Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron sorbed on clay

L. Charlet a,*, A.C. Scheinost b,c, C. Tournassat d, J.M. Greneche e, A. Géhin a, A. Fernández-Martínez a,f, S. Coudert a, D. Tisserand a, J. Brendle g

a Environmental Geochemistry Group, LGIT-OSUG, Grenoble University, 38041 Grenoble Cedex 9, France
b Rossendorf Beamline at ESRF, Grenoble, France
c Institute of Radiochemistry, FZR, Dresden, Germany
d BRGM, Environment and Process Division, 3 avenue Claude Guillemin, F-45060 Orléans Cedex 2, France
e Laboratoire de Physique de l’Etat Condensé UMR CNRS 6087, Université du Maine, F-72085 Le Mans Cedex 9, France
f Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France
g Laboratoire de Matériaux à Porosité Contrôlée, UMR CNRS 7016, Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute Alsace, 3 rue A. Werner, F-68093 Mulhouse, France

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Abstract

The mobility and availability of the toxic metalloid selenium in the environment are largely controlled by sorption and redox reactions, which may proceed at temporal scales similar to that of subsurface water movement under saturated or unsaturated conditions. Since such waters are often anaerobic and rich in Fe²⁺, we investigated the long-term (<1 month) kinetics of selenite (Se(IV)) sorption to montmorillonite in the presence of Fe²⁺ under anoxic conditions. A synthetic montmorillonite was used to eliminate the influence of structural Fe. In the absence of aqueous Fe²⁺, 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 XAS (X-ray absorption spectroscopy). When selenite was added to montmorillonite previously equilibrated with Fe²⁺ 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 (<2 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, for example by formation of surface H₂ 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, we derived an average particle size of this precipitate which does not exceed 2 nm. A comparison with the Mössbauer and XAS spectra of the clay samples demonstrates that such homogeneous precipitation can be excluded as a mechanism for the observed slow Se reduction, emphasizing the role of abiotic, heterogeneous precipitation and reduction for the removal of Se from subsurface waters.
1. INTRODUCTION

1.1. The environmental problem

Selenium is a trace element, essential to the human body. As opposed to many other trace elements however, the optimal daily uptake is very narrow and slight differences in daily uptake may lead to either toxicity (selenosis) or deficiency. Countries with a chronic selenium deficit, such as France or Finland, have implemented a program of field fertilization with selenium-doped nitrites, but the very success of these programs depends on the efficient bioavailability of soil selenium to crops. For instance, outbreaks of the Keshan deficiency disease, a type of heart disease, in China are restricted to well defined geographic regions (Fordyce, 2005) where soils unexpectedly have rather significant total concentrations in selenium (13–160 μg/g soil, Tan et al., 1994). Moreover, no significant correlation between the disease prevalence and the total soil selenium content could be established (Johnson et al., 2000). Crops grown in the region are thus unable to extract selenium from these soils, which are also high in organic matter, and this low bioavailability is attributed either to reduction of selenium to strongly adsorbed or poorly soluble forms (Hartikainen, 2005) or to selenium strongly bound to organic fractions (Johnson et al., 2000; Wen et al., 2006). The bioavailability of selenium is therefore highly dependant on local reducing conditions, such as the ones present in organic matter rich soil aggregates, and thus on the local selenium valence state (e.g., +6, +4, 0, −1, −2). The same concept applies to the deep anoxic clay rich systems considered for the disposal of nuclear waste. In these systems, very rich in Fe²⁺ due to the anoxic clay rich systems considered for the disposal of nuclear waste (e.g., 0.26 V < Eh < 0.55 V at pH 7 and 1 μmol L⁻¹ total concentration; White et al., 1991). It exists as the selenite (SeO₃²⁻) anion, which is bound to mineral surfaces (e.g. Fe and Mn oxides) (Hayes et al., 1987; Balistrieri and Chao, 1990). Earlier investigations suggested that Se⁴⁺ behaves like phosphate, forming strong inner-sphere sorption complexes (Neal et al., 1987a,b; Barrow and Whelan, 1989; Zhang and Sparks, 1990) and substituting for phosphate in apatite (Monteil-Rivera et al., 2000; Duc et al., 2003). In reducing sediments, Se⁴⁺ and Se⁶⁺ are converted to Se⁰ and reduced Se species (oxygenation states −1 and −2). The process is thought to proceed via sorption to Fe and Mn oxides, reductive dissolution of the latter minerals, mineralization of organic matter and precipitation as Se⁰, ferroselite and Se-hosting pyrite (Velinsky and Cutter, 1990, 1991; Tokunaga et al., 1997; Belzile et al., 2000). Indeed, ferroselite-pyrite associates prevail in ore deposits (Howard, 1977; Xiong, 2003). The reduction may also involve the reduction by HS⁻, pyrite and organic matter, as in Boom clay (Bruggeman et al., 2005), and it may be either microbial or inorganic. Microbial reduction of Se⁴⁺ and Se⁶⁺ to Se⁰ has been confirmed by several laboratory studies (Oremland et al., 1989; Oremland and Steinberg, 1990; Garbisu and Fujii, 1988). Earlier work suggested that Se⁶⁺ behaves like sulfate, with low sorption and high mobility (Goldberg and Traina, 1987; Hayes et al., 1987; Neal and Sposito, 1989; Balistrieri and Chao, 1990). More recent work has demonstrated the formation of Se⁶⁺ inner-sphere sorption complexes by XAS and IR spectroscopies and electrophoretic mobility measurements (Manceau and Charlet, 1994; Su and Suarez, 2000). Both outer-sphere and inner-sphere sorption complexes may in fact occur simultaneously, the partitioning between both species being controlled by pH, ionic strength and mineral surface properties (Peak and Sparks, 2002), such as the presence of specific surface sites on different Fe oxides (Manceau and Charlet, 1994).

