	Experiment title: Chemical state of arsenic in low concentration environmental samples	Experiment number: 08-01-948
	Beamline:	Date of experiment: from: 24 October 2013 to: 29 October 2013
Shifts: 15	Local contact(s): F. D’Acapito	Date of report: 31 Oct. 2013 <i>Received at ESRF:</i>
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Preliminary report:

The aim of the proposal was to constrain the chemical state (“speciation”) of arsenic in sediments and soils from two Italian regions, Sardinia and Veneto. Although of different geological nature, these samples may contain As amounts in the order of several tens or even hundreds of mg/kg, thus exceeding the limits established for soils by Italian laws (20 mg/kg for residential use, 50 mg/kg for industrial use). In both cases, local authorities expressed concern for possible adverse effects of this arsenic presence, therefore the issue is of direct applied interest.

The study involves a much larger number of samples than it was possible to handle in a single experiment, therefore this is an exploratory study that should be substantiated by additional data. Fortunately, the excellent performance of the beamline and the ring stability throughout the experiment (we experienced only a short failure on 25 October), allowed us to collect several meaningful spectra. For both areas, we investigated samples with a wide range of arsenic concentrations (6 to 560 mg/kg). For the lowest concentrations, the task was indeed challenging. To improve the quality of the data, all spectra were collected at liquid nitrogen (80° K) temperature. This setup was greatly facilitated by a) the good performance of the cooling system, that allows uninterrupted operation for several days, b) the use of a large sample holder, where up to 18 samples can be mounted, minimizing the need for warming up and opening the experimental chamber for sample changes. All sample spectra were collected at the As K edge (11867 eV) in the fluorescence mode with a 12-channel detector. Because several samples contained Fe in the order of several units percent weight, it was necessary to attenuate the strong fluorescence signal of this element by interposition of an Al foil between the chamber and the detector. For energy calibration, a reference spectrum of GaAs was collected throughout the experiment. For comparison with sample spectra, the spectra of a number of standard compounds were collected in transmission mode – InAs, NaAsO₂, Ca₃(AsO₄)₂, arsenopyrite (FeAsS), and enargite (Cu₃AsS₄), each representing a different chemical state of arsenic (see Di Benedetto et al., 2011).

The experiment was quite successful in terms of quality of the acquired spectra. We were able to achieve the minimum goal (a well resolved XANES portion) even for the most dilute samples with reasonable (up to 8 hrs) acquisition times. Comparison with standard spectra clearly emphasize the presence in most samples the presence of a main chemical state of arsenic, most probably As (V) bound to oxygen. However, in many samples a second (or more?) chemical state is clearly discernible, either as a distinct peak at lower energies, or as a shoulder on the low-energy side of the main peak. When clearly expressed, this peak seems to suggest a chemical state similar to arsenopyrite, i.e. in these samples there is a component of arsenic bound to a sulphide mineral.

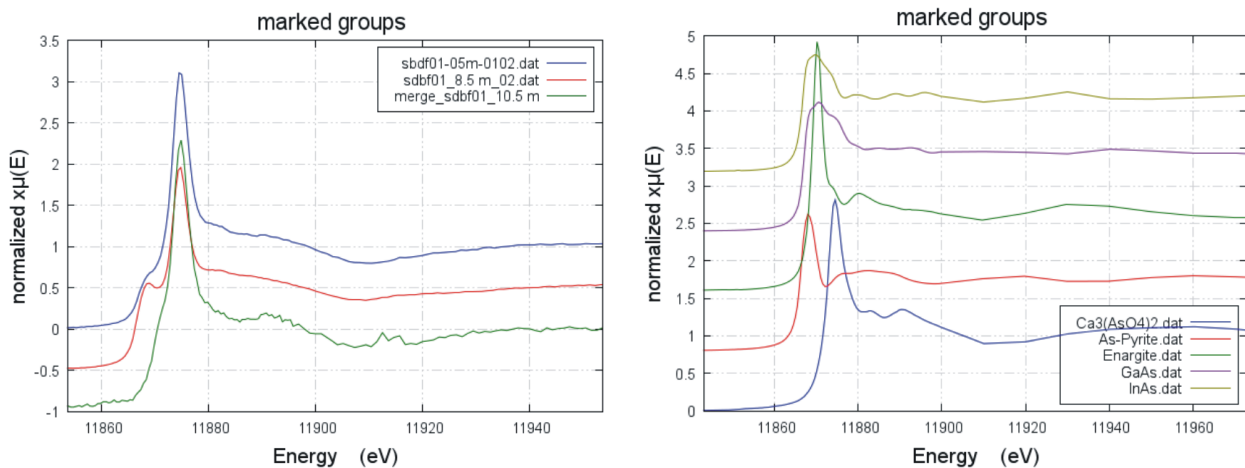


Figure 1. Left: some representative spectra of the studied samples. Right: some standard spectra

A quantitative definition of the components will be attempted by a Linear combination fit routine. The interpretation of the EXAFS portion of the spectra may present some more problems, because many spectra become noisy at $k > 6$; however, we should be able to fit at least the first shell, that will clarify when arsenic is bound to oxygen or to sulphur.

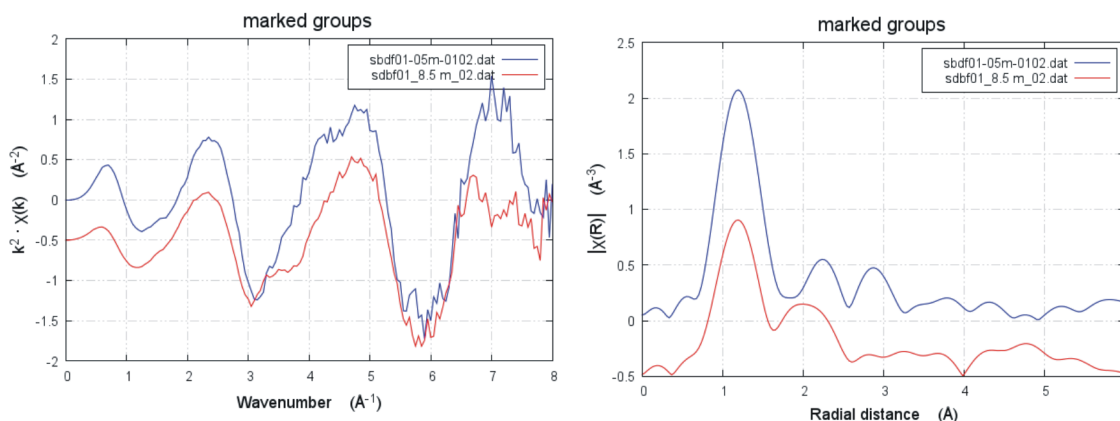


Fig. 2. Some representative spectra of the studied samples in k space (left) and R space (right)

Reference cited: Di Benedetto F., Da Pelo S., Caneschi A., Lattanzi P. (2011) - Neues Jb. Mineral. Abh., 188, 11-19

This is a preliminary report submitted immediately after the conclusion of the experiment as a support to the proposal for continuation of the experiment, and will be replaced by a more complete report upon further elaboration of the acquired data