ESRF	Experiment title: **PDF analysis of FeSe, $FeSeO_3$ and As-bearing nanoparticles of environmental relevance**	**Experiment number**: EC262
Beamline: ID15B	**Date of experiment**: from: 12/12/07 to: 16/12/07	**Date of report**: 10/3/08
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Names and affiliations of applicants (* indicates experimentalists):

*** Alejandro Fernández-Martínez**

Equipe de Géochimie de l'Environnement, LGIT-UJF, BP 53, 38041 Grenoble, France

*** Gabriel J. Cuello**

Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France

Andre Burnol

BRGM, Environment and Process Division, 3, avenue Claude Guillemin, BP 6009, 45060 Orléans Cedex 2, France

Laurent Charlet

Equipe de Géochimie de l'Environnement, LGIT-UJF, BP 53, 38041 Grenoble, France

Report

The main objective of this experiment is the use of the Pair-Distribution Function (PDF) technique:

1. To study the structure and size of ferrihydrite nanoparticles with sorbed As(III) and As(V) before and after of a reductive dissolution process.
2. To study the structure and size of FeSe and FeSeO3 nanoparticles precipitated in anoxic conditions.

The experiment was initially designed (at the time the proposal was written) to be performed at ID31, beamline equipped with energy analizers, which facilitates the data correction procedure (no Compton scattering correction, for instance). However, the assignment of beamtime in ID15B has allowed us to use the RA-PDF technique[1], revealing the excellent capabilities of the beamline, with low background in fast acquisition times, and a very good resolution. The 2D Pixium detector was used in the experiment.

The RA-PDF technique makes use of a 2-dimensional detector to collect the hole diffraction pattern at the same time. This makes the measurements much faster, in detriment in this case of some resolution, and of some extra time employed for data correction. All the inelastic scattering (and the eventual fluorescence) is so integrated within the data, which makes corrections harder. However, all the corrections are today perfectly understood and the ID15B setup has shown a resolution good enough for our nanoparticulated samples, with broad peaks and oscillations. The fast measuring times (15 seconds for each sample) allowed us to measure four times the number of samples initially proposed. In addition to the originally proposed, we have included imogolite samples (mineral nanotubes), mackinawite, calcite precipitated with Se(0) nanoparticles and some standards (Ni, LaB_6, Fe). All the samples (except the standards) present broad peaks in the diffraction patterns when measured in our lab X-ray equipment (Cu radiation). This broadening comes mainly from the fact that these samples are 'nanoparticulated', which decreases their coherent domain size. The PDF technique is perfectly adapted to study the structure of this kind of materials.

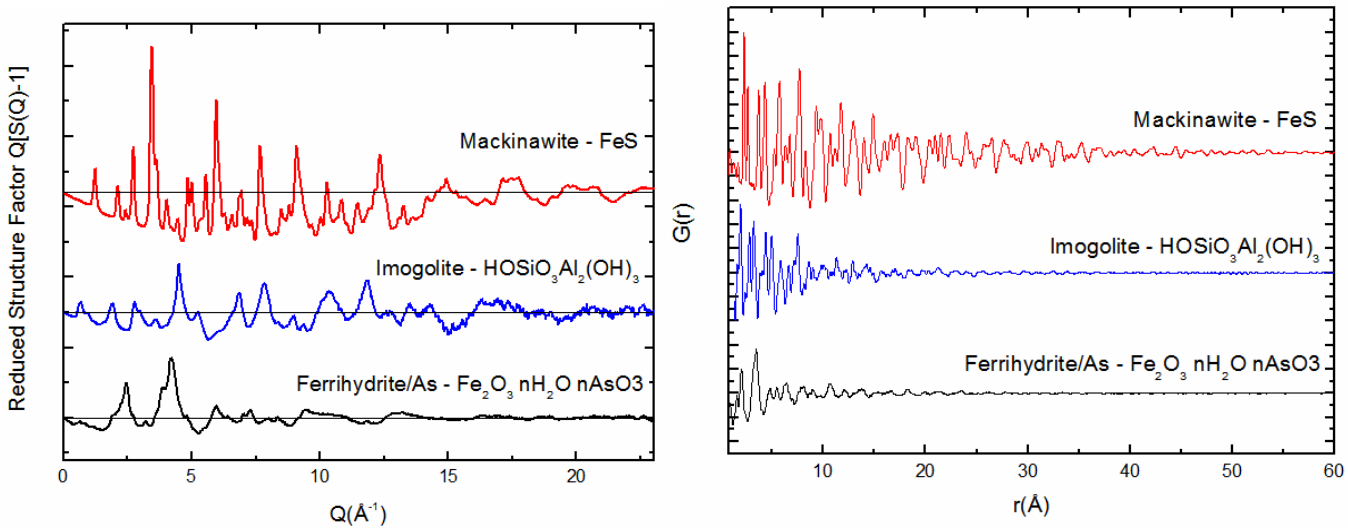

Figure 1. *Left*: Reduced structure factor Q[S(Q)-1] of Mackinawite, Imogolite and Ferrihydrite with sorbed As. *Right*: PDF functions for the same set of samples.

The Q[S(Q)-1] function for three samples is presented in Figure 1 (left). Significative diffuse scattering is observed at high Q, in the form of an oscillating signal.

The data analysis was not finished by the time this experimental report was written. However, some PDFs have been already extracted. We present in Figure 1 (right) the PDF functions for imogolite nanotubes, ferrihydrite and mackinawite. Different features can be observed: the diameter of mackinawite nanoparticles (assuming a spheroidal shape) can be estimated to be of around 6 nm, distance at which no more peaks are found in its PDF. A fit of the PDF with a refinement of a 3D structural model has been started. The interpretation of Imogolite's PDF is more difficult: Imogolite's shape (nanotube) makes that the modelling of the PDF more complicated. A detailed study of the first peaks has shown differences with the known structural model of natural Imogolite[2]. Ferrihydrite presents a size of around 25 Å in diameter, which is acceptable for a 2-lines ferrihydrite. A detailed study of the low-r peaks is going on in order to determine the presence or not of sorbed As and of other precipitates.

Data analysis is currently going on, using different software to perform fit of the obtained PDFs. In the case of Imogolite, a new structural model which fits with our data is being constructed.

The experiment has been very successful. Information on the size and local structure of the samples has been obtained. Main difficulties with the data analysis come from certain uncertinties in the exact stechiometry of some of the samples. An accurate information of the composition is required to perform Compton and other corrections.

References

[1] P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey, and S. J. L. Billinge. *Rapid-acquisition pair distribution function (RA-PDF) analysis.* Journal of Applied Crystallography, **36**, 1342-1347 (2003)

[2] P.D.G. Cradwick, V.C. Farmer, J.D. Russell, C.R. Masson, K. Wada, and N. Yoshinaga. *Imogolite, a hydrated aluminum silicate of tubular structure.* Nature, Phys. Sci., **240**, 187-189 (1972).