



Beamline:	Experiment title: Chemical state of arsenic and copper in enargite and its oxidation products	Experiment number: MA-459
	Date of experiment: from: 25.06.2008 to: 29.06.2008	Date of report: 24.11.2008
Shifts: 12	Local contact(s): Mauro ROVEZZI	<i>Received at ESRF:</i>
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Report:

Enargite, Cu_3AsS_4 , is a copper arsenic sulphide of both economic and environmental interest. It can be a copper ore, while, on the other hand, upon oxidation it can release the toxic elements copper and arsenic. For these reasons, in recent years it has been extensively studied (see Lattanzi et al., Earth Sci. Rev. 86, 62-88, 2008). As in most sulphides, the nature of the chemical bond and the exact chemical state of the elements are complex. It is generally assumed that copper is in a monovalent state (Cu(I), whereas As is in a pentavalent state (As(V), but actually there is much to clarify about the exact chemical state of copper and arsenic in enargite (see the literature in the proposal for this experiment). As pointed out above, such a knowledge is not of merely academic interest, because a detailed understanding of the oxidation process of enargite has important implications both for environmental issues and for mineral processing.

The XAS spectra at the Cu K (8979 eV) and As K (11867 eV) edges were collected at room temperature in the transmission mode. The starting materials were two carefully selected natural enargite samples, freshly broken and ground just before spectra collection. Previous experience indicates that in these conditions enargite oxidation is minimal, i.e. these samples reasonably approach the status of "pristine" enargite. Starting from these samples, two set of treated ("oxidized") samples were prepared: 1) by high energy grinding (performed by Paolo Scardi at University of Trento, Italy); 2) by heating at 250° C in oxygen atmosphere, performed at GILDA with the reaction cell described by Longo et al. (J. Synchrotron Rad. 12, 499-505, 2005). In the original proposal, this second type of treatment was planned *in situ* in the experimental hutch of the beamline, with concomitant acquisition of the XAS spectra. However, preliminary tests indicated that runs of several hours were required to achieve a recognizable reaction. Therefore, the treatment was performed *ex situ* (i.e., the enargite pellet was first placed in the cell and allowed to react, then transferred to the beamline for spectra acquisition).

The collected spectra were compared with a fairly large set of standard compounds, for a best comparison of the edge position and XANES features. These standards included, for copper: chalcocite, Cu_2S ; covellite, CuS ; chalcopyrite, CuFeS_2 ; bornite, Cu_5FeS_4 ; a tetrahedrite of approximate composition $\text{Cu}_{10}\text{Zn}_{1.4}\text{Fe}_{0.4}\text{Hg}_{0.2}\text{Sb}_{3.7}\text{As}_{0.3}\text{S}_{13}$; malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$; synthetic Cu_2O and CuO ; and metallic copper, placed downbeam of the sample chamber in all scans to set a reference point for energy calibration. A standard labeled as CuCl was also considered, but it

proved to be oxidized, and was discarded. For arsenic, the standards were: GaAs, with the same function of general reference as metallic copper for Cu; arsenopyrite, FeAsS ; a tennantite of composition $\text{Cu}_{10.4}\text{Zn}_{1.7}\text{Fe}_{0.4}\text{Sb}_{0.5}\text{As}_{3.3}\text{S}_{13}$; realgar, As_4S_4 ; synthetic NaAsO_2 , As_2O_5 , $\text{Ca}_3(\text{AsO}_4)_2$. The realgar spectrum proved fairly poor, because of a significant presence of contaminant cinnabar (HgS), giving rise to a marked absorption edge at ~ 12300 eV.

In the first two days, the experiment was hampered by beam failures (including a problem with Linac), and bugs with the beamline software. No serious troubles occurred in the last two days. Some scans of both samples and standards were actually repeated to achieve a better statistics.

The overall results are quite good and definitely interesting. Each compound shows distinctive edge and XANES regions, allowing a meaningful comparison of the chemical states.