1.2. Speciation of selenium in reductive environments

Tetravalent Se [Se⁴⁺] is the stable valence state under mildly reducing or anoxic condition (0.26 V < Eh < 0.55 V at pH 7 and 1 μmol L⁻¹ total concentration; White et al., 1991). It exists as the selenite (SeO₃²⁻) anion, which is bound to mineral surfaces (e.g. Fe and Mn oxides) (Hayes et al., 1987; Balistrieri and Chao, 1990). Earlier investigations suggested that Se⁴⁺ behaves like phosphate, forming strong inner-sphere sorption complexes (Neal et al., 1987a,b; Barrow and Whelan, 1989; Zhang and Sparks, 1990) and substituting for phosphate in apatite (Monteil-Rivera et al., 2000; Duc et al., 2003). In reducing sediments, Se⁴⁺ and Se⁶⁺ are converted to Se⁰ and reduced Se species (oxygenation states −1 and −2). The process is thought to proceed via sorption to Fe and Mn oxides, reductive dissolution of the latter minerals, mineralization of organic matter and precipitation as Se⁰, ferroselite and Se-hosting pyrite (Velinsky and Cutter, 1990, 1991; Tokunaga et al., 1997; Belzile et al., 2000). Indeed, ferroselite-pyrite associates prevail in ore deposits (Howard, 1977; Xiong, 2003). The reduction may also involve the reduction by HS⁻, pyrite and organic matter, as in Boom clay (Bruggeman et al., 2005), and it may be either microbial or inorganic. Microbial reduction of Se⁴⁺ and Se⁶⁺ to Se⁰ has been confirmed by several laboratory studies (Oremland et al., 1989; Oremland and Steinberg, 1990; Garbisu and Fujii, 1988). Earlier work suggested that Se⁶⁺ behaves like sulfate, with low sorption and high mobility (Goldberg and Traina, 1987; Hayes et al., 1987; Neal and Sposito, 1989; Balistrieri and Chao, 1990). More recent work has demonstrated the formation of Se⁶⁺ inner-sphere sorption complexes by XAS and IR spectroscopies and electrophoretic mobility measurements (Manceau and Charlet, 1994; Su and Suarez, 2000). Both outer-sphere and inner-sphere sorption complexes may in fact occur simultaneously, the partitioning between both species being controlled by pH, ionic strength and mineral surface properties (Peak and Sparks, 2002), such as the presence of specific surface sites on different Fe oxides (Manceau and Charlet, 1994).

1.3. The reactive Fe(II)–clay system

Montmorillonite is a 2:1 layer-type smectite clay mineral found in a variety of environments. It has two reactive surfaces: the siloxane basal planes, and the edges with mixed aluminoil and silanol groups. Fe²⁺ sorbs to these siloxane planes by cation exchange (Kamei et al., 1999; Charlet and Tournassat, 2005). It also sorbs to the edges via a complex pH-dependent surface complexation mechanism (Géhin et al., 2007). The sorption sites for metal ions such as Fe²⁺ can be considered as a combination of the 27 reactive edge sites distinguished for proton adsorption based on the structure and composition of an ideal montmorillonite structure with Mg and Fe (ferrous and ferric) octahedral substitutions but with no tetrahedral substitution (Fig. 1). Out of the 27 sites, five main sites are quantitatively sufficient to describe the titration curves of natural montmorillonite (Tournassat et al., 2004a,b). Fe²⁺ specific adsorption occurs at pH values as low as pH 2 or 3, depending on the montmorillonite sample, and this behavior demonstrates the extreme high affinity of clay edge site(s) for the Fe²⁺.
The use of the $^{57}$Fe isotope and Mössbauer spectroscopy has been instrumental in distinguishing adsorbed Fe$^{2+}$ from structural iron (III) (Williams and Scherer, 2004; Silvester et al., 2005). $^{57}$Fe was used to quantify the Fe(III)/Fe(II) ratio of sorbed iron (Géhin et al., 2007). At pH values where a pre-sorption edge plateau occurs ($2 < $ pH $< 7.5$), the ratio increases from 0.14 at pH 2 up to 0.74 at pH 7. As pH increases and protons are removed from the clay edge surface, more highly reactive edge sites acquire a steric configuration that stabilizes Fe(III) relative to Fe(II). This surface oxidation of Fe(II) is completely reversible, i.e. by lowering the suspension pH, the Fe(II)/Fe(III) ratio is again reduced to the value observed before raising the pH. Therefore the oxidation agent is water and the hydrogen molecules produced by the reaction remain in the vicinity of the surface complex for the reaction to be macroscopically reversible.

1.4. Aims of the present study

With this background, we investigated the long-term kinetics of Se(IV) reduction in Fe$^{2+}$-montmorillonite suspensions, employing a strictly Fe-free montmorillonite. We coupled two spectroscopic techniques, Mössbauer spectrometry and X-ray absorption spectroscopy, to explore the mechanism and reduction kinetics in the Fe$^{2+}$/Se$^{4+}$/montmorillonite system as an analog of many O$_2$-free soil and groundwater systems where the transport of selenium is of concern. Mössbauer spectrometry was not only used to
quantify the Fe(II)/Fe(III) ratio in each system but also to distinguish different species in each oxidation state. Selenium K-edge X-ray Near-Edge Structure (XANES) and Extended X-ray Absorption Fine-Structure (EXAFS) spectroscopy, evaluated by Iterative Transformation Factor Analysis (ITFA) were used to derive the number of different oxidation states, to identify the local structure of the species and to quantify their relative amounts. Molecular Dynamics calculations and a bond valence approach were used to investigate the oxidation state and structure of hydrated Fe-selenite surfaces as reference model.

2. MATERIAL AND METHODS

The present study relies on the combination of a large panel of experimental and modeling approaches. Chemical conditions and modeling with regards to Fe(II) sorption onto the synthetic montmorillonite used in this study have been described in a previous paper (Géhin et al., 2007). The effect of this sorbed Fe(II) on the Se speciation is investigated here through Se sorption kinetics where pH, Eh and Se and Fe concentrations variations were monitored. During the course of these experiments, solid samples were taken in order to perform spectroscopic measurements: XANES/EXAFS and Mössbauer spectrometry for Se and Fe speciation on the solid, respectively. The coherence between the results from all of these techniques was checked through the application of solution/solid speciation models for Se and Fe. Finally, Density Functional Theory studies were performed to verify the reliability of some features of our interpretations.

2.1. Laboratory material and methods

2.1.1. Chemicals

All solutions and suspensions were prepared with boiled, argon-degassed Millipore Milli-Q 18 MΩ water. NaOH and HCl stock solutions were made from Titrisol ampoules. CaCl₂ and FeCl₂ stock solutions were prepared from analytical grade salt. HPLC-AFS speciation analysis of Se(IV) stock solution kept in contact with air showed a slow but distinct oxidation of Se(IV) to Se(VI), hence the Se(IV) stock solution kept in contact with air was similar to Ca-saturated, purified natural MX80 Wyoming bentonite (see Géhin et al., 2007).

The cation exchange capacity of the synthetic montmorillonite was measured with the Cs–Li method (Anderson and Sposito, 1991). At pH 7.0, the permanent structural charge (Cs) was 0.44 eq/kg and the variable charge (Li) was 0.19 eq/kg, accounting for a total CEC of 0.63 eq/kg. The methods used to determine the concentration of the clay suspension are available from Tournassat et al. (2004a,b).

2.1.3. Oxygen control

All experiments were conducted at room temperature (25 ± 2 °C) in a glove box (Jacomex) with a N₂ atmosphere. The oxygen partial pressure (pO₂) was monitored continuously by a Jacomex O₂ sensor, and never exceeded 1 ppm. As discussed in detail in a companion paper (Géhin et al., 2007), the rate of Fe(II) oxidation was negligible under the present experimental conditions, where every precaution was taken to minimize the presence of oxygen in solution.

