DUBBLE – EXPERIMENT REPORT

We kindly request you to answer the questions (max 2 pages) and return the form to NWO **within 2 months of the completion of the experiment** to **dubble@nwo.nl**

Beam time number:		**Title:**
26_01_1059		**Interactions of Se with unaltered and redox-modified Boom Clay**
Beamline:	**Date(s) of experiment:**	**Date of report:**
BM26	**29/01 – 01/02/2016**	**24/4/2016**
Shifts:	**Local contact(s):**	
9	**Dr. Dipanjan Banerjee**	

1. **Who took part in the experiments?** (Please indicate names and affiliations)
   Dr. Thilo Behrends (Faculty of Geosciences, UU)
   Dr. Mariëtte Wolthers (Faculty of Geosciences, UU),
   Drs. Alwina Hoving (Faculty of Geosciences, UU)

2. **Were you able to execute the planned experiments?**
   YES; we have been able to perform the planned measurements.

3. **Did you encounter experimental problems?**
   NO, we did not encounter any significant problems. However, a technical problem at the ESRF disrupted the data acquisition at about 4:00 on 01/02/2016. Allegedly, a remote restart of ESRF servers impaired experiments at several beamlines. We were not able to restart the acquisition programme with standard procedures and the beamline scientist had to restart the beamline including new energy calibration of the monochromator so that we have not been able to collect more spectra after the incident.

   Furthermore, an unexplainable jump in the recorded beam intensity at the first ionization chamber (I0) when passing an energy of 13250 eV limited the energy range we could use for EXAFS analysis.

4. **Was the local support adequate?**
   YES local support was perfect and collaboration with dr. Dipanjan Banerjee was very valuable.

5. **Are the obtained results at this stage in line with the expected results as mentioned on the project proposal?**
   YES and No. See additional remarks for more details.

6. **Are you planning follow-up experiments at DUBBLE for this project?**
   NO this project has been finished, but proposals for new projects have been submitted.

7. **Are you planning experiments at other synchrotrons in the near future?**
   YES. Proposal for experiments at the Diamond Light Source have been submitted, too.

8. **Do you expect any scientific output from this experimental session (publication, patent, ..)**
   YES, the results from this experiment will be part of the PhD thesis of drs. Alwina Hoving and the related manuscripts are expected to be submitted until the end of the year.

9. **Additional remarks (short summary of preliminary results)**

   Samples were measured from experiments in which Boom Clay, or the silt and clay fraction of Boom Clay, were reacted with Se(IV). Prior to the experiments, the Boom Clay had been redox-modified

by chemical oxidation and reduction. Measurements from experiments from untreated Boom Clay material confirmed the results from our previous experiment 26-01-1016: Within the time scale of several days, Se(IV) became reduced to Se(0) as exemplarily shown for the unseparated and untreated Boom Clay in Fig.2. The presented relative concentrations of the three components are the result of the ITT analysis, which is part of the ITFA software [1]. For obtaining these results, all XANES spectra collected from 35 samples were complemented with a suite of spectra from reference materials. Depending on the loading of the vectors after the varimax rotation, reference spectra, which were related to vectors with low loading on the spectra from the experiments, were stepwise removed until only three spectra of reference material remained. The spectra of the data set with all sample spectra plus the remaining reference spectra can be very well reproduced using three components. The three extracted components by ITT analysis can be assigned to adsorbed Se(IV), red Se(0) and FeSe, respectively (Fig. 1). The third component, assigned to FeSe, contributes only marginal to spectra from samples of untreated Boom Clay. However, reproduction of spectra from reduced and oxidized Boom Clay material require the third component. It is expected that chemical reduction of the Boom Clay enhances the reductive capability of the material. It is therefore in line with the expectation that this could lead to the formation of Se(-II) which is the oxidation state of Se in FeSe. It is, however, surprising that the third component is the major Se fraction the most oxidized material (oxidized 2). After one treatment with H_2O_2 (oxidized 1) the kinetics and extent of Se(IV) reduction decreases. However, several treatments with H_2O_2 seem to activate a reductive constituent in the material which is capable to reduce Se(IV) to Se(-II). This implies that the capacity to reduce Se(IV) is not necessarily lost when Boom Clay is exposed to chemical oxidants such as H_2O_2. Furthermore, chemical redox-modfication of Boom Clay, including oxidation and reduction, appears to activate reductants for Se(IV) in the samples. Activation of these reductants can lead to the formation of other reduction products than Se(0) which is the dominant product of the reaction of Se(IV) with untreated Boom Clay.

