

**Experiment title:**

Study of arsenic retention onto biotite using x-ray absorption spectroscopy

**Experiment number:**

EV-6

<b>Beamline:</b>	<b>Date of experiment:</b> from: 12/06/2013 to: 17/06/2013	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Angela Trapananti	<i>Received at ESRF:</i>

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**Report:**

We have acquired the XAS spectra at the As K-edge on a series of different biotite samples (fresh and weathered).

These samples came from the Greater Augusta region of Maine where the arsenic concentrations has been found up to 325 g L<sup>-1</sup> in groundwater of both sulfidic and calcareous metasedimentary rocks. A unique aspect of this study region is that geologic formations have undergone prograde metamorphism resulting in a transition from slightly altered marine shales (phyllites and slates) towards increasingly metamorphosed schists and gneisses as one progresses from northeast to southwest across the study area. To our knowledge, this study is the first that addresses arsenic variation in rocks having undergone progressive metamorphism.

Total iron, arsenic and manganese in pulverized rock powders were first analyzed by X-ray fluorescence (XRF). Moreover, a microwave-assisted nitric acid digestion (EPA Method 3051a) was employed to assess potential mobility of arsenic. In an attempt to isolate certain minerals, rock powders underwent the following mineral separation procedure at USD. First, a hand magnet was used to separate strongly magnetic minerals, including magnetite and pyrrhotite. A few grams of this non-magnetic rock powder was then added to a 50 mL centrifuge tube and mixed with LST Heavy Liquid were left to settle until the heavy minerals sank and the lighter minerals floated.

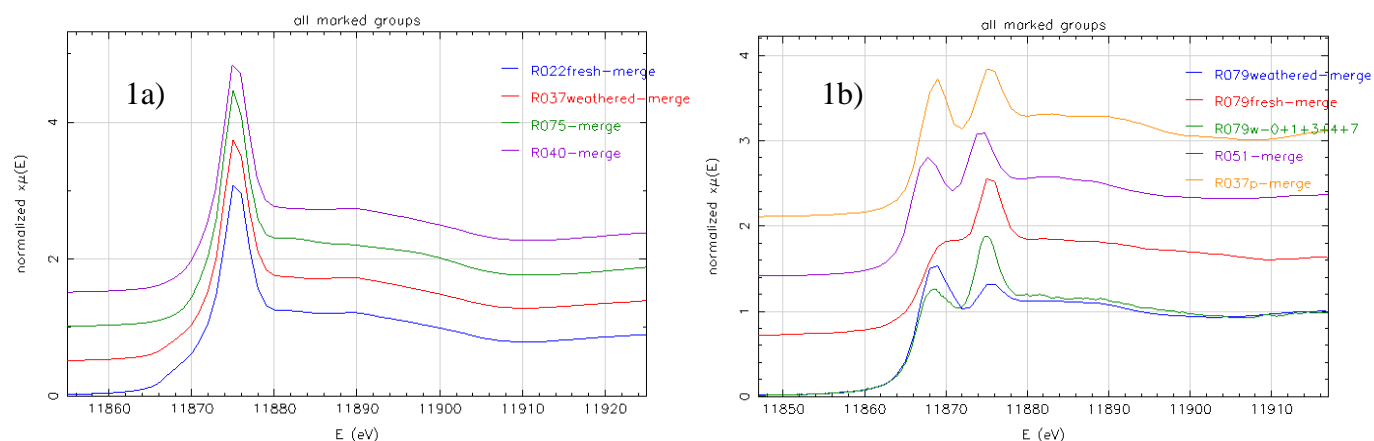
The resulting outcome was rock powders separated into magnetic, float, and sink fractions for individual analysis by As K-edge X-ray absorption spectroscopy (XAS). Unfortunately, the magnetic

fraction yielded volumes too small for XAS analysis and the presence of tungsten in the LST Heavy Liquid produced a tungsten signal overlapping the K $\alpha$  fluorescence line of arsenic.

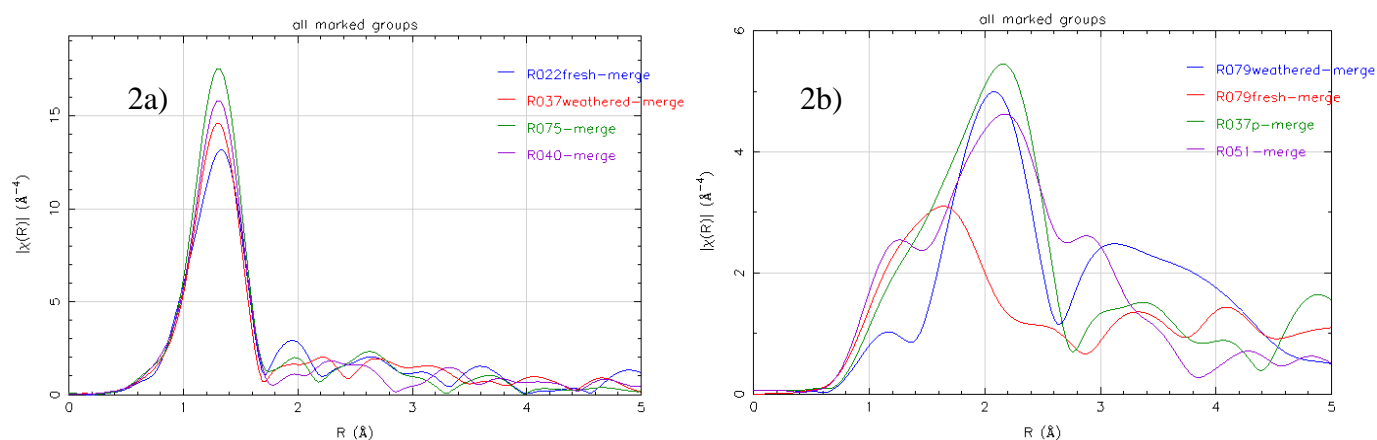
The remaining samples analyzed by As K-edge XAS were performed on bulk non-separated rock powders representing the average coordination environment and speciation of arsenic in each rock powder. Samples from the low and medium grade rocks containing the greatest arsenic concentrations were selected for XAS analysis (Arsenic concentration ranging from 100 ppm to 450 ppm).