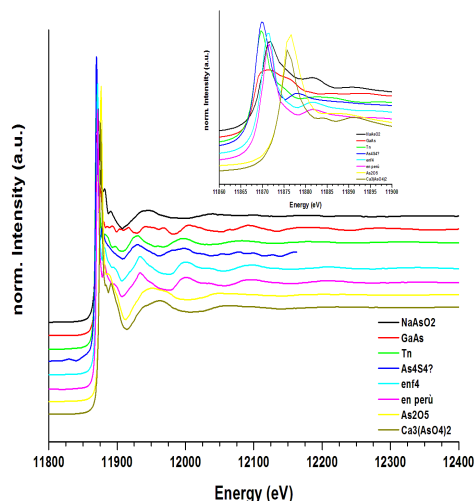


Fig. 1 – XAS spectra, As K edge

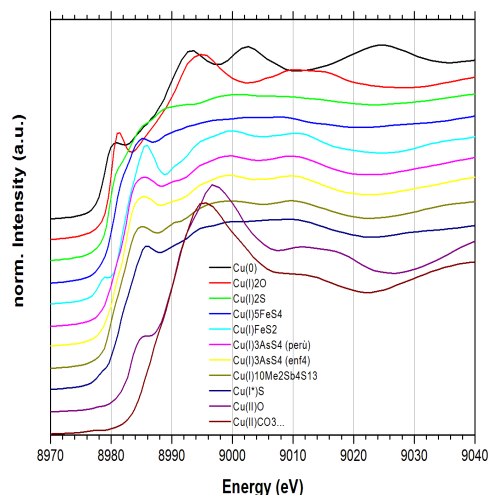


Fig. 2 – XAS spectra, Cu K edge

The most evident feature is the different edge position of compounds with nominally similar valence states: enargite, where As is considered pentavalent, is definitely different from arsenate, and more similar to arsenite; the same applies for the Cu K edge, where the nominally Cu(I) compounds (enargite, bornite, chalcocite, chalcopyrite) all have different edge and XANES features. This finding emphasizes the general concept that valence states should be considered cautiously in compounds having a complex chemical bonding such as sulphides.

Treated enargite samples show, in general, subtle differences from untreated enargite. The differences are more evident in the spectra at the As edge; the most important change is apparently recorded by the sample ground for 64 hrs in the presence of water. A quantitative analysis of both XANES and EXAFS portions of the spectra is under way.

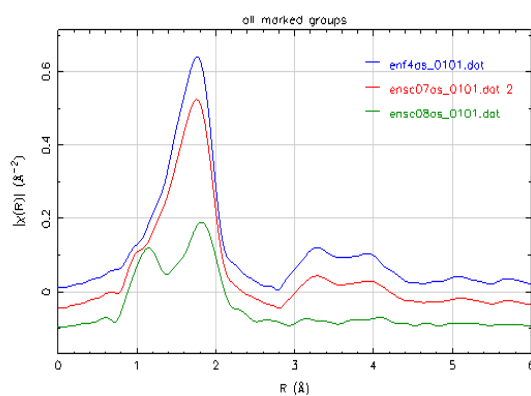
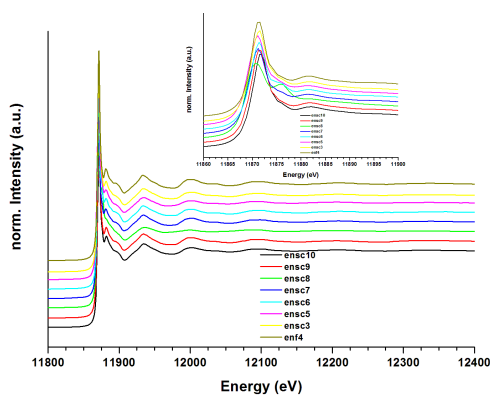


Figure 3. Left: XAS spectra at the As K edge of untreated (enf4) and treated (ensc) enargite; right: details of some spectra in R space