Extreme care was also taken to prevent sample oxidation during the transport from the glove box to the spectroscopic facilities. Small aliquots (a few mL) of suspensions were filtered (Millipore filter 0.022 μm) and the wet pastes were then transferred to Mössbauer or XAS sample holders. The sample holders were sealed with Kapton tape (XAS spectroscopy) or with epoxy resin (Mössbauer spectroscopy) and placed in small plastic boxes. All these steps were performed in the glove box. The samples were then immediately shock-frozen with liquid N₂ and transported to the spectroscopic facilities in a Dewar flask filled with liquid N₂. At the synchrotron facility, they were transferred within 2 minutes from the Dewar to a closed-cycle He cryostat with He atmosphere and 15 K temperature, which was used for the XAS measurements. At the Mössbauer facility, the samples were transferred within 1 minute from the Dewar to the Mössbauer bath cryostat with a He gas atmosphere.

2.1.4. Analyses

Inductively coupled plasma optical emission spectroscopy (ICP-AES) (Perkin-Elmer Optima 3000 DV) was used to measure total iron and selenium concentrations above 0.5 μmol L⁻¹ Fe and 7.5 μmol L⁻¹ Se. Total Se concentrations lower than 1.5 μM were analyzed by Atomic Fluorescence Spectrometry (Millenium AFS). The Ferrozine method (Viollier et al., 2000) was also used to measure Fe(II) and Fe(III) separately for concentrations up to 30 μM after dilution and to show that no oxidation of Fe(II) to Fe(III) had occurred in solution, i.e. that Fe³⁺ concentration is equal, within measurement accuracy, to Fe total concentration.
2.2. Wet chemistry and spectrometric investigations

2.2.1. Kinetic redox experiments

Fe(II)–Se(IV) redox kinetics in the presence of synthetic montmorillonite was studied in a closed reactor in free pH drift mode. The pH of the suspensions was measured in the supernatant with a pH meter (Metrohm 781 pH/Ion Meter). The montmorillonite was stored in 0.05 M CaCl₂ solution in order to avoid artifacts due to hydration after freeze drying. All the experiments were performed using the same clay stock suspension and were conducted at room temperature with 0.05 M CaCl₂ background electrolyte to minimize the Ca²⁺-by-Fe³⁺ exchange in the montmorillonite interlayer by mass effect. The clay concentration of the suspension was set to 20 g/L for all the experiments.

The montmorillonite suspension was equilibrated in a 350 ml glass reactor, wrapped with aluminum foil to avoid exposure to light (Gruebel et al., 1995), for one week at pH 6.0 with 5 mM aqueous ⁵⁷Fe²⁺ (or for the XAS sample, with regular Fe²⁺) before adding Se. Isotopically pure ⁵⁷Fe(II) (>97%) was used in order to enhance the Mössbauer signal. The reactor had three inputs, one for the pH electrode and two others for adding and retrieving solutions. At time zero an aliquot of a Se(IV) stock solution was introduced in the reactor to obtain an initial solution concentration of 0.5 mM. The pH of the suspension increased up to pH 7.2. After given reaction periods, a 10-ml sample of suspension was filtered through a 0.22-µm pore size membrane and analyzed for selenium concentration. Solutions filtered with smaller pore size membranes (0.1 µm) had the same Fe and Se concentration. This indicates that the reacted solid (wet slurry) retained all possibly formed nanoparticles. It was transferred to the respective sample holders for XAS and Mössbauer spectroscopies. The experiment was repeated, but with an initial pH of 7.6 instead of 7.2, to follow the Fe–pH relationship.

2.2.2. ⁵⁷Fe Mössbauer spectrometry

The Mössbauer spectrometer was operated in transmission geometry in constant-acceleration mode. The velocity was calibrated using a standard Mössbauer metallic Fe foil at room temperature (RT, 295 K). The values of isomer shifts (IS) are reported relative to that of the α-Fe spectrum obtained at RT.

The spectra were fitted with MOSFIT using a discrete number of independent components (single line, quadrupole doublet and magnetic sextet) composed of Lorentzian lines. The line width at half-height $\Gamma$ (mm s⁻¹), the center shift $\delta$ (mm s⁻¹) and the quadrupole splitting $\Delta E_Q$ (mm s⁻¹) were refined using a least-squared fitting procedure. Standard deviations of parameters were generally less than 0.02 mm s⁻¹ for IS and $\Delta E_Q$, 0.02 mm s⁻¹ for $\Gamma$ and about 2% for relative absorption area. For a doublet component, the two peaks were assigned with equal areas, in agreement with isotropic powdered samples, i.e. a random distribution of crystallites.

Spectral Mössbauer analysis can resolve the number of Fe sites, their valence states and the type of magnetic order, through the electric and magnetic hyperfine interactions at ⁵⁷Fe nuclei. In the present study, the Mössbauer spectra exhibit quadrupolar structure where the doublet peak separation is known as “quadrupole splitting” and may be designated $\Delta E_Q$ while the center of each component is related to the “isomer shift”, which is sensitive to the s electron density, i.e. the valence state. The method consequently enables the presence of Fe(II), Fe(III) and intermediate or mixed valence states, i.e. with localized and delocalized electrons, respectively to be established. When the hyperfine parameters are well refined, both IS and $\Delta E_Q$ serve as a fingerprint in identifying the particular mineral phase or species.

For well-crystallized materials, the typical measured peak width $\Gamma$ is 0.3–0.35. Line broadening may be attributed to either (1) an amorphous nature of the material; or (2) a lack of crystallinity (presence of atomic defects as substitution vacancies); or (3) the occurrence of superparamagnetic fluctuations originating from the presence of small magnetic particles (<20–30 nm), when the interactions between particles are weak.

2.2.3. X-ray absorption spectroscopy

Selenium K-edge XAS spectra were collected at the Rosendörfer Beamline (BM20) at the ESRF. Both the X-ray Absorption Near-Edge Spectroscopy (XANES) region around the absorption edge and the Extended X-ray Absorption Fine Structure (EXAFS) region above the absorption edge were recorded. A Si(111) double crystal monochromator (DCM) was used with electronic beam flux stabilization (MOSTAB) through a fast feedback loop between the pitch movement of the 2nd crystal and the output signal from the I₀ ion chamber. The energy of the DCM was calibrated relative to the Au K-edge of metallic gold (11,919 eV). Collimation, vertical focusing and the suppression of higher-order harmonics was achieved with two Pt-coated cylindrical mirrors before and after the DCM.

The samples were measured in fluorescence mode using a 13-element Ge detector (Canberra) with digital signal processing (XIA DXP-2X4T-M). A low-vibration, closed-cycle He cryostat (CryoVac) cooled the samples to 15 K and excluded O₂ from the sample environment, thereby suppressing sample redox processes due to O₂ diffusion and photoreduction and improving spectral quality due to reduction of the thermal contributions to the Debye–Waller factors. Several scans were combined for improved signal quality. The energy of each scan was corrected using a simultaneously monitored Au(0) foil and the dead time of the fluorescence detector was corrected by employing the nonlinear relation between the count rates of SCA, $r$, and ICR: $r = \rho \exp(-\tau)$, with the deadtime ($\mu$s), $\tau$, and the proportionality constant, $\kappa$ (SixPack, http://www.stanford.edu/~swebb).

