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|   | <b>Experiment title:</b><br><b>EXAFS investigation of sorbed selenium oxyanions onto maghemite and influence of aqueous iron(II)</b> | <b>Experiment number:</b><br>20-01-707 |
| <b>Beamline:</b><br>BM 20  | <b>Date of experiment:</b><br>from: 20.07.2011                      to:        23.07.2011<br>(9 shifts)                              | <b>Date of report:</b><br>10.2.2012    |
| <b>Shifts:</b><br>9  | <b>Local contact(s):</b><br>Andreas C. Scheinost   | <i>Received at ESRF:</i>               |
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## Report:

For the first time, the mechanism leading to the retention of selenium(VI) and selenium(IV) onto maghemite  $\gamma\text{-Fe}_2\text{O}_3$  (a polymorph of hematite  $\alpha\text{-Fe}_2\text{O}_3$ ), as well as the nature of the sorbed species were elucidated by XAS spectroscopy. The starting maghemite suspensions consisted of  $5 \times 10^{-5}$  M Se(IV) and  $10^{-4}$  M Se(VI) in NaCl 0.1 M as background electrolyte. The pH-dependence sorption of selenium(IV) and selenium(VI) onto maghemite was studied from pH 3.5 to 8.0 and from pH 3.5 to 4.0, respectively. After 3 days of stirring to reach sorption equilibrium, the samples were ultracentrifuged during 30 minutes at 32,000 rpm and loaded as a wet paste in a sample holder, which was then sealed with Kapton tape. Great care was taken to exclude  $\text{O}_2$  during sample transport and storage by keeping them in liquid  $\text{N}_2$ . At the beamline, they were rapidly (2 min) transferred to the closed-cycle He cryostat, where they were kept at 15 K for the XAS measurements. XANES and EXAFS spectra of Se reacted maghemite were recorded on the Se K edge ( $E_0 = 12\,658$  keV) in fluorescence mode at the Rossendorf Beamline at ESRF (Grenoble, France). Corrections of energy and fluorescence deadtime as well as averaging of scans (4 to 12 depending on Se loading) were performed with SixPack, while data reduction steps and shell fitting were performed with WinXAS 3.1. The theoretical scattering phases and amplitudes were calculated using the scattering code FEFF8.2.

Fig. 1 shows the Fourier transform magnitude corresponding to radial structure functions (RSF) for selenium(VI) (left) and selenium(IV) (right) adsorbed onto maghemite, respectively. Concerning Se(VI), a strong peak at about  $1.3 \text{ \AA}$  (not corrected for phase shift) was observed, which was fit with four Se-O paths at  $1.65 \text{ \AA}$ , typical for the tetrahedral coordination of selenate. At around  $3 \text{ \AA}$ , there is another broad FT peak visible, at a distance of  $3.38 \text{ \AA}$ , with a coordination number of  $\sim 0.3$ , in line with former results of selenate sorption to Fe oxides (Hayes et al., 1987; Manceau and Charlet, 1994). This Fe-Se distance was previously interpreted – along with a Se-Fe coordination number of two – as bidentate binuclear corner-sharing complex. Results obtained by IR spectroscopy, the ionic strength dependence observable during batch experiments and the absence of the  $\text{pH}_{\text{IEP}}$  shift in zeta potential measurements all suggested the formation of outer-sphere (OS) sorption complexes. Selenate OS complexes do not show Se-Fe interactions, because their distances would be too far and too disordered to be detectable by EXAFS spectroscopy, but show only the Se-O backscattering from the coordination shell. Since this

coordination number for Fe-Se is 0 for the OS complex, and 2 for the binuclear corner-sharing complex, the fraction of the binuclear complex is  $0.3/2 = 0.15$ . The majority of Se, 85%, was therefore assumed to be present as OS complex.

Concerning Se(IV), the Fourier transform magnitude is dominated by a strong peak at about 1.3 Å (uncorrected for phase shift), which arises from backscattering of the oxygen atoms in the coordination sphere. This peak was fitted with 3 Se-O paths with a length of 1.71 Å, confirming the structure of the pyramidal selenite  $\text{SeO}_3^{2-}$  unit (Charlet et al., 2007; Peak et al., 2006). Beyond this coordination sphere, two peaks (depending on pH) clearly rise above the background noise level ( $R > 3.5$  Å). The shorter Se-Fe distance of 2.9 Å (labeled ES)) is in line with a bidentate mononuclear edge-sharing ( $^1\text{E}$ ) linkage between one  $\text{SeO}_3^{2-}$  pyramid and one  $\text{FeO}_6$  octahedron, while the longer Se-Fe distance of 3.37 Å (labeled CS) is in line with a bidentate binuclear corner-sharing ( $^2\text{C}$ ) linkage between one  $\text{SeO}_3^{2-}$  pyramid and two  $\text{FeO}_6$  octahedra. This co-existence of  $^1\text{E}$  and  $^2\text{C}$  inner-sphere surface complexes of selenite on Hydrous Ferric Oxide (HFO) and magnetite was also suggested by Manceau and Charlet (1994) and (Missana et al., 2009). According to factor analysis, the samples at pH 3.5 and 4.0 contain a mixture of both species. the sample at pH 6 represents an intermediate in speciation, with a higher ratio of  $^1\text{E}$  over  $^2\text{C}$ . However, sample pH 8.0 only contains the  $^1\text{E}$  configuration.

