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Selenium solid phase speciation in Boom Clay batch conditions

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This Se research proposal had two main objectives. On the one hand it was necessary to confirm the formation of elemental Se and  $\text{FeSe}_x$  by interaction of selenite with pyrite and troilite. On the other hand the reduction of selenite to elemental Se in the Boom Clay system had to be confirmed spectroscopically.

## 1. Experimental Setup

To minimise the oxygen concentration in the reaction vessels, all experiments (except where explicitly mentioned) were carried out in a controlled atmosphere glove box. The glovebox atmosphere used for the preparation of Boom Clay and Boom Clay extract samples consisted of a mixture of  $\text{N}_2$  (99.6%) and  $\text{CO}_2$  (0.4%). This particular  $\text{CO}_2$  content was used to simulate the *in situ* Boom Clay  $\text{CO}_2$  partial pressure which is in equilibrium with the *in situ* observed carbonate concentration and solution pH. This glove box was situated in a temperature-controlled room (22°C) and the box atmosphere was recirculated over a Jacqomex purifying system (Cu sorbent) in order to remove excessive oxygen. The mean concentration of  $\text{O}_2$  in the glove box throughout the experiments was approximately 2 ppm (Teledyne oxygen sensor micro fuel cell class A-2C). The glovebox atmosphere used for the preparation of the other samples consisted of a mixture of  $\text{N}_2/\text{H}_2$  95/5 %. The box atmosphere was recirculated over a Jacqomex purifying system (Cu sorbent) in order to remove excessive oxygen. In addition to the Cu based system, also a Pt based catalytic convertor was installed in the glovebox in order to minimise the oxygen level.

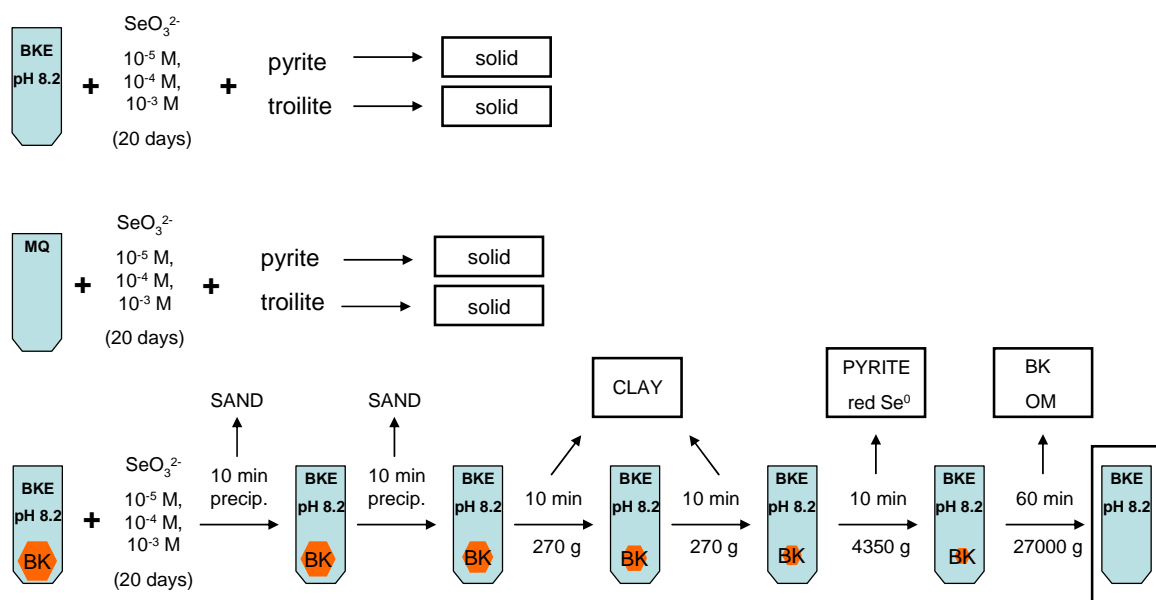
- The *Boom Clay sample* used (Boom Clay core TD25-26 06-10) for the preparation of Boom Clay and Boom Clay extract samples originated from the HADES laboratory (HADES boring campaign, january 2006, test drift ring 25-26 vertical) in the underground research facility (URF) at SCK-CEN (Mol, Belgium) and was obtained during a drilling campaign using steel sampler pipes. The sample was stored in its sampler pipe at 4°C until September 2007 when it was removed from its sampler pipe using a hydraulic press and immediately repacked in vacuum in a PE/AL/PET foil (UCB) in order to avoid oxidation. After repacking the clay core was kept in a stainless steel container at room temperature in the  $\text{N}_2/\text{CO}_2$  glovebox described above.
- All *chemicals* used were of analytical grade and the water used was deionized, filtered by a Water Purification System (Milli-Q) and finally vacuum boiled out before introduction in the glove box, where it was equilibrated with the box atmosphere by 2 hours of stirring.
- *Synthetic Clay Water* (SCW) was used as the standard electrolyte in all Boom Clay/Boom Clay extract experiments. Its composition is based on analysis of waters collected in Boom Clay piezometers [26](1) and consists of a 1170 mg/L  $\text{NaHCO}_3$ , 10 mg/L NaCl, 0.3 mg/L  $\text{Na}_2\text{SO}_4$ , 25 mg/L KCl, 22 mg/L  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solution which is saturated with  $\text{CaCO}_3$ . After one week of equilibration in the 0.4%  $\text{CO}_2$  glove box atmosphere, the SCW is filtered (0.22  $\mu\text{m}$ ) and as such it is the inorganic equivalent of *in situ* Boom Clay groundwater.
- *Boom Clay extract* was prepared by equilibrating SCW with the Boom Clay solid phase at a solid liquid ratio of 250 g/l for 1 week. After equilibration the supernatant solution was centrifuged twice for 2 hours at 22000g.

- $^{75}\text{Se}$   $\text{Na}_2\text{SeO}_3^-$  spike solution was purchased from Polatom. The spike contained 0.280 mL selenite solution with a radioactive concentration of 132.200 MBq/ml and a specific activity of 1258.60 Mbq/mg Se at reference date 25/07/2007. The selenate content ( $\text{SeO}_4^{2-}$ ) was below 0.2 percent.

