



	Experiment title: Selenium liquid phase speciation in Boom Clay conditions	Experiment number: 20-01-706
Beamline: BM20	Date of experiment: from: 25-01-2011 to: 29-01-2011	Date of report: 31-01-2012
Shifts: 12	Local contact(s): Andre Rossberg	<i>Received at ESRF:</i>

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Report:

XAS-based studies of the interaction of selenite with FeS₂ and FeS at circum-neutral pH have shown that selenite is reduced to Se⁰ and FeSe_x, respectively [1-5]. Pyrite (FeS₂) is one of the main minerals governing the redox conditions of the BC solid phases, so it is expected that selenite will be reduced to Se⁰ in Boom Clay conditions. Provided there is no interaction with the mobile Boom Clay organic matter this condition should effectively limit the Se solution concentration to the solubility of Se⁰.

Previously cryo-XAS (15K) measurements were performed on different solid phase fractions of Boom Clay batch systems, separated after equilibration with three concentrations of selenite (10⁻⁵, 10⁻⁴, 10⁻³ M) for one month with the complete BC batch systems in a glovebox [5]. Based on the XANES/EXAFS analysis, all solid phase fractions contained Se⁰, confirming the reduction of selenite to metallic selenium in BC lab systems.

Initial experiments on Boom Clay batch systems equilibrated with an initial Se(IV) concentration of 5x10⁻⁵ M indicated the presence of 5x10⁻⁶ M selenium species in supernatant solution after 1 month. Despite of this very low concentration, XANES spectra could be recorded on the flash-frozen solution. Comparison of this XANES edge with known reference spectra indicated the presence of a low oxidation state (-II, -I or 0) selenium species different from both the Se⁰ phase adsorbed to the Boom Clay solid and from any of the available solid Se references (amorphous/crystalline elemental Se, achavalite (FeSe), ferroselite (FeSe₂). Also, no evident match was indicated upon comparison of this spectrum with the extensive library of organic and inorganic Se XANES spectra recorded by Ryser *et al.* [6] in the framework of their study on selenium bearing minerals in mine waste-rocks from the US Western Phosphate Resource Area.

Since XANES fingerprinting did not allow to identify the dissolved non-selenite species present in the supernatant solutions of Boom Clay batch systems equilibrated with selenite, new experiments were designed in an attempt to obtain EXAFS spectra for this species. Based on the equilibrium data reported by Breynaert *et al.* [5] Boom Clay batch systems were equilibrated in an anoxic glove box with respectively 5x10⁻⁵M and 5x10⁻⁴M of selenite for 20 weeks. Upon recovery of the supernatant solutions three approaches were tested to obtain more concentrated supernatant solutions.

A first approach was partial lyophilisation, performed at 0.4 mbar on supernatant samples flash frozen in round-bottom flasks equipped with wide-bore valves to guarantee the anoxic atmosphere during the transfer from the glove box to the freeze-drying apparatus. In order to minimise unwanted sample alterations, only partial lyophilisation was performed. Upon thawing, this approach allowed to recover a liquid, more concentrated sample without addition of any component. 5 hours of lyophilisation yielded a sample solution with a concentration factor between 40 and 60 as compared to the original supernatant solution.

The second approach to concentrate the samples assumed that the dissolved selenium species were mostly adsorbed to the dissolved Boom Clay organic matter and was based on the known interaction of the hydrophobic parts of natural organic with XAD-8 resin. In contrast with the classical dissolved organic matter concentration/separation schemes based on XAD-8, the supernatant solutions were not acidified before transfer to the XAD column. Although this alteration to the procedure did not assure complete protonation and hence decreased the hydrophobic properties as compared to the original procedure, the alteration was made in order to minimise any changes to the selenium speciation. Radioactive assay of ^{75}Se spiked samples indicated no adsorption of Se or organic matter on this resin.

The third sample concentration scheme targeted the ion exchange properties of the Boom Clay organic matter and any anionic selenium species present in the solution. Similar to the XAD-8 procedure, aliquots of the supernatant solution was run through a DOWEX 1X8 anion exchange column. [7]. Before preparation of the non-radioactive XAS samples tests were run using 1ml aliquots of ^{75}Se spiked supernatant solutions. Radioactive assay of the percolate of these column adsorption tests indicated complete adsorption of the ^{75}Se species and dissolved organic matter on the column.

Normalised XANES spectra for supernatant solutions of Boom Clay batch systems equilibrated with SeO_3^{2-} are shown in Figure 1. Spectrum X shows the spectrum for an un-concentrated supernatant solution sampled after 4 weeks of equilibrating a Boom Clay batch system with $5 \times 10^{-5} \text{M}$ of SeO_3^{2-} . Spectra D1 and D2 were recorded on samples from comparable batch systems equilibrated with $5 \times 10^{-4} \text{M}$ of SeO_3^{2-} sampled after 20 weeks and concentrated on a Dowex 1X8 resin. Spectrum D4 was recorded on a sample taken from a batch system equilibrated with $5 \times 10^{-5} \text{M}$ SeO_3^{2-} , sampled after 20 weeks and concentrated on a Dowex 1X8 column. All XANES spectra seem to be related and cannot be matched to a combination of reference spectra of FeSe_2 , FeSe , Se^0 and SeO_3^{2-} .

