ESRF	Experiment title: **Role of microorganisms on oxidation state and trapping mechanisms of As by iron oxides.** **Rôle des microorganismes sur l'état d'oxydation de l'arsenic et son piégeage par les oxydes de fer**	**Experiment number**: 30-02-633
Beamline:	**Date of experiment**: from: 12 june 2003 to: 17 june 2003 01 october 2003 to : 07 october 2003	**Date of report**: 10 / 03 /2004
Shifts:	**Local contact(s)**: Olivier Proux, Jean-Louis Hazemann	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Guillaume MORIN*, François GUYOT* , sophie LEBRUN*, Georges ONA-NGUEMA* LMCP UMR7590 - Paris6&7 – IPGP, 140 rue de Lourmel 75015 Paris

Philippe BARANGER, BRGM, 3, avenue Claude Guillemin - BP 6009 - 45060 Orléans Cedex 2

Jean-Christian PERSONNÉ, Hydrosciences, UMR 5569 CNRS- Montpellier II-IRD, CC57, 34095 Montpellier cedex 05.

Violaine BONNEFOY, UPR 9043 CNRS, Lab.Chimie Bacterienne, 31 ch. Joseph Aiguier, 13402 Marseille Cedex 20

Report:

EXAFS and XANES data were recorded at the As-K edge (11 869 eV) using a Si(220) monochromator at the BM30B/FAME beamline. Data were essentially collected at 10K. Most data were recorded in fluorescence mode using a 30 elements Ge - array detector completed by a 3$\Delta\mu$ Ge filter to attenuate elastic scattering and Fe fluorescence from our Fe-rich samples. Thanks to dynamic horizontal focusing by the second monochromator crystal, we had a very high flux at 12 keV, despite FAME is a bending magnet beamline. By comparison with previous experiments we carried out on other beamlines with samples having similar chemical compositions, the flux on the sample on FAME was not more than an order of magnitude lower than that delivered by high flux undulator beamlines as ID26. Thanks to horizontal focusing, energy resolution was also very good, about 0.5 eV.
EXAFS and XANES data were recorded in step-scan mode after recording few quick-XANES spectra in order to check for unwanted photo-oxydation or reduction of the samples under the beam.

From an experimental point of view, we showed thanks to quick-XANES data that the photo-oxydation of As(III) by Fe(III) under the beam is severely slowed at liquid He temperature (Figure 1). It is also noticeable that the rate of As(III) oxidation thoroughly increases with increasing Fe(III)/As(III) ratio in the sample, as illustrated in Figure 2.

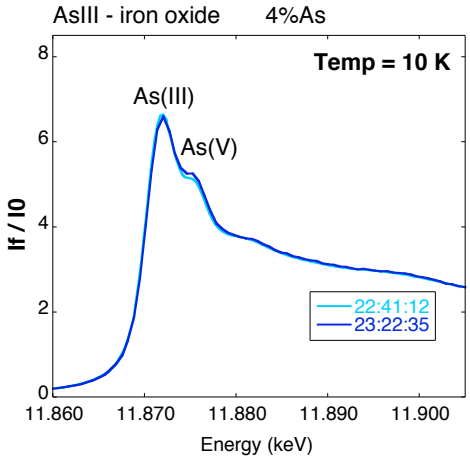

Figure 1. As K-edge XANES spectra recorded in fluorescence mode at 10K in oct 2003 at FAME. The sample consists of an iron-oxide containing 4 wt% As. The rate of As(III) photo-oxidation is enough slow at this temperature (compared to 300K, Figure 2) to record full EXAFS data in 40 mn step scans without changing the As oxidation state.