For this first series of experiments the sample preparation was specifically designed to allow XAS measurements at the lowest Se dosage accessible by this technique in order to: 1) spectroscopically confirm the solid phase Se speciation in pyrite and troilite systems at Se concentrations as low as reasonably achievable; 2) determine spectroscopically the solid phase Se speciation in different mineral fractions present in the Boom Clay; 3) gain additional proof for the conceptual model for the geochemistry of the different Se species under Boom Clay conditions; 4) to obtain direct (e.g. spectroscopic) information on the thermodynamically stable Se species under Boom Clay conditions.

Before use, the troilite ( $< 100\ \mu\text{m}$ ) and pyrite ( $< 5\ \mu\text{m}$ ) solid phases were washed three times with 0.1M HCl for 15 minutes, rinsed three times with degassed acetone and subsequently dried under vacuum.

Pyrite and troilite batch systems were prepared in duplicate in polypropylene centrifuge tubes at a solid liquid ratio of 66.67 g/l with three initial concentrations of selenite ( $10^{-5}$ ,  $10^{-4}$  and  $10^{-3}$  M) in both Boom Clay extract and pure MilliQ solution. Before phase separation, (2 hours, 22000g) all samples were equilibrated for 20 days on and end-over-end shaker in their respective glovebox.



**Figure 1: Schematic overview of the XAS sample preparation for the Boom Clay, pyrite and troilite containing samples.**

Boom Clay batch systems were prepared in triplicate in polypropylene centrifuge tubes by suspending 4g of Boom Clay in 20 ml of SCW. After 18 days of pre-equilibrating the systems on and end-over end shaker, 0.5 ml of selenite solution was added to the systems resulting in three initial selenium concentrations ( $5 \times 10^{-5}$ ,  $5 \times 10^{-4}$ ,  $5 \times 10^{-3}$  M). After 20 days of equilibration on an end-over-end shaker different solid phase

fractions were separated from the systems (Figure 1). The main part of the sand fraction was removed after 10 minutes of gravitational precipitation. After decantation followed by a second, identical, gravitational precipitation step, a light-colored clay fraction was obtained by centrifugation of the supernatant for 2x10 minutes at 270g. The remaining supernatant was then centrifuged for 10 minutes at 4350g yielding a dark mineral fraction believed to contain mainly pyrite and coarse particulate organic matter. A final solid phase fraction was obtained by centrifugation of the remaining supernatant at 27000g for 60 minutes.

After their isolation, the solid phase fractions were centrifuged a second time at 27000g for 60 minutes and subsequently decanted to obtain pastes with a lower water content allowing to minimize the amount of dissolved selenium in the XAS samples. The XAS samples were prepared in small Plexiglas sample holders (2.5x2.5x20 mm sample slit), sealing both sides with kapton tape. After shock-freezing the samples in liquid nitrogen inside the glovebox, the frozen samples were stored in liquid nitrogen until insertion into the cryostate (15K) for the XAS measurement.

XAS measurements were performed at the ROBL and DUBBLE beamlines at the ESRF (Grenoble, France) using a cryostate (15K) in order to: 1) prevent oxidation of the sample 2) prevent beam induced changes to the Se speciation during the measurement. Most of the spectra were obtained in fluorescence mode. The monochromator energy was calibrated with a gold foil (K-edge at 11919 eV) because of its greater inertness and hence reliability in comparison to elemental Se.

## **2. Results and Discussion**

Previous experiments concerning the behaviour of selenite in the Boom Clay system have indicated an adsorption/reduction mechanism for the interaction of selenite with the Boom clay solid phase. Upon addition of selenite to Boom Clay batch systems, the Se concentration in solution decreased as function of time and Se increasingly becomes associated with the solid phase of the Boom Clay batch systems. Indications were found that the interaction of selenite with pyrite or pyrite containing solid phases such as Boom Clay leads to the formation of a  $\text{Se}^0$  solid phase. The presence of other phases such as illite or natural organic matter in more complex systems like Boom Clay was reported to slow down the sorption/reduction kinetics of  $\text{Se(IV)}$  with respect to the behaviour in presence of pyrite only. In addition, evidence has been obtained for the existence of significant concentrations of dissolved non-selenite Se species (up to  $\sim 10^{-7}\text{M}$  in the systems studied). Considering the solubility of low oxidation state (0, -II) Se phases that can be formed in these systems, an association of Se with humic substances was put forward as a likely identification for the dissolved non-selenite Se species observed.

In all previous studies, the identification of the non-selenite, solid and liquid phase, selenium species in the Boom clay system has always been based on circumstantial evidence such as solubility, or comparison with the spectroscopically identified speciation of Se in model systems used for the interpretation of the behaviour of Se in Boom Clay conditions. The XAS experiment described in this report was designed to fill the gap remaining, by allowing a positive identification of the Se species present in different solid phase fractions of the Boom Clay system (Figure 1), after equilibration of selenite in Boom Clay batch systems for one month. It has been previously

demonstrated that this timeframe allows to reach equilibrium or at least steady-state conditions in such systems [14].

During the XAS campaigns XAS measurements were performed on the solid phase of the reference phases pyrite and troilite, in addition to the different solid phase fractions (clay, pyrite, organic) of the Boom Clay systems. Both XANES and EXAFS spectra were obtained for the solid phase of the reference systems (troilite, pyrite) equilibrated with  $1 \times 10^{-3}$  M of selenite (Table 1). XANES spectra were obtained for the different solid phase fractions (preliminary designated as clay, pyrite, organic) of the Boom Clay systems equilibrated with  $5 \times 10^{-5}$ ,  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  M of selenite, except for the organic matter fraction from the system equilibrated with  $5 \times 10^{-3}$  M. From this point forward these fractions will be referenced by their respective names (O – V) listed in Table 2. EXAFS spectra were obtained for all fractions of the BC systems equilibrated with  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  M of Se(IV) (P,Q,S,T,V) (Table 2).