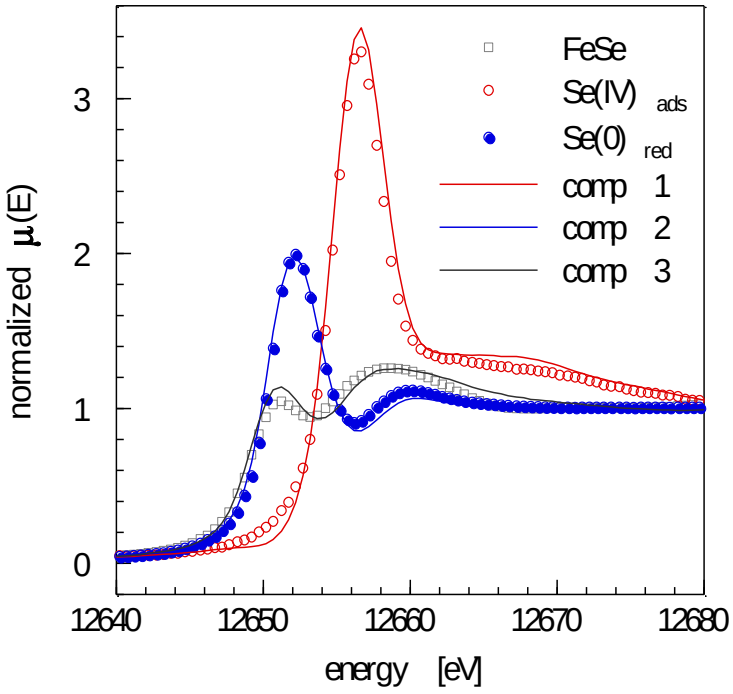

Fig.1. Three components extracted by ITT analysis from the Se XANES spectra in comparison with spectra of reference materials which were added to the data set. The three components can be interpreted as adsorbed Se(IV), red Se(0) and FeSe.

[1] Rossberg, A.; Reich, T.; Bernhard, G. (2003) Anal. Bioanal. Chem., 376, 631-638

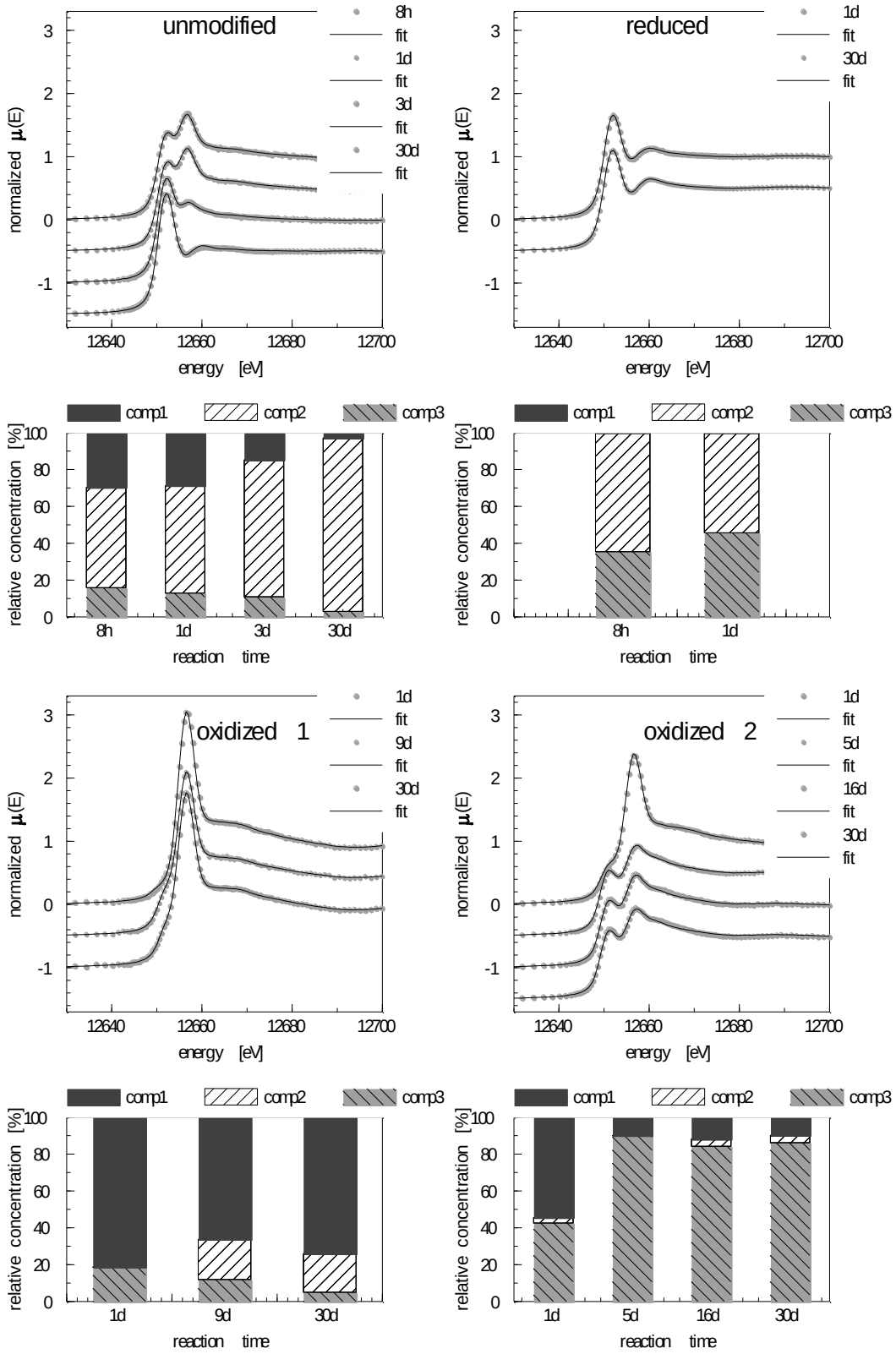

Fig 2. Se XANES spectra collected from samples which were retrieved after different reaction times from experiments in which Se(IV) had been added to Boom Clay suspensions. In addition to untreated, unseparated Boom Clay(unmodified), Boom Clay material after chemical reduction (reduced) and after one (oxidized 1) and several (oxidized 2) treatments with H_2O_2 were used. The lines are the reproduction of the spectra by using three components. The relative concentration of the components in shown in the bar charts below the XANES spectra.