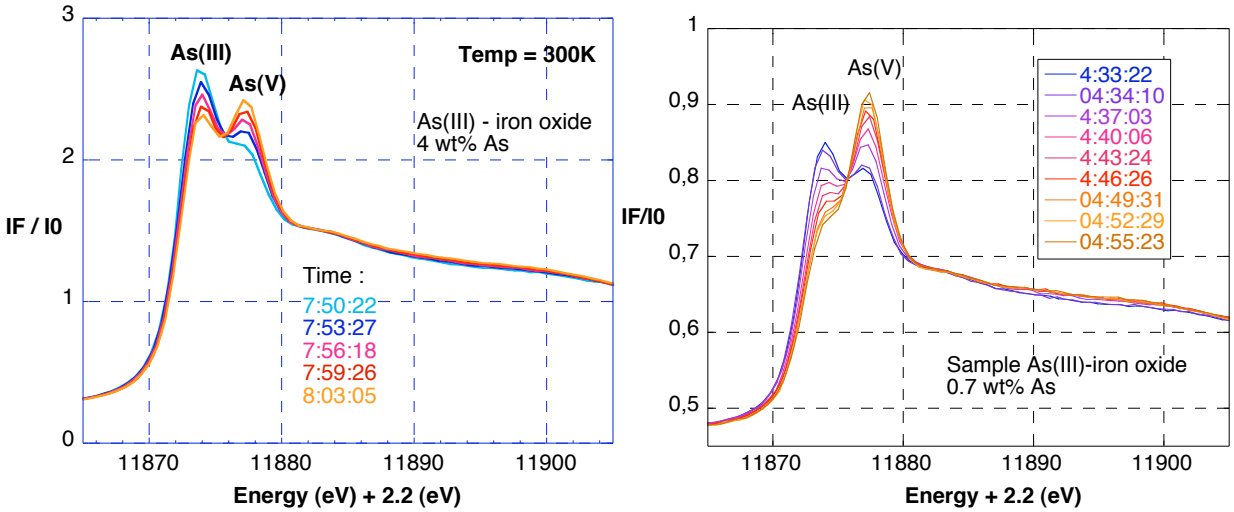

Figure 2. As K-edge quick-XANES spectra recorded in fluorescence mode at 300K on ID26 in 2002. The samples consists of iron-oxides containing 4 and 0.7 wt% As. (Left sample is the same as in figure 1). The rate of As(III) photo-oxidation under the beam increases whith decreasing As(III) concentration in the sample.

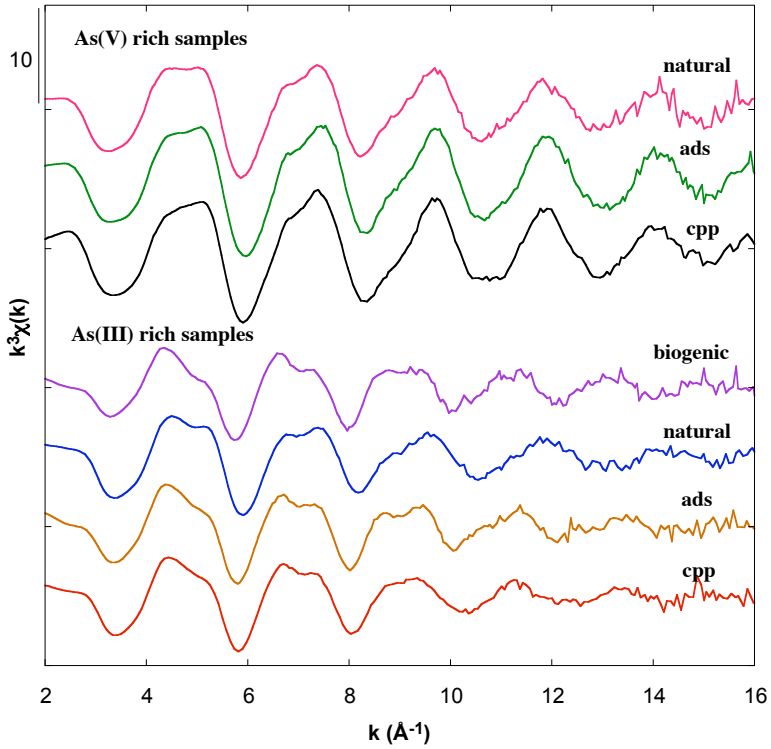

Figure 3. Representative As K-edge EXAFS spectra recorded in fluorescenece mode at 10K during the oct. 2003 run. Samples consists of iron-oxides containing 1 to 4wt% As. Although BM30B deliver a high flux on the samples, 5 to 10 scans of 40 mn in k-scan mode were necessary to get reliable S/N ratios because of the very high Fe K fluorescence background. The set of samples shown here includes natural and synthetic arsenic doped iron oxyhydroxides produced by iron and/or arsenic oxidizing bacteria in acid mine drainage environment. Arsenic coprecipitates with - and sorbs onto - bacterially produced iron-oxides, the redox state of arsenic in the solid depending on the ability of bacteria to oxidize As(III) into As(V). Natural samples are compared to synthetic ones prepared by biotic or abiotic pathways. Natural samples contain a mixtture of AsIII and AsV. This difficulty will be overcomed by using linear decomposition of the spectra.

Abstracts

Morin et al. 2004. Structure and reactivity of nano-crystalline As-Fe oxy-hydroxides in acid mine drainage. Goldschmidt Conf. Copenhague.

Lebrun et al. 2004 Mineralogy of As-Fe precipitates in acid mine drainage. the role of acidophilic bacteria. EGU Nice.

Ona-Nguema et al. 2004 Biolmineralogical processes controlling arsenic mobility in anoxic environments. EGU Nice