 ROBL-CRG	Experiment title: Reduction of Eu and Se by Fe(II) at the clay edge surface	Experiment number: 20-01-652
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Report:

Charlet, L., Scheinost, A. C., Tournassat, C., Greneche, J. M., Géhin, A., Fernández-Martínez, A., Coudert, S., Tisserand, D., and Brendle, J. (2007). Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron sorbed on clay. *Geochimica et Cosmochimica Acta*, in review.

Abstract:

The mobility and availability of the toxic metalloid selenium in the environment is largely controlled by sorption and redox reactions, which may proceed at temporal scales similar to that of subsurface water movement at saturated or unsaturated conditions. Since such waters are often anaerobic and rich in Fe^{2+} , we investigated the long-term (≤ 1 month) kinetics of selenite (Se(IV)O_3^-) sorption to montmorillonite in the presence of Fe^{2+} at anoxic condition. A synthetic montmorillonite was used to eliminate the influence of structural Fe. In the absence of aqueous Fe^{2+} , selenite was sorbed as outer-sphere sorption complex, covering only part of the positive edge sites, as verified by a structure-based MUSIC model and Se K-edge X-ray absorption spectroscopy. When selenite was added to montmorillonite previously equilibrated with Fe^{2+} solution, however, slow reduction of Se and formation of a solid phase was observed with Se K-edge XANES (x-ray absorption near-edge spectroscopy) and EXAFS (extended x-ray absorption fine-structure) spectroscopy. Iterative transformation factor analysis of XANES and EXAFS spectra suggested that only one Se reaction product formed, which was identified as nano-particulate Se(0) . Even after one month, only 75 % of the initially sorbed Se(IV) was reduced to this solid species. Mössbauer spectrometry revealed that before and after addition and reduction of Se, 5 % of total sorbed Fe occurred as Fe(III) species on edge sites of montmorillonite ($\approx 2 \text{ mmol kg}^{-1}$). The only change observed after addition of Se was the formation of a new Fe(II) species (15 %) attributed to the formation of an outer-sphere Fe(II)-Se

sorption complex. The combined Mössbauer and XAS results hence clearly suggest that the Se and Fe redox reactions are not directly coupled. Based on the results of a companion paper, we hypothesize that the electrons produced in the absence of Se by oxidation of sorbed Fe(II) are stored, e.g. by formation of surface H_2 species, and are then available for the later Se(IV) reduction. The slow reaction rate indicates a diffusion controlled process. Homogeneous precipitation of an iron selenite was thermodynamically predicted and experimentally observed only in the absence of clay. Interestingly, half of Fe was oxidized in this precipitate (Mössbauer). Since DFT calculations predicted the oxidation of Fe at the water-FeSe solid interface only and not in the bulk phase, the average particle size of this precipitate does not exceed 2 nm. A comparison with the Mössbauer and XAS spectra of the clay samples demonstrates that such homogenous precipitation can be excluded as mechanism for the observed slow Se reduction, emphasizing the role of abiotic, heterogeneous precipitation and reduction for the removal of Se from subsurface waters.

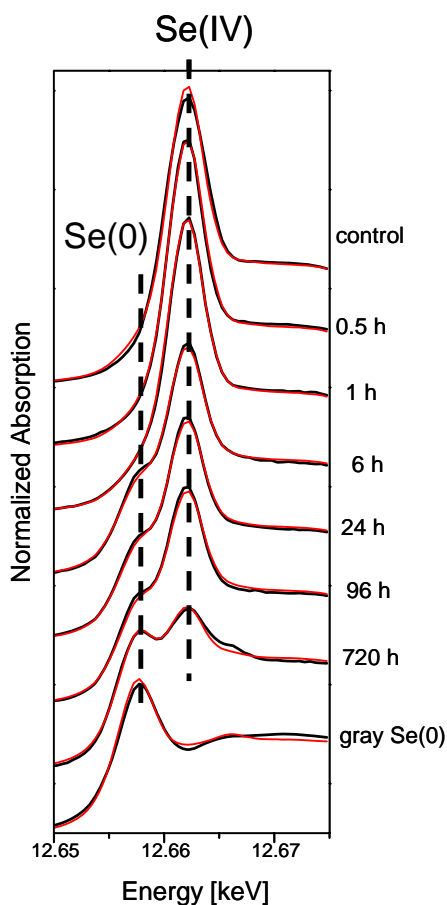


Fig. 1. Time-resolved Se-K edge XANES spectra of the Se(IV)- Fe^{2+} -montmorillonite system (black lines) and spectral reconstruction with two components (ITFA). As references, the spectra of a control without Fe^{2+} and of gray Se(0) are shown.

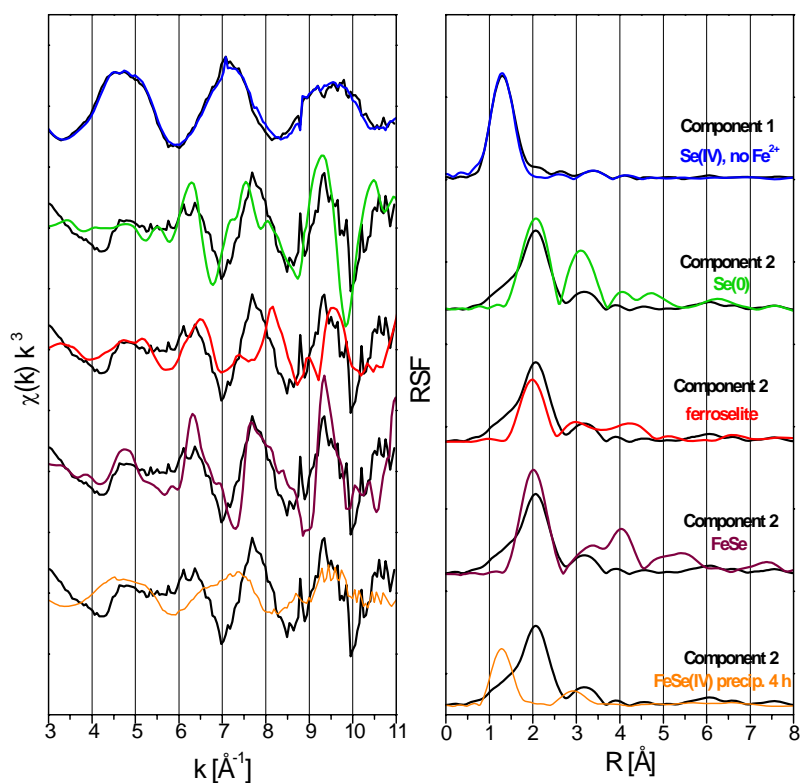


Fig. 2. Se-K edge EXAFS spectra of ITFA-derived spectral components of component/species 1 and 2 (black lines) in comparison to selected references (colored lines).