 ROBL-CRG	<b>Experiment title:</b> Selenium solid phase speciation in Boom Clay conditions	<b>Experiment number:</b> 20-01-677
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 04-07-08 to: 08-07-20	<b>Date of report:</b> 23-12-2008
<b>Shifts:</b> 9	<b>Local contact(s):</b> Andreas SCHEINOST	<i>Received at ROBL:</i>
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### Report:

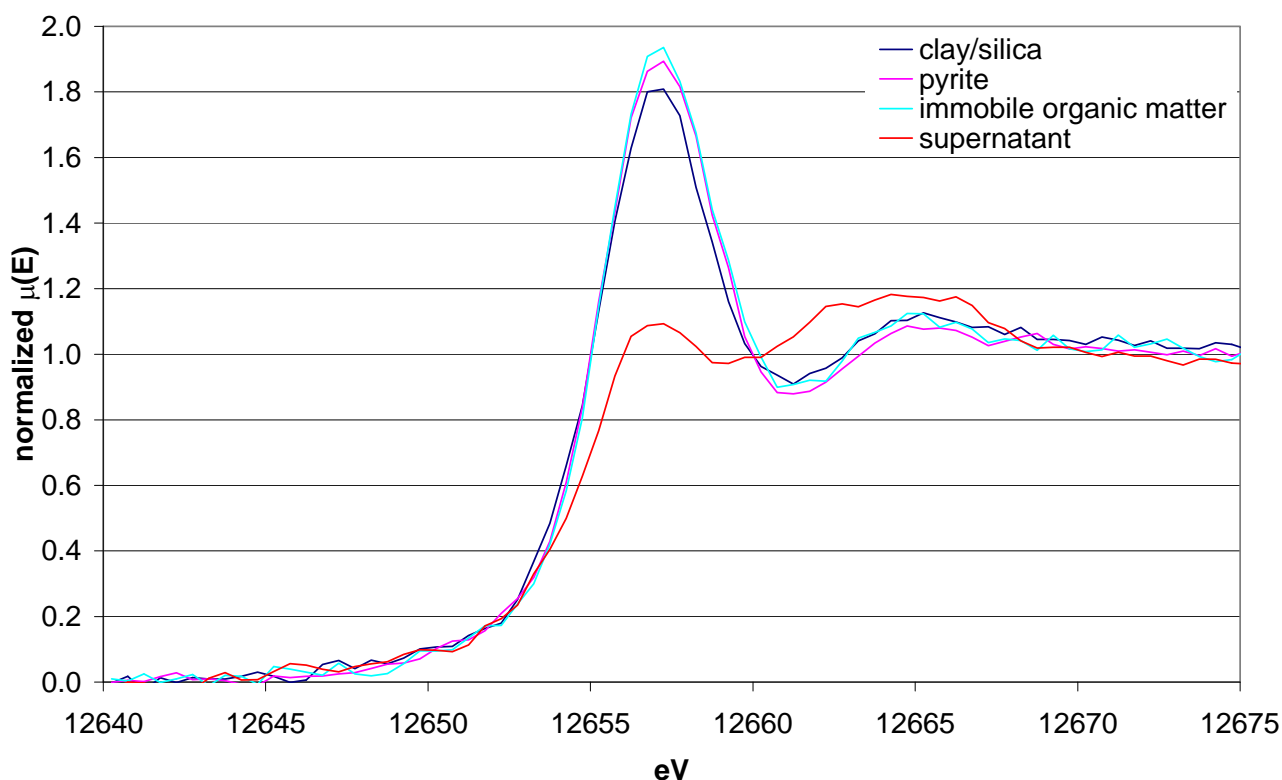
According to the latest performance assessment calculations for the current geological storage scenario for high level radioactive waste in the Belgian Boom Clay formation, Se will contribute the highest dose to man. Since the mobility and consequently also the dose contribution is highly related to the speciation of selenium, the knowledge on its behaviour in the far field of the Boom Clay formation is very important for the safety case of the future Belgian high level waste disposal program.

Previous XAS-based results on the interaction of selenite with FeS<sub>2</sub> and FeS at circum-neutral pH have shown that selenite is reduced to respectively Se<sup>0</sup> and FeSe<sub>x</sub> (Breynaert et al., 2008; Scheinost and Charlet, 2008; Scheinost et al., 2008). Since pyrite (FeS<sub>2</sub>) is one of the main minerals governing the redox conditions of the Boom Clay solid phases, it is expected that selenite will be reduced to Se<sup>0</sup> in the Boom Clay system, thereby effectively limiting the solution concentration to the solubility of Se<sup>0</sup>, provided that there is no interaction with the mobile Boom Clay organic matter.

During the present experiment, cryostat (15K) XAS measurements were performed on different fractions of Boom Clay batch systems, separated after equilibration with three concentrations of selenite (10<sup>-5</sup>, 10<sup>-4</sup>, 10<sup>-3</sup> M) for one month with the complete Boom Clay batch systems in a glovebox. After the equilibration period each batch system was separated into 4 solid phase fractions (sand, clay/silica, pyrite, immobile organic matter) and one supernatant by respectively: 1/ gravitational precipitation (2x10 minutes), 2/ centrifugation at 270 g ( 2x 10 minutes), 3/ centrifugation at 4350g (10 minutes) and 4/ centrifugation at 27200g (60 minutes). XAS measurements were done on solid phase fractions 2 to 4 and on the supernatant.

Based on the XANES/EXAFS analysis, all solid phase fractions contained Se<sup>0</sup>, confirming the reduction of selenite to metallic selenium in the Boom Clay system. Except for the samples equilibrated with 10<sup>-5</sup> M of selenite, different levels of unreduced selenite were also observed in addition to Se<sup>0</sup>. This was confirmed by the results obtained for the supernatant phases of systems

equilibrated with  $10^{-4}$  and  $10^{-3}$  M of Se, where the dominant speciation was found to be selenite. For the system equilibrated with  $10^{-5}$  M of Se, the equilibrium solution concentration dropped down to  $5 \times 10^{-6}$  M of Se. Despite of the low equilibrium concentration, XANES measurements were possible and unexpectedly indicated the presence of a selenide phase (FeSe or and organic selenide), although  $\text{Se}^0$  was observed on the respective solid phase fractions (Figure 1). This indicates that the theoretically expected reduction of Se(IV) to Se(-II) is indeed possible in Boom Clay batch systems, although Se(-II) has not been experimentally observed before in the Boom Clay system.



**Figure 1:** XANES spectra (15K) of different fractions of a Boom Clay batch system equilibrated with  $5 \times 10^{-6}$  M Se(IV) for 1 month.

## Conclusions

XAS based solid phase speciation has demonstrated that selenite [Se(IV)] is reduced to  $\text{Se}^0$  on the Boom Clay systems solid phase. After 1 month equilibration of  $10^{-5}$  M of selenite in Boom Clay batch systems, a selenide phase (FeSe or and organic selenide) was observed in the supernatant solution, although  $\text{Se}^0$  was observed on the different solid phases.

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- Scheinost A. C. and Charlet L. (2008) Selenite reduction by mackinawite, magnetite and siderite: XAS characterization of nanosized redox products. *Environ. Sci. Technol.* **42**, 1984–1989.
- Scheinost A. C., Kirsch R., Banerjee D., Fernandez-Martinez A., Zaenker H., Funke H., and Charlet L. (2008) X-ray absorption and photoelectron spectroscopy investigation of selenite reduction by FeII-bearing minerals. *J. Contam. Hydrol.* **102**, 228-245.