Quantitative speciation was performed by applying Iterative Transformation Factor Analysis (ITFA) to the normalized XANES spectra and to the k²-weighted chi spectra (Rossberg et al., 2003). This method combines principal component analysis (PCA) and iterative target test (ITT) to derive real spectra of endmember species and their relative contribution to each sample spectrum, i.e. the full quantitative speciation. The advantage in relation to standard methods (PCA followed by target test and linear
combination fit in separate steps) is the higher reliability and the possibility of extracting the real spectra of endmember species, even in the absence of appropriate reference spectra.

To determine the short-range structure of extracted species, EXAFS shell fitting was performed using FEFF 7 and WinXAS (Ankudinov and Rehr, 1997; Ressler, 1998). Based on the fits of reference minerals, the error of the first shell coordination numbers is better than ±25%, and the error of distances is ±0.01 Å.

The following reference samples were available. First a natural achatavite sample was used, nominally Fe \textsubscript{II}Se, from Cerro de Cachenta, Mendoza (Argentina); the EXAFS range of this sample was restricted to 10 Å\textsuperscript{-1} because of a high Pb content. A synthetic Fe \textsubscript{II}Se sample (AlfaAesar) consisted predominately of tetragonal Fe \textsubscript{II}Se\textsubscript{2}, in addition to minor amounts of hexagonal Fe \textsubscript{II}Se (achavalite) and hexagonal Se(0) as confirmed by XRD collected under an O\textsubscript{2}-free atmosphere. The XAS spectrum of ferroselite, orthorhombic Fe\textsubscript{II}Se\textsubscript{2}, was provided by Dan Strawn, University of Idaho. A sample of trigonal, grey Se(0) was obtained from the School of Mines Mineralogy Museum, Paris. As solid Se(IV) reference, Na\textsubscript{2}SeO\textsubscript{3} \textsubscript{Æ} 5H\textsubscript{2}O purchased from Merck was used. Finally, an FeSeO\textsubscript{3} precipitate was obtained by reacting 50 mM Se(IV) with 50 mM Fe\textsuperscript{2+} at pH 5. The precipitate was filtered after 4 h, and repeatedly washed with deionized water. The XANES and EXAFS spectra of these references are shown in Figs. 2, 8 and 10.

2.3. Modeling approaches

2.3.1. Bond valence model

The solid compound FeSeO\textsubscript{3} was studied by Density Functional Theory (DFT) based Molecular Dynamics (MD) simulations, using the Vienna \textit{ab initio} Simulation Package (VASP) (Kresse and Hafner, 1993). Details of the calculations can be found elsewhere (Cuello et al., 2007). Mulliken Population Analyses have been performed with DMol\textsuperscript{3} (Delley, 1990) in order to study the optimized structure of the bulk of FeSeO\textsubscript{3}. A Double Numerical plus Polarization (DNP) set (Delley, 1990) has been used as basis set for the atomic orbitals. The Perdew–Burke–Ernzerhof exchange correlation functional (Perdew et al., 1996) has been used to calculate the exchange-correlation energy. These calculations project the charge density into the numerical basis set of atomic orbitals, that gives a value for bond populations (order) and atomic charge.

The results of the simulations have been interpreted in terms of the 2nd Pauling’s rule of electrostatic valence (Pauling, 1929). It states that the total strength of the valence bonds that reach an ion from all neighboring atoms is equal to the charge of the ion (\(V_i\)):

\[ V_i = \sum_j s_{ij} \]

where \(V_i\) is the charge of the \(i\) ion and \(s_{ij}\) is the strength of the bond between a neighboring \(j\) atom and the \(i\) ion. The more commonly used model for the calculation of the bond strength is that from Brown and Altermatt (1985) that relates \(s_{ij}\) to the bond lengths by this expression:

\[ s_{ij} = \exp\left(\frac{(R_0 - R_{ij})}{b}\right) \]

with \(R_0\) is the bond length between the atoms and \(R_0\) and \(b\) are parameters fitted by analyzing several known structures.

The Bond Valence approach is implemented into the MUSIC model for surface complexation in order to predict proton affinity constants based on structural parameters (Hiemstra et al., 1989a,b, 1996).

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**Fig. 2.** Selenium K-edge XAS spectra of Se(IV) sorbed to synthetic montmorillonite at pH 6.0 in the absence of Fe\textsuperscript{2+}, in comparison to selected references with Se oxidation states of IV, 0, I and II (left, XANES; middle, EXAFS; right, Fourier transform of EXAFS).
2.3.2. MUSIC surface complexation model and Fe sorption model

The clay MUSIC model of Tournassat et al. (2004a,b) is a non-electrostatic model, as previously developed by (Baeyens and Bradbury, 1997), which aims at integrating the complexity of the edge sites in both structural and chemical terms. The MUSIC approach (Hiemstra et al., 1989a,b, 1996) has been used to obtain the protonation/deprotonation pK of the edge sites. At pH values below 7–8, this model suggested that two main sites control the change in positive edge charge due to their relative amount and pK:

\[
\begin{align*}
\text{Si-O}^{-1/2} - \text{Al} + \text{H}^+ & \iff \text{Si-OH}^{+1/2} - \text{Al} & \log K_1 &= -7.2 \\
\text{Al-OH}^- - \text{Al} + \text{H}^+ & \iff \text{Al-OH}_2^+ - \text{Al} & \log K_2 &= -4.8
\end{align*}
\]

Acid–base and complexation reactions occurring both at edge sites and at cation exchange sites were used, as in the earlier Baeyens and Bradbury model. Due to the large variety of different edge sites, some edge sites were grouped together in the model and some sites were neglected due to their low density at the edges. Despite the numerous approximations relative to the contribution of different edge faces and thus to the different edge surface populations, the MUSIC approach successfully described the surface proton charge of montmorillonite and the apparent CEC variations as a function of pH (Tournassat et al., 2004a,b). This model was tested for the prediction of Se adsorption as a function of pH. The sorption of Fe was not modeled using the MUSIC approach mainly because it is still not possible to attribute the sorption behavior of Fe to specific chemical–structural sites. Therefore, we used a simple specific sorption model for Fe as described in the companion paper (Géhin et al., 2007).