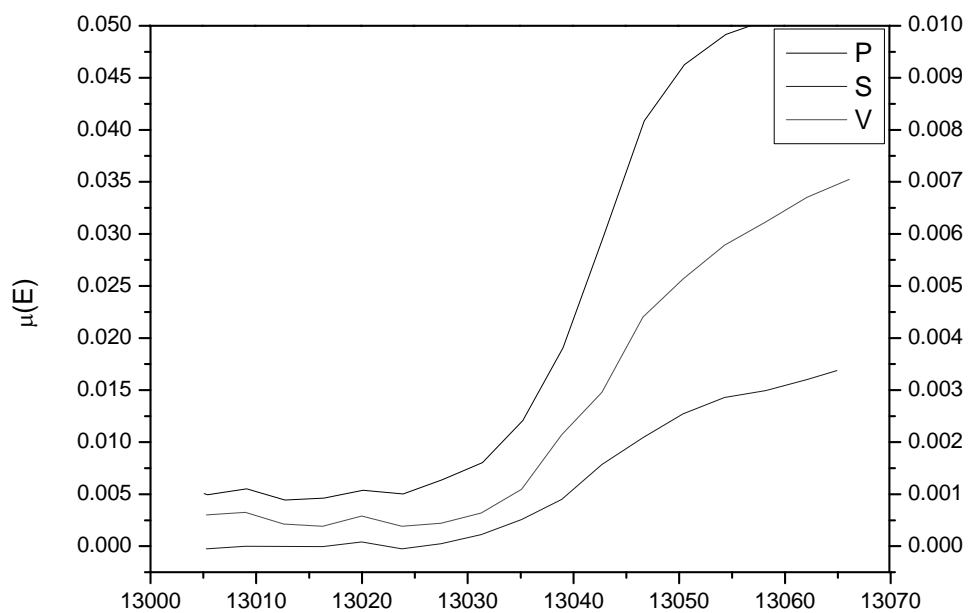
*Table 1: Overview of the XAS samples taken from the troilite and pyrite systems shown in Figure 1*

sample	mineral phase	initial Se(IV) conc.	XANES	EXAFS
E	Troilite	$1 \times 10^{-3}$ M	+	+
K	Pyrite	$1 \times 10^{-3}$ M	+	+

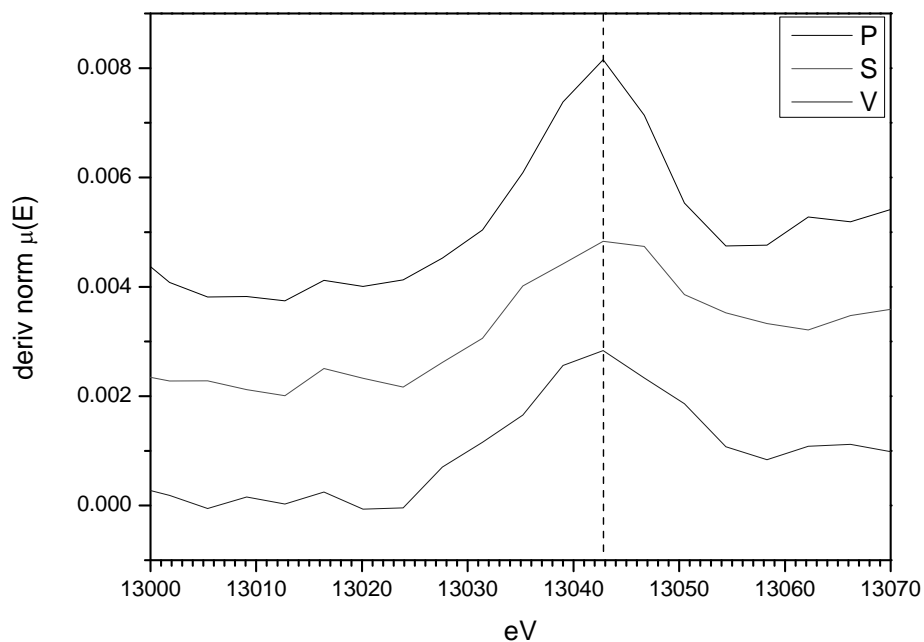
*Table 2: Overview of the XAS samples taken from the fractions of the Boom Clay systems shown in Figure 1*

sample	Fraction	initial Se(IV) conc.	XANES	EXAFS
O	Clay	$5 \times 10^{-5}$ M	+	-
P	Clay	$5 \times 10^{-4}$ M	+	+
Q	Clay	$5 \times 10^{-3}$ M	+	+
R	Pyrite	$5 \times 10^{-5}$ M	+	-
S	Pyrite	$5 \times 10^{-4}$ M	+	+
T	Pyrite	$5 \times 10^{-3}$ M	+	+
U	organic matter	$5 \times 10^{-5}$ M	+	-
V	organic matter	$5 \times 10^{-4}$ M	+	+

The k-range of the EXAFS spectra of the solid phase BC fractions is limited to  $\pm 10$  k due to the presence of an absorption edge from Pb at 13043 eV. The presence of this feature in the data inhibits the extraction of EXAFS data beyond this edge energy. Although the XAS measurements were recorded in fluorescence mode, the influence from the Pb L3 edge (Figure 2, Figure 3) significantly distorts the EXAFS signal due to the interference of a Pb fluorescence L-line with the measurement of the Se fluorescence K line at 11.2 keV. The Pb content in the samples is probably associated with pyrite in the samples, since galena (PbS) is an impurity, commonly present in natural pyrite samples.



**Figure 2:** X-ray absorption at the Pb L3 edge for the solid phase fractions [P: clay, S: pyrite, V: organic matter]



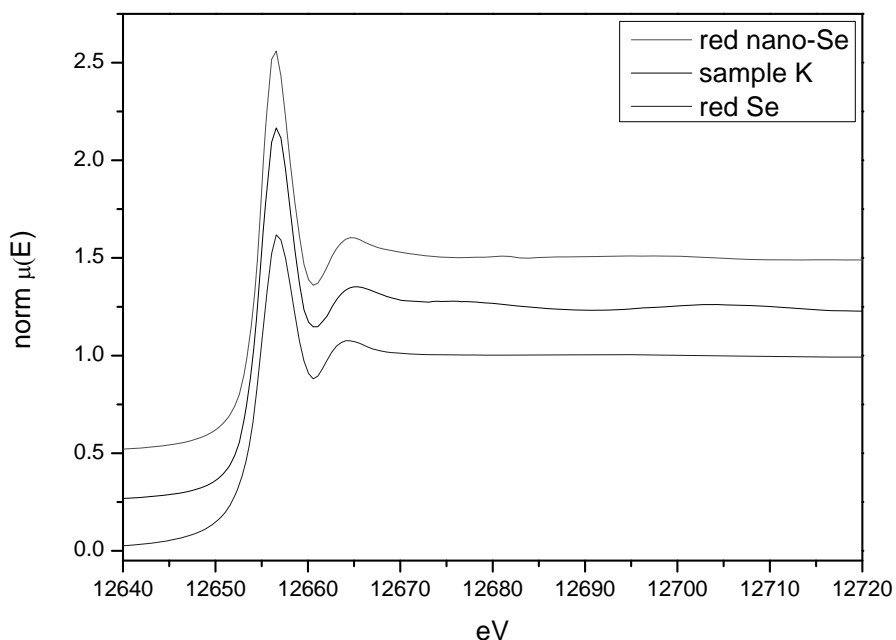
**Figure 3:** first derivative of the normalised Pb L3 XANES spectra for the solid phase fractions [P: clay, S: pyrite, V: organic matter (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-4} M$ . The maximum of the first derivative is located at 13043 eV.