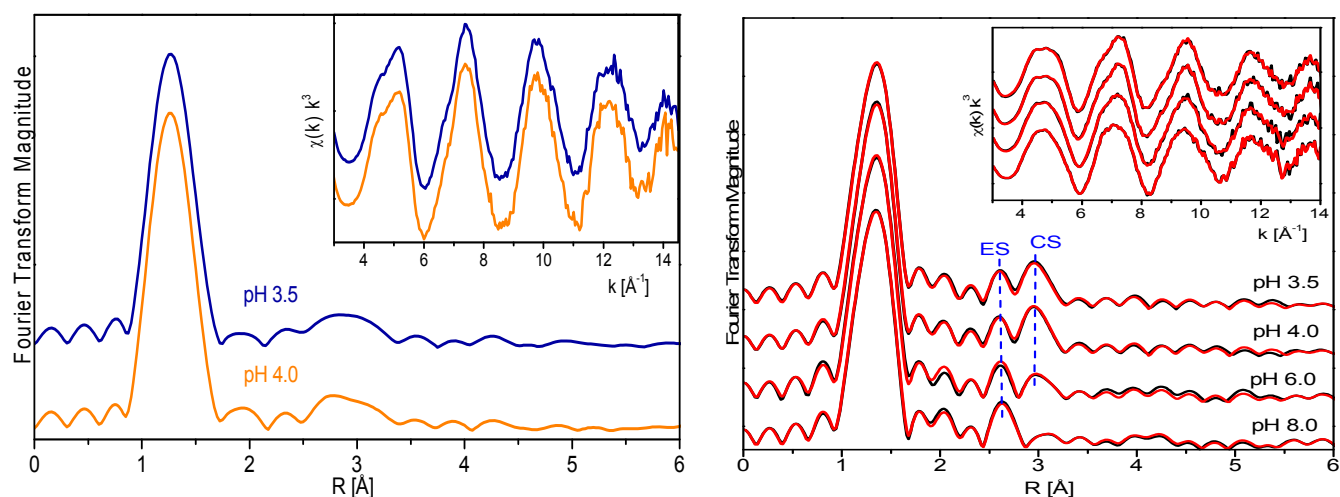


Fig. 1. Fourier transforms of Se(VI) (left) and Se(IV) (right) sorbed onto maghemite.

**Acknowledgements:** We are grateful to Dr. C. Hennig, Dr. D. Banerjee and Dr. A. Rossberg for their experimental support.

### References:

- Charlet, L., Scheinost, A. C., Tournassat, C., Greneche, J. M., Gehin, A., Fernandez-Martinez, A., Coudert, S., Tisserand, D., and Brendle, J., 2007. Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron sorbed on clay. *Geochim. Cosmochim. Acta* **71**, 5731-5749.
- Hayes, K. F., Roe, A. L., Brown, G. E., Hodgson, K. O., Leckie, J. O., and Parks, G. A., 1987. In situ X-ray absorption study of surface complexes: Selenium oxyanions on  $\alpha$ -FeOOH. *Science* **238**, 783-786.
- Manceau, A. and Charlet, L., 1994. The mechanism of selenate adsorption on goethite and hydrous ferric-oxide. *J. Colloid Interface Sci.* **168**, 87-93.
- Missana, T., Alonso, U., Scheinost, A. C., Granizo, N., and Garcia-Gutierrez, M., 2009. Selenite retention by nanocrystalline magnetite: Role of adsorption, reduction and dissolution/co-precipitation processes. *Geochim. Cosmochim. Acta* **73**, 6205-6217.
- Peak, D., Saha, U. K., and Huang, P. M., 2006. Selenite adsorption mechanisms on pure and coated montmorillonite: An EXAFS and XANES spectroscopic study. *Soil Sci. Soc. Am. J.* **70**, 192-203.