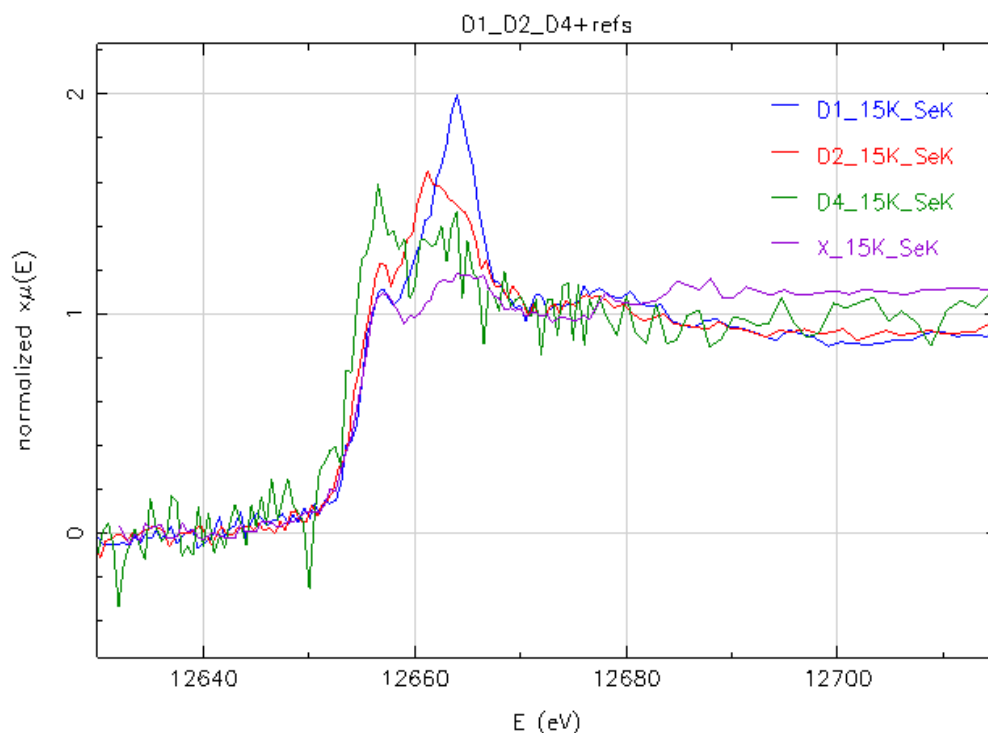


Figure 1: XANES fingerprints for selenium containing supernatant solutions sampled from Boom Clay batch systems equilibrated with SeO_3^{2-} .

All XANES edge energies, determined as the energy of the first inflection point, are in the range of 12654 – 12656 eV and as such confirm the presence of reduced selenium species (-2,-1,0).

Since the fingerprint of sample D1 shows features that might be attributed to the presence of SeO_3^{2-} , a linear combination fit was performed for this sample using spectrum X and a spectrum for SeO_3^{2-} dissolved Boom Clay extract to impose the pH conditions representative for Boom Clay batch systems (Figure 2). The best possible linear combination fit shown in figure 2 readily indicates the absence of Se(IV) in sample D1. XANES fingerprinting analysis of the XAS spectra recorded for the dissolved non-selenite species does not allow to explain the unknown fingerprint as any combination of known species. In conclusion: colloidal species of FeSe_2 , FeSe , red amorphous Se^0 and the known crystalline elemental selenium phases can be excluded as candidates for the identification of the dissolved non-selenite species. Due to the co-adsorption behaviour of the dissolved species on the DOXWEX anion exchanger, no further conclusions can be made about the potential association of this species with dissolved Boom Clay organic matter.

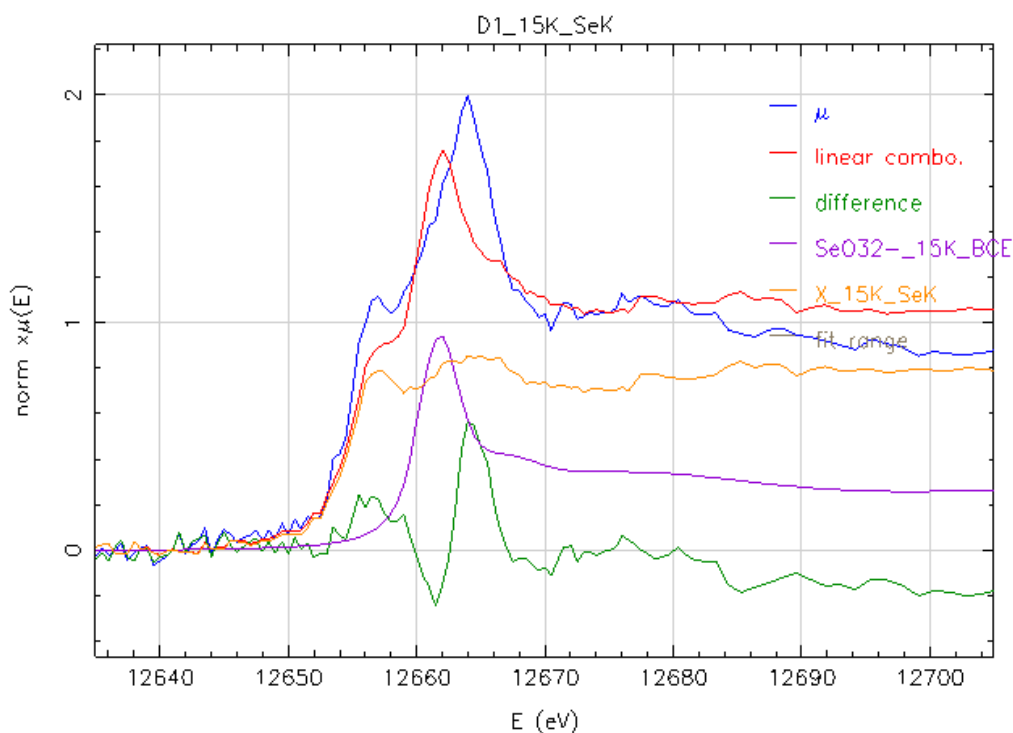


Figure 2: Best possible linear combination fit for sample D1 using SeO_3^{2-} as one of the references.

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