XAS based identification of unknown products is possible in two ways. Since the overall shape and the structural features of XANES spectra (i.e., the XANES fingerprint) are related to the molecular structure of the compound, this fingerprint provides a first means of identification of unknown compounds by comparison with the fingerprint of known references. Using the EXAFS spectrum is a second, alternative route of identification for unknown compounds. This route is however much more prone to errors

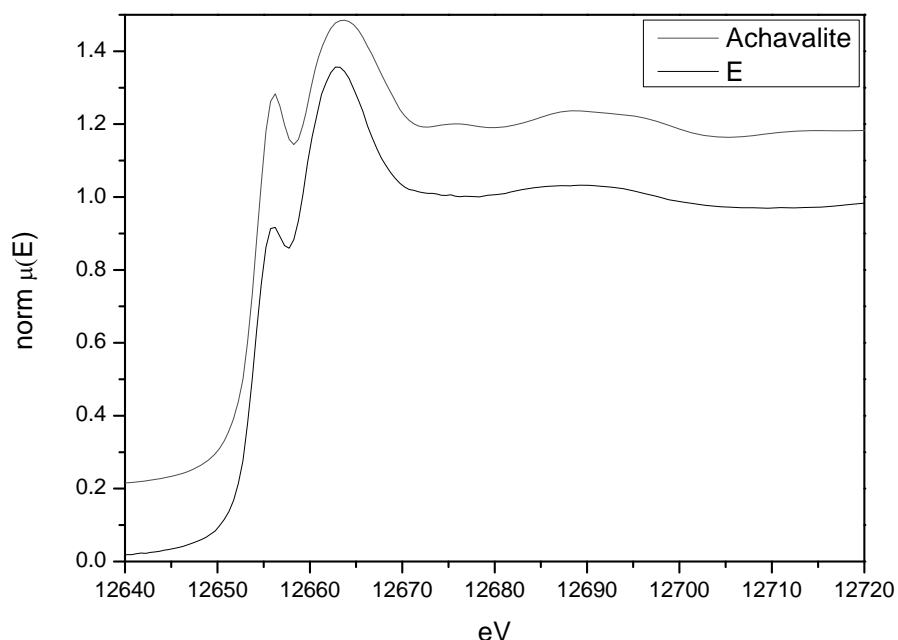
since it requires extracting the EXAFS spectrum from the atomic background absorption, a procedure potentially introducing unwanted artefacts in the spectrum.

Figure 4 shows the normalised XANES spectrum for the solid phase reaction product of Se(IV) with pyrite (sample K) together with the spectrum of nano-particulate and macro-crystalline red (monoclinic)  $\text{Se}^0$  references. Sample K was prepared from the solid phase of a batch system containing pyrite equilibrated for 1 month with an initial selenite concentration of  $5 \times 10^{-3}$  M. Comparison of the spectra allows identifying the solid phase speciation of sample K as nanoscale red Se particles. The slight difference in the white line intensity between sample K and the nanoparticulate reference can be attributed to a larger particle size of the  $\text{Se}^0$  particles in sample K as compared to the reference. These data confirm the previous study, identifying of the solid phase reaction product for the reduction of selenite by pyrite as a type of monoclinic metallic selenium [17].

The normalised XANES spectrum for sample E is shown in Figure 5 together with the spectrum of an achavalite (trigonal  $\text{FeSe}$ ) reference sample. Sample E was prepared from the solid phase of a batch system containing troilite equilibrated for 1 month with an initial selenite concentration of  $5 \times 10^{-3}$  M. The XANES fingerprint for this sample and especially the typical ratio between the first two maxima in the XANES spectrum allows for the unequivocal identification of the solid phase reaction product as a form of iron selenide. This confirms the previous experimental results identifying the solid phase reaction product for the interaction of selenite with troilite as  $\text{FeSe}_x$ , based on the analysis of the EXAFS spectrum of the reaction products [17].



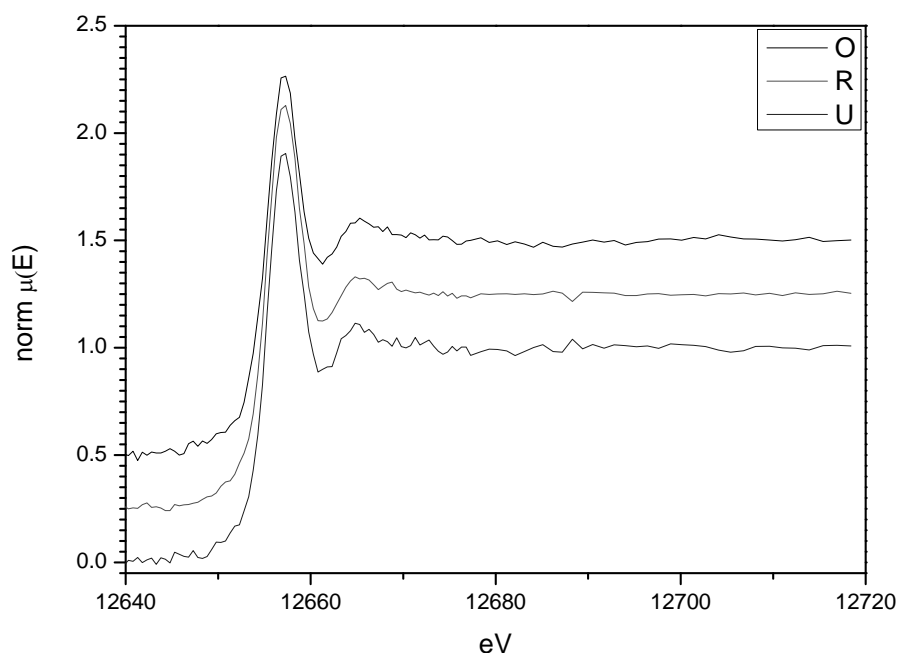
**Figure 4:** normalised XANES spectra for a nanoparticulate red  $\text{Se}^0$  reference, sample K [pyrite equilibrated for one month with an initial selenite concentration of  $5 \times 10^{-3}$  M (Figure 1, Table 1)] and a macro-crystalline red Se reference. The spectra were offset in steps of 0.25 abs.