3. RESULTS AND DISCUSSION

3.1. Adsorption of single ions (SeO\(_4\)\(^{2-}\) or Fe\(^{2+}\)) on clay edges

Adsorption of selenium oxyanions on clays is generally considered to be very low and to be affected to a greater extent by pH than by type of mineral, although the 2:1 mineral montmorillonite exhibits smaller sorption capacity than the 1:1 mineral kaolinite (Bar-Yosef and Meek, 1987). The permanent negative electric field near the surface of montmorillonite is more effective in screening the positive charge of clay edges (Tournassat et al., 2004a,b), thus restricting anion accessibility to the edge adsorption sites (Bar-Yosef and Meek, 1987; Chang and Sposito, 1996; Avena, 2002). Depending on whether the electric edge surface potential is explicitly taken into account or not, montmorillonite of Zero Net Proton Charge (PZNPC) varies from pH 4.5 (Bourg et al., 2007) to pH 7.3 (Tournassat et al., 2004b), and the presence of positively charged edge sites varies accordingly.

The EXAFS spectrum of the Se(IV) reacted montmorillonite in the absence of Fe\(^{2+}\) (Fig. 2) was used to determine the structure of the sorption complex. The fit suggests only one oxygen coordination shell, with the refined values close to the expected coordination number of three and an average distance of 1.70 Å, in line with the Se species SeO\(_4\)\(^{2-}\). In spite of the long k range (2–14 Å\(^{-1}\)) and the measurement at 15 K, which suppresses thermal atomic vibrations, no further atomic shell beyond the O coordination sphere was detected. Therefore we can exclude the presence of more than 5% of inner-sphere complexes. Hence, on synthetic montmorillonite at pH 6.0, outer-sphere selenite sorption prevails, presumably to positively charged edge sites.

This result is in contrast to that of Peak et al. (2006), who observed prevalently inner-sphere sorption of selenite to a natural montmorillonite. While their interpretation based on EXAFS data may be biased by a short k range and higher noise level, their careful interpretation of the XANES region provides compelling evidence for the prevalence of inner-sphere complexes. By comparison, the XANES of our sample of selenite
Table 1
List of reactions and their equilibrium constants as used in the non electrostatic, smectite MUSIC model (Tournassat et al., 2004b) and in the Fe sorption model of Géhin et al. (2007)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Log $K$</th>
<th>Site conc. (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$XNa + H^+ \Leftrightarrow XH + Na^+$</td>
<td>$0^a$</td>
<td></td>
</tr>
<tr>
<td>$XNa + Ca^{2+} \Leftrightarrow XCa + 2 Na^+$</td>
<td>$0.5^a$</td>
<td></td>
</tr>
<tr>
<td>$XNa + CaCl^{+} \Leftrightarrow XCaCl + Na^+$</td>
<td>$2.5^a$</td>
<td></td>
</tr>
<tr>
<td>$2XNa + Fe^{2+} \Leftrightarrow X_2Fe + 2Na^+$</td>
<td>$0.4^a$</td>
<td></td>
</tr>
<tr>
<td>$XNa + FeCl^{+} \Leftrightarrow XFeCl + Na^+$</td>
<td>$2.3^a$</td>
<td></td>
</tr>
<tr>
<td>Edge protonation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Si - O^{1/2} - Al + H^+ \Leftrightarrow Si - OH^{1/2} - Al$</td>
<td>$-7.2$</td>
<td>$31$</td>
</tr>
<tr>
<td>$Al(OH)^{-} - Al + H^+ \Leftrightarrow Al(OH)^{2-} - Al$</td>
<td>$-4.8$</td>
<td>$34$</td>
</tr>
<tr>
<td>Selenium adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Si - OH^{1/2} - Al + HSeO_3^- \Leftrightarrow Si - OH^{1/2} - Al \cdot HSeO_3^-$</td>
<td>$16.5$</td>
<td>$0.5 \times (1.5 \times 31)$</td>
</tr>
<tr>
<td>$Al(OH)^{2-} - Al + HSeO_3^- \Leftrightarrow Al(OH)^{2-} - Al \cdot HSeO_3^-$</td>
<td>$16.5$</td>
<td>$0.5 \times (1.5 \times 34)$</td>
</tr>
<tr>
<td>Fe sorption on clay edges$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fe^{2+} + s^1 \equiv 3[(OH^-)_2 \Leftrightarrow s^1 \equiv 3[(OH^-)(O_2^-)_2Fe^{2+} + 2H^+]$</td>
<td>$1$</td>
<td>$1.4$</td>
</tr>
<tr>
<td>$s^1 \equiv 3[(OH^-)(O_2^-)_2Fe^{2+} + 2H_2O \Leftrightarrow s^1 \equiv 3[(OH^-)_2Fe^{3+} (OH^-)<em>2 \cdot (H_2)</em>{0.5} + 2H^+]$</td>
<td>$-7.8$</td>
<td></td>
</tr>
<tr>
<td>$Fe^{2+} + s^2 \equiv 3[(OH^-)^- \equiv s^2 \equiv 3[(OH^-)(O_2^-)_2Fe^{2+} + 2H^+]$</td>
<td>$1$</td>
<td>$2.8$</td>
</tr>
<tr>
<td>$s^2 \equiv 3[(OH^-)(O_2^-)_2Fe^{2+} + 2H_2O \Leftrightarrow s^2 \equiv 3[(OH^-)_2Fe^{3+} (OH^-)<em>2 \cdot (H_2)</em>{0.5} + 2H^+]$</td>
<td>$-13$</td>
<td></td>
</tr>
<tr>
<td>$2 \equiv wOH + Fe^{3+} + H_2O \Leftrightarrow wOH_{2FeOH^+} + 3H^+$</td>
<td>$-19.5$</td>
<td>$80$</td>
</tr>
</tbody>
</table>

$^a$ After Charlet and Tournassat (2005), Gaines and Thomas thermodynamic convention.

$^b$ From Cs-Li method (Anderson and Sposito, 1991).

$^c$ Model from Géhin et al. (2007).

Fig. 5. Kinetics of Se(IV) reduction at the surface of the Fe(II)-sorbed montmorillonite (Experimental conditions 20 g clay L$^{-1}$, 5 mmol L$^{-1}$ Fe(II), 0.5 mmol L$^{-1}$ Se(IV), 0.05 M CaCl$_2$). (Top) Speciation derived from XANES spectra (see Fig. 9, speciation normalized to unity). (Middle) Percent sorbed Fe and Se. (Bottom) pH.
sorbed to montmorillonite (Fig. 2 left, orange) is clearly different, being more similar to the structures with delocalized Se-O double bonds (e.g. SeO$_2^-$ and HSeO$_3^-$) than to the structures with a localized double bond (e.g. H$_2$SeO$_4^-$), thereby confirming the prevalence of outer-sphere complexes. Therefore, the evident difference of sorption mechanisms in this former study may be due to differences in experimental conditions. While we have been working at comparable ionic strength, the pH was lower in Peak’s study (4.5) as compared to our study (6.5). Furthermore, the former study employed a natural montmorillonite, while we employed a synthetic sample. Whether or not these differences, may be responsible for the observed differences, seems to be purely speculative.