As-K edge ( $E=11867$  eV) x-ray absorption spectra (XAS) were collected at the GILDA-BM08 beamline in fluorescence geometry. Considering the aperture of the main slits (1 mm) at the source (bending magnet) and the monochromator crystals (Si 311), the energy resolution was estimated to be 0.5 eV at 12 KeV. As K $\alpha$  fluorescence intensity was measured at room temperature using a 13-element ultrapure Ge multidetector (ORTEC). Arsenic deposited on a membrane was used as reference after the sample. A minimum of three spectra with long integration time for energy point (20 s) were collected for each sample, and averaged, after interpolation, to improve the statistics of the data, while up to 9 scans have been collected on the lower concentrated samples.

We expected different As oxidation states in the fresh and weathered samples. In fact, the fresh samples should be dominated by the more toxic As speciation (3+), while the weathered rocks should contain As mainly in the 5+ oxidation state. For this purpose, the XANES spectra related to the fresh and weathered samples were acquired as showed in the Figure 1. We can note that, despite the sampling of the rocks, both R022 fresh and R037 weathered contain only the As(V) component, while the contribution of the As(III) speciation was expected in the R022 fresh sample (Fig. 1a).



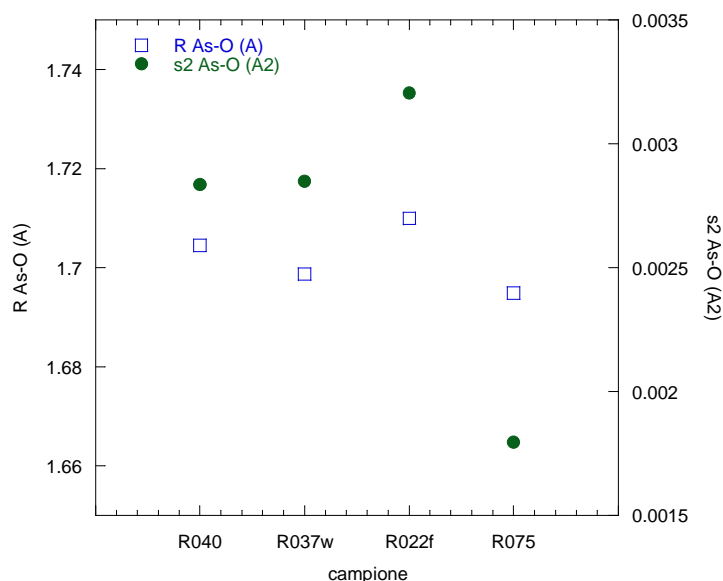
**Figure 1** XANES spectra of the more concentrated As rocks. On the left side, the XANES spectra of the samples with prominent As (V) speciation (1a). On the right side, the XANES spectra of the samples with mixed valence (1b).



**Figure 2** The Fourier Transforms related to the same samples analyzed in the Fig.1.

For the samples reported in the Figure 1a the main peak at  $1.3\text{\AA}$  is related to the As-O bond, where the absorber atom is surrounded by 4 O atoms at the real distance of  $1.7\text{\AA}$ . The further contributions at higher

distances mainly due to the scattering with Fe, Mg, Mn and O are strongly suppressed, indicating that a large disorder occurs in the structure of these samples. The As-O distances and the related mean-square relative displacements (MSRDs) are shown in Figure 3. Comparing these results with the Charnock study on the As contaminated garnet (from the Central Oslo rift) [1], where the As 5+ replaces the Si 4+ site, we find a good agreement. Since we know that the rock powder measured are extracted from a region where biotite is the main mineral in the soil, we can conclude that also in the biotite the As 5+ atoms replace the Si 4+ site, as shown by the As-O distances obtained by fitting procedure. On the other hand, it was very difficult to extract quantitative informations on the local atomic distribution around the As atom for the samples reported in Figure 1b. In fact, despite the high number of spectra for each sample and the long integration time (20 s/pt), it was not sufficient to minimize the noise for  $K > 9 \text{ \AA}^{-1}$ . Several contributions seem to affect the Fourier transform in the spatial range  $1.3 \text{ \AA} < R < 3.0 \text{ \AA}$ . In particular we can distinguish the As-O and As-S contributions comparing the spectra directly with the standards.



**Figure 3** As-O distances and related MSRDs in the samples reported in the Fig.2b.

The EXAFS analysis on the samples with mixed valence state could provide important informations on the mechanics of As release in groundwater.

[1] J. M. Charnock et al., *American Mineralogist* **92**, 1856 (2007).