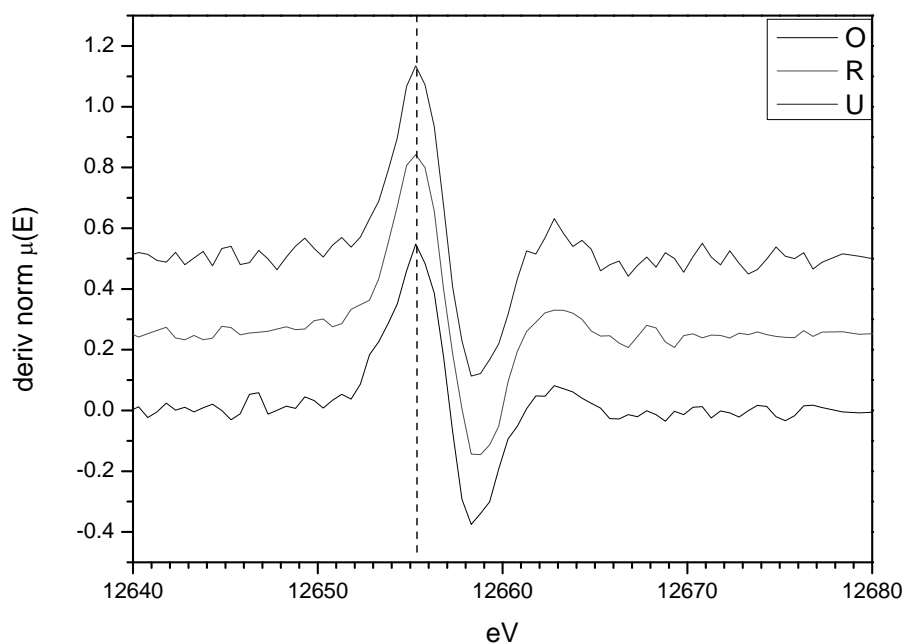
**Figure 5:** normalised XANES spectra an achavalite reference (trigonal FeSe) and for sample E: troilite equilibrated with an initial selenite concentration of  $5 \times 10^{-3} \text{ M}$  (Figure 1, Table 1)]. The spectra were offset in steps of 0.2 abs.

Figure 6 and Figure 7 show respectively the normalised XANES spectra and the first derivative of these spectra for all solid phase fractions of the Boom Clay batch system equilibrated for one month with an initial selenite concentration of  $5 \times 10^{-5} \text{ M}$  [samples O, R, U. (Figure 1, Table 2)]. As can be seen in the figures the noise levels in the data are relatively high due to the low concentration of Se in the samples. Due to the relatively high attenuation of the signal by the Boom Clay components, an initial concentration of  $10^{-5} \text{ M}$  of selenite is probably the lowest Se dosage experimentally accessible with X-ray Absorption spectroscopy. The normalised XANES spectra for the three fractions (clay, pyrite, organic matter) shown in Figure 6 are clearly identical, indicating that all solid-phase size fractions within this Boom Clay batch system are in redox equilibrium with each other. The comparison of their XANES fingerprint with those of the monoclinic red Se references and the solid phases reaction products for the interaction of selenite with pyrite allows to identify the speciation of Se in these fractions as a form of red monoclinic selenium. This is confirmed by the energy position of the maximum of the first derivative of the normalised XANES spectra located at 12655.2 eV. This energy is typically observed for low oxidation state selenium species such as Se[0], Se[-1] and Se[-II]. Interestingly, the edge jump (not normalized) for the organic fraction (sample U) was about fivefold the edge jump for the other 2 fractions, indicating either the presence of a much higher concentration of Se in this fraction, or a lower attenuation of the signal by the other components in the sample.





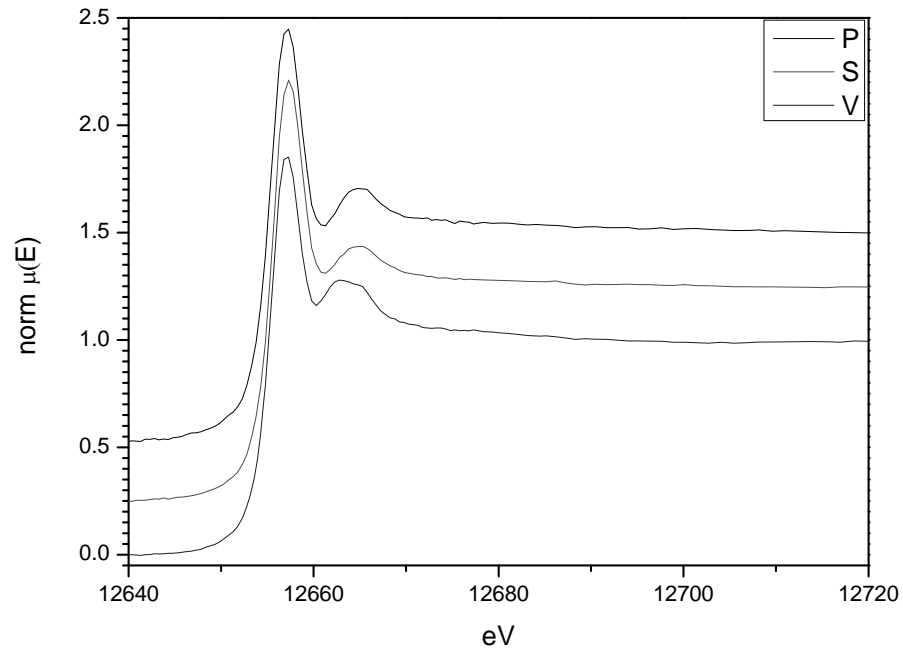
**Figure 6:** normalised XANES spectra for the solid phase fractions [O: clay, R: pyrite, U: organic matter (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-5} \text{ M}$ . The spectra are offset with an 0.25 abs interval.



