ESRF	Experiment title: **Se(IV) / Fe(II) on imogolites: sorption and redox processes**	**Experiment number**: CH2300
Beamline: BM20	**Date of experiment**: from: 3/2/07 to: 6/2/07 from: 12/2/07 to: 12/2/07	**Date of report**: 20/2/07
Shifts: 9	**Local contact(s)**: Andreas Scheinost	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*** Alejandro Fernández-Martínez, * Gabriel J. Cuello**

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

*** Laurent Charlet**

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

*** Gabriela Román-Ross**

Universidad de Girona, Dpt. de Química, Campus de Montilivi 17071 Girona, España

*** Fabrizio Bardelli**

BM8-GILDA, European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France

Report:

The main objectives of this proposal were (1) to study the structure of complexes of Se and Fe sorbed on Imogolite and (2) to elucidate, by XANES analysis, what kind of redox reactions (if any) are taking place on the system Fe^{2+}/SeO_3^{2-}/Imogolite.

The first objective has an interest in parallel to the study of the Fe/Se/Imogolite system itself: the structure and charge distribution of Imogolite, a nanotubular clay material, is not well known. Some authors claim the existence of a permanent charge of different sign on the inner (-) and outer (+) surfaces. The nature (in the absence of isomorphic substitutions in the structure of the clay) of this permanent charge is under study.

The study of a serie of Se/Imogolite and Fe/Imogolite samples at different pH values may help us to understand this charge distribution. We have measured 3 different samples of Se/Imogolite at pH 4, 7 and 9. EXAFS data at Se K-edge show a low frequency from a first shell of O atoms, covalently bonded into the structure of Selenite (SeO_3^{2-}). Fourier transform of Se EXAFS oscillations show the presence of a second shell. The high frequency signal is more appreciable at low pH (pH 4). This could be indicating a tendency towards inner-sphere complexation; further measurements at more pH values could help us to complete this investigation. The analysis of XANES data shows as well a difference between XANES signal of sample at pH 9 and pH 4. Se sorbed on Montmorillonite and in Na_2SeO_3 solid have

been shown for comparison. Further reference data of SeO_3^{2-} in solution will be measured in next experimental rounds.

The outer surface of Imogolite is a curved Gibbsite sheet, while the inner surface has SiOH groups. Data of Se sorbed on silica are presented in Figure 1, showing a first shell and apparently the existence of an outer sphere complexation. Reference samples of Se sorbed on Gibbsite are going to be measured in next experimental rounds for comparison with present data.

In the case of Fe one Fe/Imogolite sample has been measured in fluorescence mode, showing a noisy spectrum from which a XANES analysis can be done. The Fe^{2+} ion is expected to diffuse into the nanotubes' internal pores which may be preventing a good detection of the fluorescence signal. Further samples are going to be measured at different pH in order to clarify the complexation structures formed on the Imogolite surface. A reference sample of $FeCl_2$(l) has been measured. More reference samples of Fe^{2+}/Silica are going to be measured.

Once the structure of this complexes is precisely determined, the study of 5 samples with different times of reaction SeO_3^{2-} vs. Fe^{2+}/Imogolite will be measured. The combined EXFAS/XANES analysis of these data will give light into the nature of redox reactions. We expect to complete this work in a future experiment at BM20.

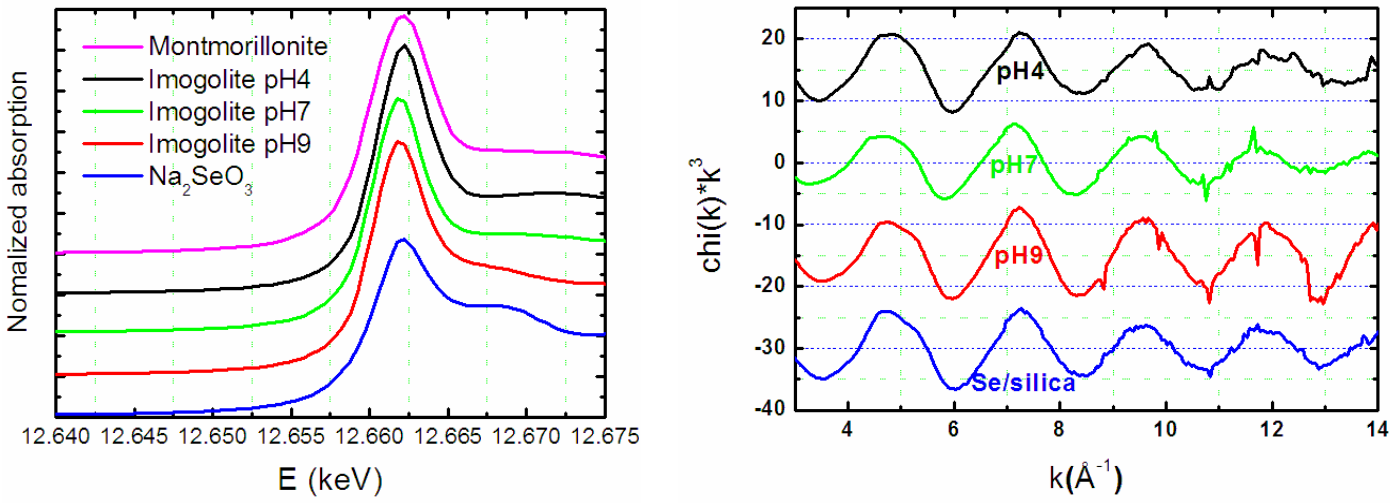

Figure 1. XANES and EXAFS spectra of SeO32- sorbed on Imogolite and on different reference materials.

The experimental apparatus at BM20 is perfectly suitable for this experiment. It allows a very fast exchange of the sample into the closed-cycle He-cryostat, keeping a cold atmosphere of 15 K.