Sulphur  $K$ -edge XANES spectra in minerals: contributions to settle the crystal chemical bases of a data bank. *15th ESRF Users' Meetg.*, Grenoble/France, February 8-9.