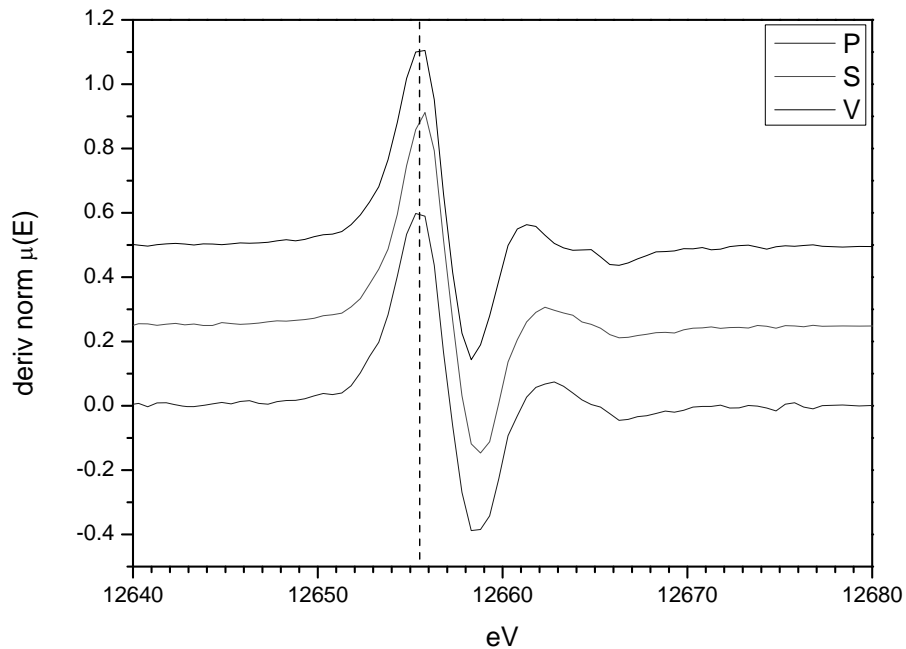
**Figure 7:** first derivative of the normalised XANES spectra for the solid phase fractions [O: clay, R: pyrite, U: organic matter (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-5} \text{ M}$ . The maximum of the first derivative is located at 12655.2 eV.

The normalised XANES spectra and their first derivative are shown in Figure 8 and Figure 9 for all solid phase fractions of the Boom Clay batch system equilibrated for one month with an initial selenite concentration of  $5 \times 10^{-4} \text{ M}$  [samples P, S, V. (Figure 1, Table 2)]. From the figures it can be seen that the XANES fingerprint for the three solid phase fractions is similar, but not identical. The energy position of the maximum of the

first derivative of the normalised XANES spectrum (Figure 9) is located at 12655.5 eV. This energy position in combination with the overall XANES fingerprint provides clear evidence for the presence of elemental selenium in all three fractions.

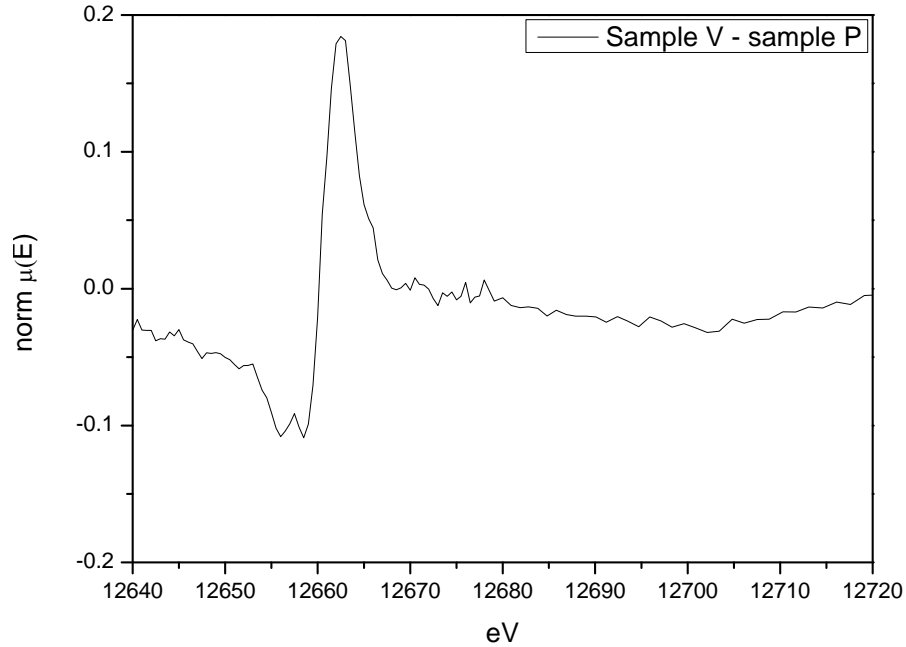


**Figure 8:** normalised XANES spectra for the solid phase fractions [P: clay, S: pyrite, V: organic matter (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-4} M$ . The spectra were offset in steps of 0.25 abs.

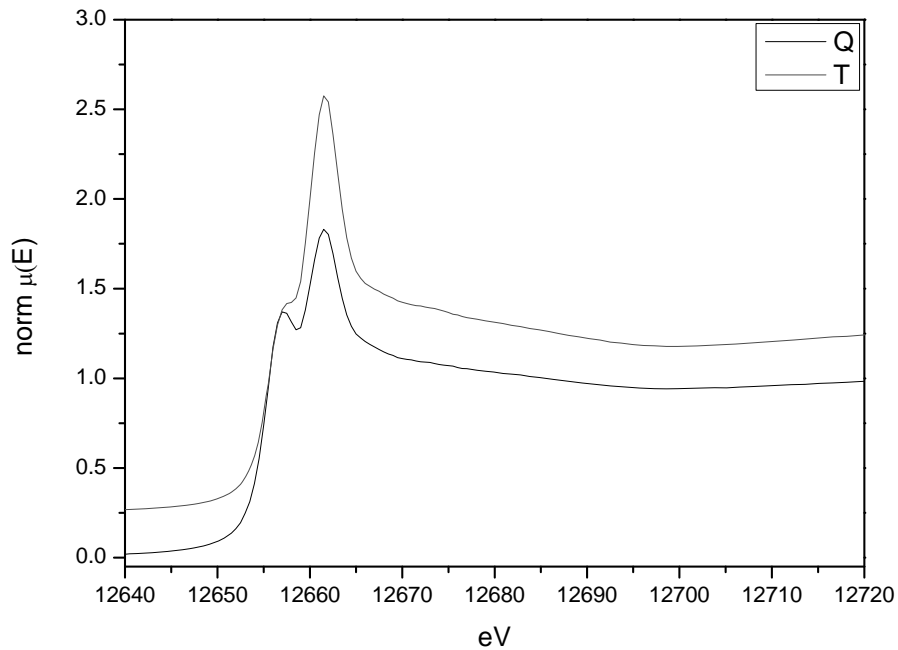


**Figure 9:** first derivative of the normalised XANES spectra for the solid phase fractions [P: clay, S: pyrite, V: organic matter (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-4} M$ . The maximum of the first derivative is located at 12655.5 eV.