The macroscopic adsorption of Se(IV) was predicted using the data from Boult et al. (1998) in 10 mM NaCl (Fig. 3). The data indicates that for a relatively high concentration of Se (10$^{-4}$ mol L$^{-1}$, similar to $5 \times 10^{-4}$ mol L$^{-1}$ used in our experiments), the relative sorption is small (20%), reaching a sorption plateau below pH 5 (Fig. 3). The maximum sorption capacity of 1 mmol g$^{-1}$ is in agreement with previously published values (1.5 mmol g$^{-1}$ at pH 6–7, Tan et al., 1994). The observed sorption edge is typical for weakly sorbing anions. The starting point of the sorption edge corresponds to the pH value, where the net charge of the functional groups at montmorillonite edge sites is expected to become positive based on the smectite MUSIC model (Tournassat et al., 2004a,b). The model predictions are therefore in agreement with the EXAFS data, supporting an outer-sphere complexation with positively charged edge sites.

The model of Tournassat et al. (2004a,b) was used to predict the Se sorption data. The simplest approach consists in defining Se sorption reactions with the same specific association constant for the two sites in the form of:

\[
\text{Si-OH}^{1/2+}Al + \text{HSeO}_3^- \rightleftharpoons \text{Si-OH}^{1/2+}Al \cdots \text{HSeO}_3^- \\
\log K_1 = 16.5
\]

\[
\text{Al-OH}_2^{1/2+}Al + \text{HSeO}_3^- \rightleftharpoons \text{Al-OH}_2^{1/2+}Al \cdots \text{HSeO}_3^- \\
\log K_4 = 16.5
\]

The associated log $K$ value was fitted in order to reproduce the start of the edge at pH 7–8. However, this simplistic model predicted a much higher sorption in agreement with the high surface density for these sites ($\sim 30$ mmol g$^{-1}$ for both sites, Tournassat et al., 2004a,b). In fact, only 1.5% of the available sites were necessary to obtain the fit shown in Fig. 3. This can be seen as the consequence of the negative structural charge of the clay that screens the positive charge of the edges (e.g. Chang and Sposito, 1996; Avena, 2002).

In contrast to selenite, Fe$^{2+}$ is strongly sorbed by montmorillonite (Fig. 4, after Géhin et al., 2007). An adsorption edge is observed, which starts above pH 7. Below the sorption edge, much less Fe$^{2+}$ is sorbed, following a pH-independent pre-edge plateau (Fig. 4). According to the $^{57}$Fe Mössbauer results, this sorption plateau at low pH cannot be entirely attributed to cation exchange as for other metallic cations such as Zn or Ni (e.g. Baeyens and Bradbury, 1997). Instead, specific sorption and oxidation phenomena occur at pH values as low as pH 3 (Géhin et al., 2007). Based on the Mössbauer results, the sorption data could be successfully fitted using the model given in Table 1 (Fig. 4, insert). The sorbed Se and Fe concentrations observed during the kinetic experiment are presented in Fig. 5. They are in good agreement with the sorption model. This is shown in Fig. 6, which shows the amount of sorbed Fe(II) in absence of Se using the experimental conditions of the present experiments modeled after Géhin et al. (2007). Fig. 7 shows the amount of Se(IV) in absence of iron as derived from the smectite MUSIC model (Table 1), together with the predicted amount of sorbed Fe(III) in absence of Se (see Section 3.2).

![Fig. 6. Modeled Fe sorption by specific sites (full line), and cation exchange sites (dotted line) of synthetic montmorillonite (Experimental conditions: 20 g$_{clay}$ L$^{-1}$, [Fe]$^T$ = 5 mM, [CaCl$_2$] = 50 mM). Dotted dash line: total sorbed Fe. Symbols: total sorbed Fe at the beginning and end of the kinetic experiment.](image)

![Fig. 7. Modeled Se(IV) sorption on specific sites of synthetic montmorillonite in the absence of Fe and predicted amount of sorbed Fe(III) in the absence of Se after Géhin et al. (2007) (Experimental conditions: 20 g$_{clay}$ L$^{-1}$, [Fe]$^T$ = 5 mM, [CaCl$_2$] = 50 mM, [Se]$^T$ = 0.5 mM). Symbols denote measured sorbed amounts of Se and Fe during the kinetic experiment.](image)
3.2. Mössbauer results of the clay–Fe(II)–Se(IV) system

Fig. 8 shows the paramagnetic Mössbauer spectra of selected samples recorded at 77 K and their deconvolution into different Fe(II) and Fe(III) species. The corresponding hyperfine parameters are given in Table 2. Montmorillonite reacted with Fe²⁺ only, i.e. without selenite, shows two doublets D₁ and D₂ assigned to Fe(II) species (Fig. 8a, spectrum taken from Géhin et al., 2007). This species has been identified as FeCl⁺ and Fe²⁺ bound to cation exchange sites (Charlet and Tournassat, 2005; Géhin et al., 2007). In addition, there is a third doublet D₃ corresponding to about 23% of Fe(III). Given the strictly anoxic conditions and the absence of any redox active metals in aqueous solution, in the montmorillonite solid and at the respective interface, the occurrence of this Fe(III) species is surprising. In a companion paper, Géhin et al. (2007) investigated this Fe redox phenomenon at the water–montmorillonite interface in detail and suggested that the oxidative agent responsible for this reversible oxidation is water.

Mössbauer spectra of the Fe(II)–clay samples reacted with selenite for 1 h and 5 days are shown in Figs. 8b and c, respectively. The D₁, D₂ and D₃ doublets have hyperfine parameters similar to those in the absence of Se, suggesting that they represent similar species. In both samples, the two exchangeable Fe(II) species prevail (D₁ + D₂: 79–86%). However a striking fact appears which a priori could contradict the role of selenium as an electron acceptor: 23% of the total sorbed iron is oxidized in the absence of selenium, whereas only 4% of the sorbed iron is oxidized in the presence of selenium. This apparent contradiction is in fact due to differences in the experimental conditions used to prepare the Fe(II)–clay and the Se(IV)–Fe(II)–clay samples. In the Se-rich samples (this study), we used a roughly 10 times higher total Fe(II) concentration (5 mmol L⁻¹) compared to the Se-free sample (study of Géhin et al., 2007) where [Fe(II)]₉ = 630 μmol L⁻¹. Note that in both studies the clay concentration (20 g L⁻¹) and hence the site concentration (90 μmol L⁻¹) were the same.

According to our sorption model under the present experimental conditions (Figs. 6 and 7), sorbed Fe(III) corresponds to 4–5.6% of the total sorbed Fe (pH 5.75–6.25). This value compares well with the 4–6% determined by Mössbauer spectrometry, suggesting that the addition of Se(IV) did not change the amount of this sorbed Fe(III) species. Furthermore, the Mössbauer spectra show little evolution within 1 h and 5 days, hence the Fe speciation remains more or less constant, giving no indication for a slow Fe(II) oxidation after addition of selenite (Fig. 8).

