



Experiment title: Electronic state of sulphur atoms with an unusual metal surrounding in tetrahedrites		Experiment number: ME-589
Beamlne: ID 21	Date of experiment: from: March 5, 2003 to: March 11, 2003	Date of report: 2003.08.29
Shifts: 18 #	Local contact(s): Dr. Jean Susini and Dr. Barbara Fayard	<i>Received at ESRF:</i>
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# Beam time shared by two projects: ME-589 and CH-1457 (separate report)		

Report:

Tetrahedrites are an important group of economically valuable sulphosalt minerals with ideal simplified formula $(M^{1+})_{10}(M^{2+})_2(M^{3+})_4[S_{13}]$ where M^{1+} ions are mainly Cu with some Ag, divalent ions being Cu, Zn, Fe, Hg, Cd, Pb, and trivalent ions Sb, As, Bi, and very seldom Te.

The cubic crystal structure of tetrahedrite (*s.l.*) contains two formula units per unit cell. The atomic array derives from the arrangement in sphalerite – the prototype of “tetrahedral structures” where each one of the constituting atomic species (Zn^{2+} and S^-) is surrounded by a tetrahedron of species with opposite sign – by leaving unoccupied (vacant) four out of sixteen cubic closest-packing anion positions, and further replacing this tetrahedral cluster of vacancies (4□) by one sole S-atom.

This replacement process provides pyramidal and triangular coordination to some of the metal ions, and gives rise to a *peculiar coordination* and *binding situation* for *one out of thirteen sulphur atoms* in the chemical formula. The S-atom replacing a tetrahedral cluster of packing vacancies becomes octahedrally coordinated by six close Cu/Ag and additionally, by four Sb/As^{III} (themselves in pyramidal coordination by S^-) with the lone pair probably oriented towards that peculiar central S-atom. Such crystal chemical insight [1] emphasizes the decisive role that S K-edge XANES plays in providing a comprehensive interpretation for tetrahedrite geochemical behaviour – a feature with significant economic implications.

X-ray absorption experiments at ID-21 had then the purpose of studying the influence of the environment (*geometry and nature of metal ions coordinating sulphur*) and of *bonding effects* through changes observed in the *profile of sulphur K-edge* using *minerals with well known structure as model compounds* for different binding situations. A very good resolution was required for that purpose.

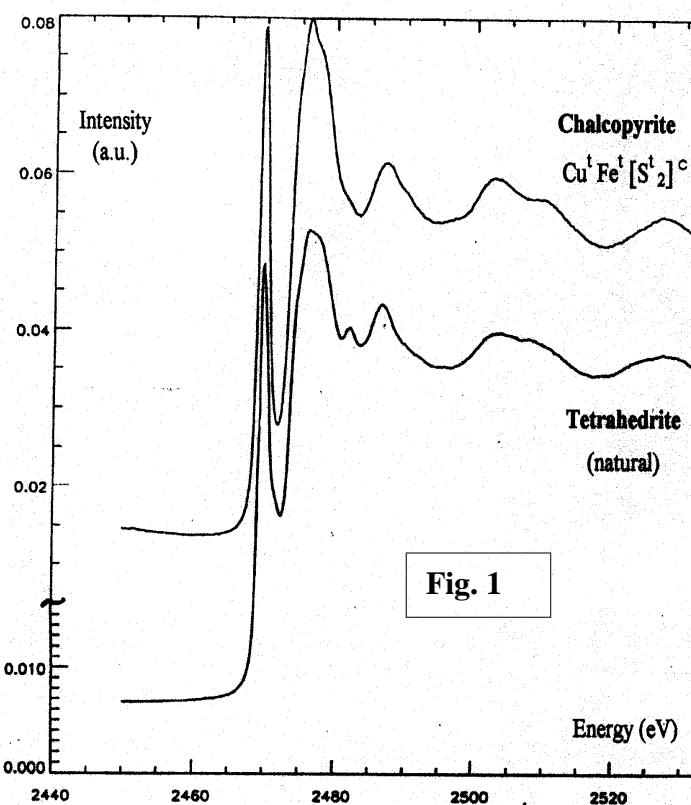


Fig. 1

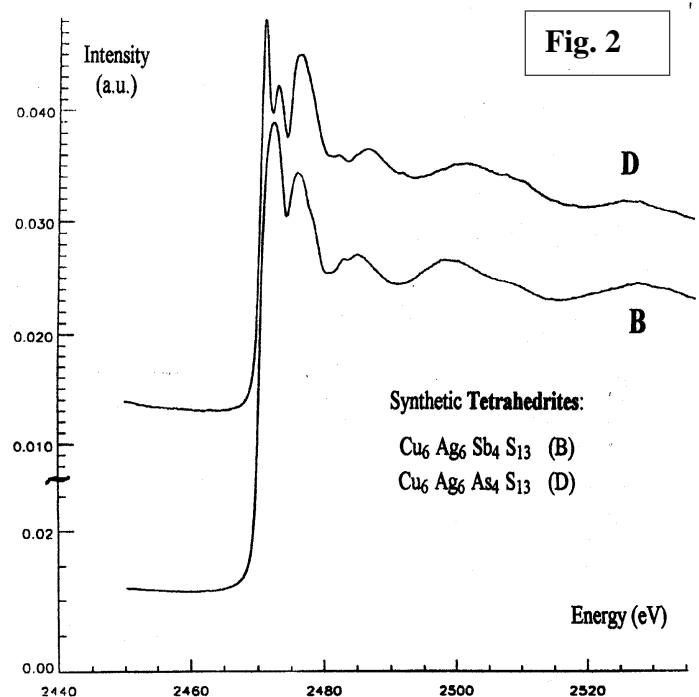


Fig. 2

The following sulphide minerals were studied: the *model compounds* galena (Pb S), sphalerite (Zn S), chalcopyrite (Cu Fe S_2) – the three minerals displaying a cubic closest packing of anions –, pyrite (Fe S_2), arsenopyrite (Fe As S), stibnite ($\text{Sb}_2 \text{S}_3$) and auripigment ($\text{As}_2 \text{S}_3$); various *natural tetrahedrites* with different chemical constitution and geological provenance, plus *synthetics* with extreme Cu/Ag and As/Sb proportions in the system Cu-Ag-As-Sb-S (the chemical homogeneity of these samples was previously checked by μ -PIXE at the Nuclear Research Institute in Lisbon).

A total of 112 scans between 2.45 and 2.53 KeV were performed to collect S *K*-edge XANES spectra (4-5 scans were enough to obtain a good quality for the spectrum).

The figures above illustrate the general trend of S *K*-edge XANES spectra from tetrahedrites, compared to the prototype mineral (chalcopyrite). The white line present in the spectra reproduced in fig.1 does not seem to occur with similar intensity in those collected from pure synthetic tetrahedrites (fig.2). The post-edge region presents interesting details in both cases.

Theoretical calculations and spectra modelling with FEFF8.10 program [2] are now in progress for the prototype minerals (model compounds), prior to an attempt for interpreting tetrahedrite spectra.

[1] M.O. FIGUEIREDO & J.A. FERREIRA (2002) Crystal chemistry of tetrahedrites revisited: considerations on significant geochemical outputs. *9th Int. Symp. Experim. Mineral. Petr. Geochem.* Zürich, March 24-27 (poster).

[2] A. ANKUDINOV, B. RAVEL & J. REHR (2000) Manual of FEFF8.10 program. *The FEFF Project*. Dept. Phys., Univ. Washington, Seattle, USA, 62 p.