In Figure 10, showing the difference between the XANES spectra for samples P and V, the XANES fingerprint of selenite can be easily recognised. Linear combination fitting of the XANES spectrum for sample V with that for sample P and a selenite reference spectrum also indicates the presence of 5 to 10 % of selenite in the former sample. It should be noted that in contrast with the previous series of samples, the edge jump for the clay fraction (sample P) was about 10-fold that for the other two fractions.

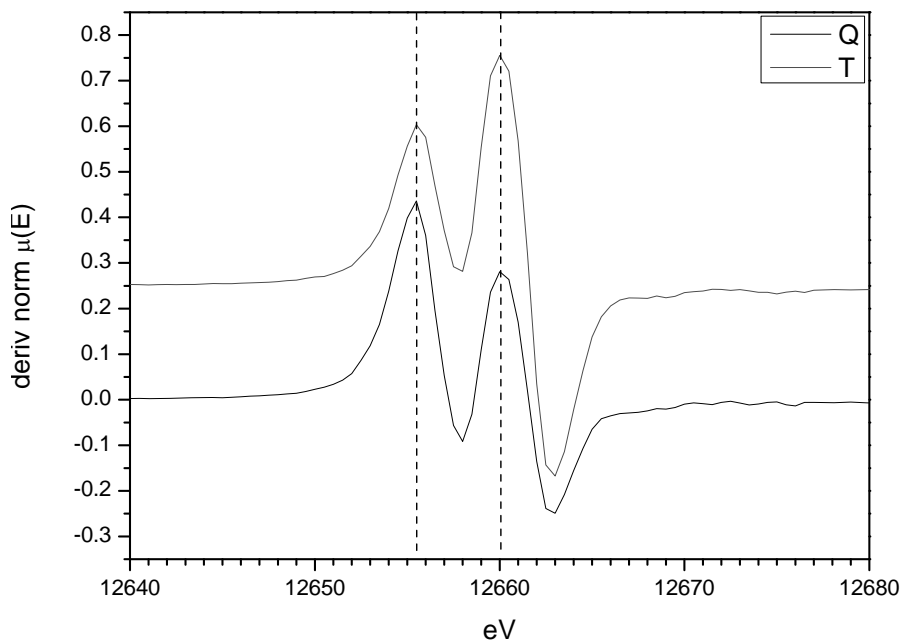


**Figure 10:** Difference between the normalised XANES spectra for sample V and Sample P

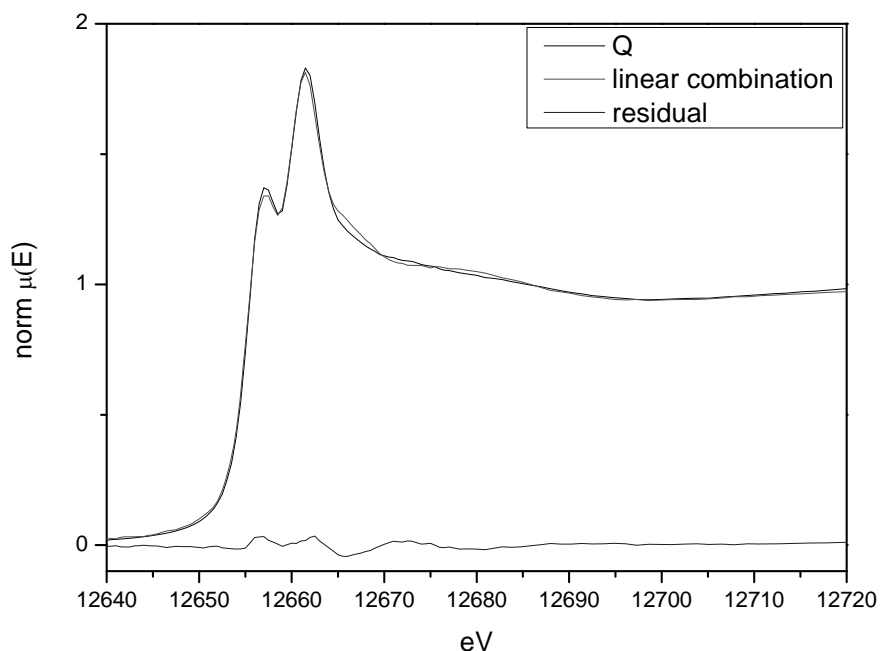


**Figure 11:** normalised XANES spectra for the solid phase fractions [Q: clay, T: pyrite (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-3} M$ . The spectra were offset in steps of 0.25 abs.

Figure 11 and Figure 12 show respectively the normalised XANES spectra and its first derivative for samples Q and T (Figure 1, Table 2), the clay and pyrite fractions of a Boom Clay batch system equilibrated for one month with an initial concentration of  $5 \times 10^{-3}$  M of selenite. In Figure 12 two distinct maxima at respectively 12655.5 and 12660 eV can be observed. These energy positions are typical for respectively low and high oxidation state selenium [12655.5 eV : Se(0,-I,-II) and 12660 eV : Se(IV)]. In line with this observation, the XANES spectrum for sample Q can be fit with a linear combination of the spectrum for sample P (60%) and a selenite reference spectrum (36%), indicating that about 40% of the selenium is present in the sample as Se(IV) (Figure 13).



**Figure 12:** first derivative of the normalised XANES spectra for the solid phase fractions [Q: clay, T: pyrite (Figure 1, Table 2)] equilibrated with an initial selenite concentration of  $5 \times 10^{-3}$  M. The maxima of the first derivative are located at respectively 12655.5 and 12660 eV.



**Figure 13:** Linear combination fit of the XANES spectrum for sample Q, with the spectrum for sample P (60%) and a selenite reference spectrum (36%).