After addition of selenite, a new Fe species is present, as indicated by the D₄ component in the Mössbauer spectra (Fig. 8b and c). Its center shift values are indicative of Fe(II). The quadrupole splitting is even larger than that of the outer-sphere FeCl⁺ sorption complex (Charlet and Tournassat, 2005; Géhin et al., 2007). Since this component is linked to the addition of selenite, it may represent a Fe(II)-selenite outer-sphere complex sorbed to the basal planes of montmorillonite. The relative abundance decreases from 15% to 10% between 1 h and 5 days. In conclusion, none of the four observed Fe species suggests a coupled Fe–Se redox reaction after addition of selenite.

3.3. XANES of the clay–Fe(II)–Se(IV) system

The evolution of selenite reduction over reaction time was monitored using Se K-edge XANES spectroscopy.

![Fig. 8. 77K Mössbauer spectra of Fe(II)-sorbed synthetic montmorillonite before (a) and after a 1-h (b) and a 5-day (c) reaction time with selenite. Spectra (d) and (e) are of an iron selenite precipitate aged for 1 h and 5 days. Spectrum (f) is of a natural montmorillonite MX80 saturated with a ~0.035 mol L⁻¹ ⁵⁷FeCl₂ solution. Spectrum (a) is taken from Géhin et al. (2007), spectrum (f) from Charlet and Tournassat (2005).](image)
The precipitation of FeSe or FeSe$_2$ as suggested by Bruggeman et al. (2005) can be excluded. Hence SeO$_3^{2-}$ is reduced to Se(0) in the presence of sorbed Fe.

Table 2
Mössbauer hyperfine parameters of the spectra presented in Fig. 7

<table>
<thead>
<tr>
<th>Site</th>
<th>$\delta \pm 0.02$</th>
<th>$\Delta E_Q \pm 0.02$</th>
<th>RA $\pm 2$</th>
</tr>
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<tbody>
<tr>
<td>Without Se$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_1$</td>
<td>1.33</td>
<td>3.37</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_2$</td>
<td>1.30</td>
<td>2.91</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>D$_3$</td>
<td>0.43</td>
<td>0.70</td>
</tr>
<tr>
<td>With Se (1 h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_1$</td>
<td>1.37</td>
<td>2.98</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_2$</td>
<td>1.38</td>
<td>3.38</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_3$</td>
<td>1.37</td>
<td>3.76</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>D$_3$</td>
<td>0.46</td>
<td>0.60</td>
</tr>
<tr>
<td>With Se (5 days)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_1$</td>
<td>1.39</td>
<td>3.05</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_2$</td>
<td>1.39</td>
<td>3.42</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>D$_3$</td>
<td>1.39</td>
<td>3.76</td>
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<tr>
<td>Fe(III)</td>
<td>D$_3$</td>
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<tr>
<td>Fe exchanged clay$^b$</td>
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<tr>
<td>Fe(II) as FeCl$^+$</td>
<td>D$_1$</td>
<td>1.38</td>
<td>3.43</td>
</tr>
<tr>
<td>Fe(II) as Fe$_{2+}$</td>
<td>D$_2$</td>
<td>1.40</td>
<td>3.10</td>
</tr>
<tr>
<td>Ferrous selenide</td>
<td>Fe(II)</td>
<td>1.33</td>
<td>2.76</td>
</tr>
<tr>
<td>(1.3 h)</td>
<td>Fe(II)</td>
<td>1.34</td>
<td>3.23</td>
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<tr>
<td></td>
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<td></td>
<td>Fe(III)</td>
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<tr>
<td>Ferrous selenide (77K)</td>
<td>Fe(II)</td>
<td>1.34</td>
<td>2.69</td>
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<td></td>
<td>Fe(II)</td>
<td>1.33</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>Fe(III)</td>
<td>0.49</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Fe(III)</td>
<td>0.43</td>
<td>1.13</td>
</tr>
</tbody>
</table>

$\delta$ (mm s$^{-1}$) isomer shift with respect to metallic Fe(0) at room temperature; $\Delta E_Q$ (mm s$^{-1}$) quadrupole splitting; RA (%) relative abundance.

$^a$ Data and fit from (Géhin et al., 2007).

$^b$ Data and fit from (Charlet and Tournassat, 2005).

Fig. 9 shows the spectra of the Fe$^{2+}$-reacted montmorillonite samples after six time periods, plus a control without Fe$^{2+}$ and three reference phases. The XANES spectra of the control and of the Fe$^{2+}$ clay after short reaction periods are dominated by a white line at 12662 eV, which is characteristic for tetravalent Se, hence represents as discussed above the adsorbed initial SeO$_3^{2-}$ outer-sphere sorption complex. With increasing time, the amplitude of the Se(IV) lines decreases, whereas a shoulder grows on its low-energy wing, which finally forms a separate peak at 12,657 eV after 1 month. This peak represents a reduced Se species.

In order to determine the number of spectral contributions, their identity and relative contribution, we analyzed the spectral data set with Iterative Transformation Factor Analysis (ITFA) (Rossberg et al., 2003). In contrast to using edge positions as proxies of oxidation state, this method has the advantage of making use of the combined information of oxidation state and coordination geometry contained in the XANES spectra. The seven clay spectra are superpositions of only two spectral components, as is demonstrated by the close fit between the experimental data (black) and their reconstruction with two Eigenvectors (red lines). Hence only the initial Se reactant and one reduced Se reaction product is present. A comparison with four references demonstrates that only grey Se(0) is a likely candidate for the reaction product. The precipitation of FeSe or FeSe$_2$ as suggested by Bruggeman et al. (2005) can be excluded. Hence SeO$_3^{2-}$ is reduced to Se(0) in the presence of sorbed Fe.

3.4. EXAFS of the clay–Fe(II)–Se(IV) system

The evolution of Se reduction over reaction time was also monitored by Se K-edge EXAFS spectroscopy, revealing information on the local structure of the species (Fig. 10). Note that we were not able to collect an EXAFS spectrum for the sample reacted for 1 month. The k$^3$-weighted EXAFS spectra reveal the formation of the reduced Se species by a splitting at 7 Å$^{-1}$ of the regular sinusoidal oscillations representing the O coordination sphere. This feature represents an additional backscattering wave, corresponding to a peak at 2.2 Å in the Fourier transform (distance not corrected for phase shift). The height of this peak increases with reaction time (Fig. 10).

Similar to the analysis of XANES spectra, we applied ITFA to the set of k$^3$-weighted EXAFS spectra (3–11 Å$^{-1}$), hence investigating the expected change in local structure with time. As for the XANES spectra, the PCA of the EXAFS spectra showed only two significant components (Fig. 10). When Se(0) was included in the analysis however, the fit of the clay samples with longer reaction times was not adequate. This suggests that the structure of the reduced species is similar to but not identical with the Se(0) reference. To test this hypothesis, we performed ITT without the Se(0) reference, in order to extract the real
spectrum of the second, Se(0)-like component (Scheinost et al., 2005). By fixing only the concentration of the Fe²⁺-free control to unity, ITT failed to converge. Therefore, we iteratively fixed for the 96 h sample the relative concentration of the second component to values between 0.3 and 0.7. In agreement with the results from XANES (Fig. 9), a relative concentration of 0.5 produced the most consistent result in terms of a minimum fit error and a minimum contribution of a SeO₃²⁻ oxygen shell (Fig. 10 and Table 5).

