



	<b>Experiment title:</b> Structural characterisation and crystal chemistry of As in a geogenic anomaly (Val di Pecora, Southern Tuscany, Italy)	<b>Experiment number:</b> ME-1182
<b>Beamline:</b> BM-08	<b>Date of experiment:</b> from: 18/11/2005                      to: 21/11/2005	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Mauro Rovezzi	<i>Received at ESRF:</i>
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## Report:

### Introduction

The present experiment was aimed to assess the speciation of Arsenic in a complex and heterogeneous natural travertine host, mainly constituted by calcite,  $\text{CaCO}_3$ . Specific goals to be pursued during the assigned time were:

- 1) the determination of the existence of As(III) in the proposed host, through the shift of the As K-edge
- 2) the determination of the structural coordination for As(V), and eventually for As(III) in the carbonate environment

The natural investigated sample comes from the Val di Pecora (Southern Tuscany, Italy), a case study area for arsenic mobilization in travertines and other Quaternary sediments and rocks largely from natural, non-anthropogenic sources.

### Experiment

The samples provided for the experiments are listed in Table 1. They consist of a set of seven standards (including one natural scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), and three natural samples: one travertine sample (F1b) and two Fe-oxide rich samples taken from sediments above (siliciclastic horizon, T2) and below (fan deposit, C5) the travertine in the stratigraphic sequence. In order to check for any preferential partitioning of arsenic between carbonate-rich and Fe-oxide rich assemblages in the travertine, in addition to bulk sample we have also analyzed two fractions separated by from Frantz Isodynamic Magnetic Separator, labelled, respectively, as “magnetic” and “non-magnetic”.

**Table 1 – investigated samples**

Standard Compounds	Working label	origin	As at%	Mode
As <sub>2</sub> O <sub>5</sub>	S1	commercial	28.57	Transmission
As <sub>2</sub> O <sub>3</sub>	S2	commercial	40	Transmission
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	S3	commercial	15.38	Transmission
NaAsO <sub>2</sub>	S4	commercial	14.29	Transmission
NaH <sub>2</sub> AsO <sub>4</sub> ·7H <sub>2</sub> O	S5	commercial	12.5	Transmission
FeAsO <sub>4</sub> ·2H <sub>2</sub> O	S6	natural	8.33	Fluorescence
"FLUORESCENCEeOOH"(As)	S7	synthetic	0.03	Fluorescence
Samples	Working label	origin	As at%	Mode
F1b, Calcite-As "bulk"	KF1	natural	0.05	Fluorescence
F1b, "non-magnetic" fraction	KF2	natural	~0.05	Fluorescence
F1b, "magnetic" fraction	KF3	natural	~0.05	Fluorescence
Fan deposit C5	C5	natural	0.24	Fluorescence
Interlayered sediment TR2	TR2	natural	0.12	Fluorescence

The materials studied in Transmission mode were prepared as pellets mixing together a few mg of each sample with cellulose. The remaining samples, analysed in Fluorescence mode, were prepared as thin films deposited onto Millipore paper disks from aqueous (deionized water) suspensions. After deposition, the films were sealed by Kapton tape. In all cases, the optimum weights were computed through the "XAFS mass" program.

The spectra were collected at the As K edge (11876.7 eV). Most samples were analyzed by both transmission and fluorescence modes; only the best obtained results are indicated in Table 1. A 13-element HP-Ge detector was employed. To minimize instrumental noise, the chamber was cooled with liquid nitrogen down to about 80° K.

Spectra were acquired from 11800 to 13100 eV, in 0.8 to 10 eV steps, counting times 3 to 10 seconds per step. For samples with low counting rates, scans were repeated 2 to 4 times. The overall data acquisition for each sample required 1 to 5 hrs.

Owing to small problems during the spectral acquisition (beam absence; modification of the experimental set up), only the standards S1 through to S5 and the samples KF1 through to KF3 were investigated with an adequate count statistics. Preliminary spectra were, however, collected on all the remaining samples.

## Results

A preliminary elaboration of raw data was performed by means of a FORTRAN software (by C. Meneghini and F. Bardelli) dedicated to the extraction of the EXAFS signal avoiding spurious modulations of the EXAFS spectrum. A selection of the results is reported as graphs in Figs. 1 and 2. Although further refinement of the analytical data is needed for a more detailed interpretation of the results, some preliminary points can be evinced :

## A) Standards

- 1) the five standards spectra, which have been obtained in Transmission mode, are of very good quality (Figg 1-3);
- 2) a relevant difference of the As(III) standards with respect to the As(V) standards is evident both in the edge position and in the XANES region, in agreement with the marked structural differences of the two classes of compounds.

## B) Natural Samples

- 3) the natural samples' spectra are still of good quality, although affected by a larger noise (Fig. 2) with respect to standards.
- 4) the study of the first coordination shell is, in any case, fully allowed
- 5) a non-negligible fraction of As(III) can be devised from the edge position of the KF1 and KF3 samples, at least. In this latter sample, the trivalent Arsenic constitutes the main valence state.

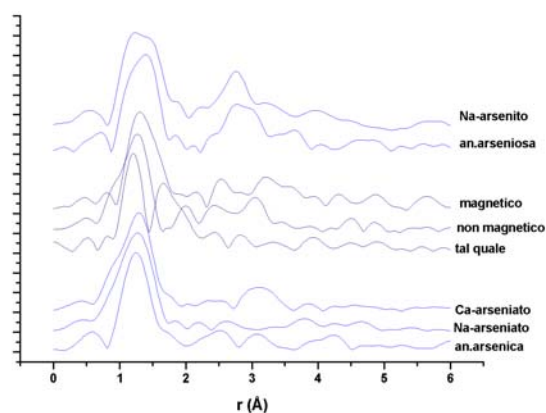
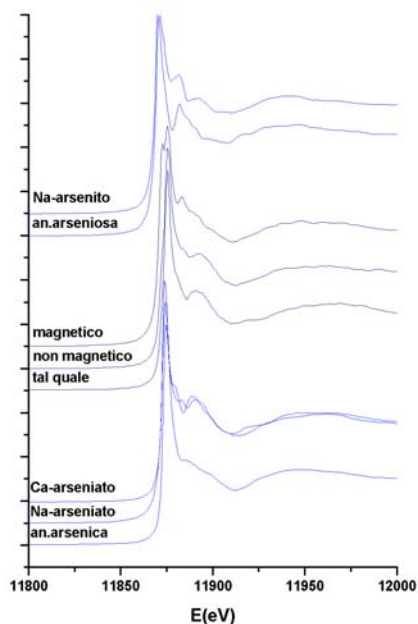


Figure 1

Figure 2

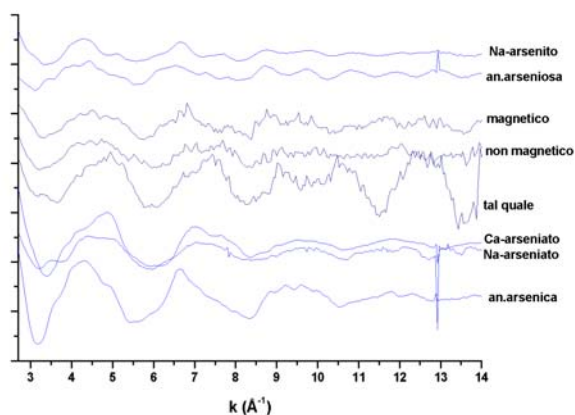


Figure 3