The XANES data for different solid phase fractions of the Boom Clay batch systems indicate the formation of elemental selenium in all system. Corresponding with the higher initial Se(IV) dosage, increasing amounts of selenite are observed in the fractions from batch systems equilibrated with  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  M of selenite, indicating an incomplete reduction of Se(IV). At present, it is unclear if the observed amount of Se(IV) originates from selenite dissolved in the interstitial water present in the samples or if it is present in the samples as selenite sorbed on the solid phase of the Boom Clay batch systems. In any case, without additional experimental data the presence of an unknown amount of selenite in the samples prevents the analysis of the EXAFS spectra for the samples containing selenite in addition to the reduced selenium phase. The EXAFS analysis of selenite containing spectra should be possible after obtaining additional experimental data. Firstly, the distribution of selenium between the supernatant and the different solid phase fractions will have to be measured in the XAS samples and verified in additional batch systems replicated with radioactive Se. Secondly, the amount of interstitial supernatant solution in the samples has to be determined. And finally, XAS data on the supernatant phases (measured but presently not reported) would be highly recommendable to allow for a reliable EXAFS analysis based on fitting linear combinations of the speciation in the different phases present within the samples (solid and liquid phase).

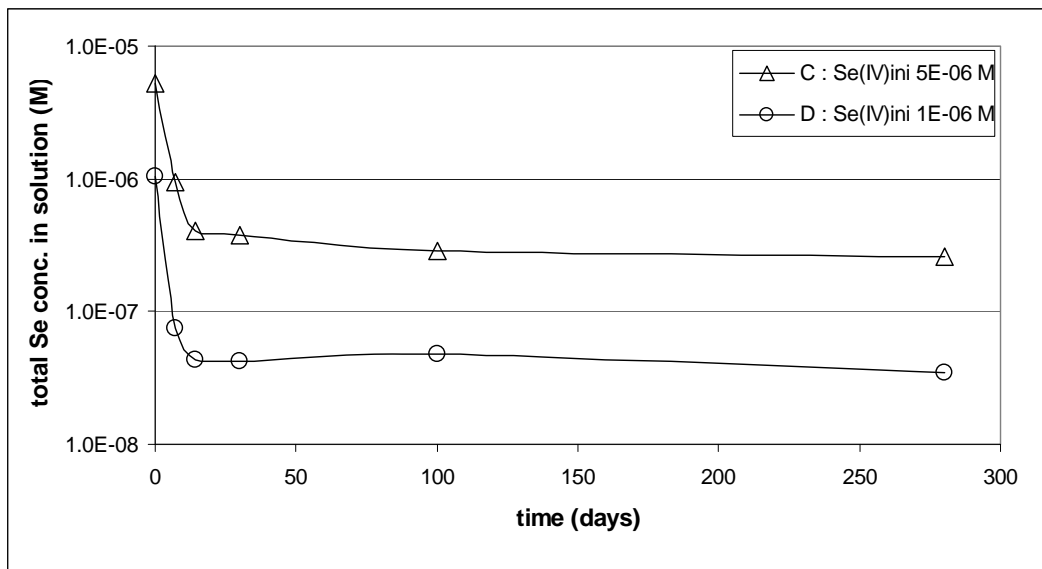
The missing mass balance for the Boom Clay batch systems that would enable the allocation of Se to different fractions in the system can still be obtained by Se analysis of the XAS samples that have been stored frozen after the XAS measurements. In addition it is recommended to repeat the sample preparation using radioactive selenium in order to allow following the distribution of Se over the different fractions of the batch system as function of time. Such information can be used for comparison of the Se distribution in the batch systems used for XAS sample preparation with previous experiments designed to determine this distribution in similar Boom Clay batch systems as function of time, initial Se dosage and solid/liquid ratio. This will allow relating the XAS evidence to

previous experiments in order to verify previous conclusions. Additionally, such information will facilitate the publication of the present results in a peer-reviewed journal.

Table 3 and Figure 14 show some data for batch Boom Clay systems from previous experiments with a Se dosage comparable to the conditions used for the preparation of the completely reduced samples O, R and U. It can be seen in the figure that an equilibrium distribution was reached after 25 days that remained stable until the end of the experiment (280 days). A similar behaviour can be expected for the batch system used for preparing the XAS samples O, R and U since the Se(IV) dosage used was only slightly higher than the dosage for the  $5 \times 10^{-6}$  M sample shown in Figure 14. Previously, the speciation of the relatively high supernatant concentration of Se was interpreted as selenite since it was thought that the 'equilibrium' liquid phase speciation of Se in Boom Clay batch systems was governed by the solubility [ $\sim 10^{-9}$  M] of elemental selenium formed by the reduction of selenite with pyrite. The new XAS data for samples O, R and U confirm the reduction of Se(IV) to elemental selenium.

**Table 3:** Overview of the solid/liquid ratio, initial Se(IV) concentration and Se(IV) dosage used for the preparation of both the completely reduced XAS samples (O, R and U) and similar batch systems used in previous experiments to evaluate the Se distribution as function of time, Se dosage and S/L ratio [14].

S/L g/l	[Se(IV)] <sub>ini</sub> M	Se(IV) dosage Mol/g	Sample
21.0	5.00E-06	2.38E-07	Previous experiment, Figure 14
21.0	1.00E-06	4.76E-08	Previous experiment, Figure 14
156.6	5.00E-05	3.19E-07	O,R,U



**Figure 14:** evolution of the total Se concentration in solution as function of time for Boom Clay batch systems ( $0.05 \text{ kg L}^{-1}$  equilibrated with an initial selenite concentration of respectively  $1 \times 10^{-6}$  and  $5 \times 10^{-6}$  M).

### 3. Conclusion

In the present series of experiments XAS based evidence was provided confirming previous findings concerning the speciation of the solid phase reaction products formed by the reduction of selenite with (FeS). It was found that an iron selenide phase is formed with a XANES fingerprint similar, but not identical to achavalite (trigonal iron selenide). In presence of pyrite (FeS<sub>2</sub>), the reduction of selenite does not lead to the formation of Se(-II); instead monoclinic red selenium is formed indicating that the redox state of the most reduced sulphur species in the system determines the oxidation state of the reaction product after reduction of selenite.

Since pyrite is one of the main reducing solid phases determining the redox state of the Boom Clay formation, it was believed that this phase will determine the final speciation of Se in the Boom Clay formation. This was confirmed by the XANES fingerprint of the solid phase Se species formed on the different fractions of the Boom Clay solid phase (clay, pyrite, organic matter) upon complete reduction of selenite in Boom Clay batch systems equilibrated for one month with an initial selenite concentration of  $5 \times 10^{-5}$  M.