3.5. Solubility product analyses

The combined pₑ–pH values measured during the course of the kinetic experiment are depicted in Fig. 11. The values fall in the Se(0) stability domain, in agreement with XANES data. Linear regression of the pₑ–pH data yields a slope of −3.11 and an intercept of +22.52. The slope is close to the theoretical −3.0 value, which has been derived for aqueous and sorbed Fe(II)/FeOOH(s) (see for example Silvester et al., 2005). Therefore the measured redox potential appears to be governed by the Fe(II)/Fe(III) couple:

Fe(OH)₃(s) + 3H⁺ + e⁻ = Fe²⁺ + 3H₂O Kₘ K₉Fe

where Kₘ is the solubility product of the Fe(OH)₃(s) solid phase and K₉Fe is the Fe²⁺/Fe³⁺ one electron redox reaction constant (log K₉Fe = 13.05 at 25 °C). The line intercept and the activity of Fe²⁺(aq) yield a Kₘ value of 10⁶.7. This value is in between the ferrihydrite solubility products given in the Inl database (10⁵.6) and that given in the Minteq v.4 database (10⁵.7) provided with PHREEQC2 (Parkhurst and Appelo, 1999). The high solubility of the Fe(OH)₃(s) solid phase polymers formed by oxidation of the Fe²⁺ ions sorbed on the montmorillonite edges can be interpreted in terms of crystal size. Based on the dependence of the solubility product on crystal size and on surface tension (Ernstun and Turkevich, 1960) and on the 10⁻².⁷ crystallized goethite solubility product (Langmuir, 1969) one obtains 13.3 Å wide Fe(III) polymers, assuming goethite spherical nanoparticles with 20.6 cm³ mol⁻¹ molar volume and 1.6 J m⁻² surface tension (Steefel and Van Cappellen, 1990).
Such clusters could be hidden in the ferric part of the Mössbauer spectra as quadrupole doublets. Their size is close to 1.6 nm, i.e. to the size observed by Small Angle X-ray scattering for Fe(III) clusters formed during the hydrolysis of FeCl₃ solutions. These clusters are constituted of 24 Fe(III) atoms and possess a local structure similar to that in α-FeOOH/β-FeOOH (Bottero et al., 1994).

Until now we assumed the reaction products to be pure Fe(III) solid phases. However, the Fe⁴⁺ activity could also be controlled by mixed-valence amorphous Fe-oxides (MVA Fe-oxides) with solubility relations that resemble hydrated-magnetite (Schwab and Lindsay, 1983; Brennan and Lindsay, 1998). Under the assumption of metastable equilibrium, the stoichiometry of mineral species controlling Fe²⁺ activity may be inferred from the slope of the data plotted as [pc + pH] versus [log(Fe²⁺) + 2 pH] (Thompson et al., 2006). While equilibrium with an Fe⁴⁺ mineral (e.g., ferrihydrite) yields a slope of −1, magnetite (FeFe²⁺⁴⁺O₄) gives a slope of −0.67. Linear regression of our data yields a slope of −0.98, also consistent with an Fe(III) precipitate. Furthermore, the activities of Fe²⁺ and H⁺, and therefore the slope of the best fit line in Fig. 11, are also affected by Fe²⁺ adsorption–desorption equilibrium, as described in Table 1. Because of this ambiguity regarding the impact of surface adsorbed Fe²⁺, standard thermodynamic predictions that redox dynamics in natural systems are in equilibrium with mixed Fe²⁺–Fe⁴⁺ solids must be interpreted cautiously.

3.6. Evidence of formation of nano Se(0) clusters

Fig. 12 shows the EXAFS spectra of the ITFA-derived two components in comparison with references. Component 1 represents the Se⁴⁺ outer-sphere complex. As already suggested by the ITFA procedure, there is some deviation between component 2 and the k³-weighted EXAFS spectrum of Se(0). When comparing the two Fourier transforms, both spectra reveal backscattering shells at similar distances (2 and 3.2 Å, uncorrected for phase shift). However, the second shell of component 2 is significantly smaller than that of Se(0), suggesting a smaller coordination number or larger Debye–Waller factor.

To further investigate the structural relationship between component 2 and trigonal Se(0), we fitted both spectra in the same data range of 3 ≤ k ≤ 11 Å⁻¹ (Table 4). In comparison to the trigonal Se(0) reference, atomic distances are slightly smaller in component 2. Furthermore, the coordination of the second shell is significantly smaller. Even though the coordination numbers are clearly biased by the short k-range, one can infer a relatively small average cluster size for the newly formed precipitate. The larger Debye–Waller factors suggest a larger structural disorder (all samples were measured at 15 K, where thermal vibrations are negligible) for species 2. All features together suggest that the reduced species consist of nano-sized clusters with a higher structural disorder than Se(0).

Based on a comparison of their EXAFS spectra, ferroselite and the FeSe⁴⁺ precipitates are not likely candidates for species 2 (Fig. 10), while tetragonal FeSe seems to provide a reasonable match of the EXAFS spectra. Nevertheless, FeSe can be excluded for two reasons. First, the Fourier transform shows that its second Se shell is at a larger distance in comparison to component 2 and Se(0), which is further supported by the FT data (Table 3). Second, the XANES spectrum of FeSe clearly deviates from those of component 2 and Se(0) (Fig. 8). Hence the
water/FeSeO₃ interface

Fe selenite. The solid was precipitated by mixing equal volumes of 0.03 mol L⁻¹ FeCl₂ and Na₂SeO₃ and aged for up to 5 days. The solution remained oversaturated with respect to the published solubility product of FeSeO₃ (Kₛₛ = 10⁻⁹.99, Seby et al., 2001). Other solids like Na₂Fe(SeO₃)₂, Fe₂(SeO₃)₂ or Fe₂(SeO₃)₃·6H₂O may precipitate as well, but to the best of our knowledge no solubility product has been published for these phases. X-ray diffraction patterns after various aging periods exhibit very broad bands (data not shown), corresponding to poor crystallinity, which prevented the phase identification by this method.

XANES spectra recorded at the Se K-edge show no reduction of selenium after a 1 h reaction time, and about 25% reduction after 4 h (shoulder at the low energy side in Fig. 9). The predominant oxidation state remains IV. The corresponding Mössbauer spectra (Fig. 8 and Table 2) show 50% Fe(III), whereas Fe(III) never exceeded 4% of total iron in the reacted clay systems. The EXAFS spectrum of the 4-h precipitate shows a selenite-like oxygen coordination sphere (1.9 O at 1.69 Å) and an additional backscattering shell fitted with 1.1 Fe atoms at a distance of 3.35 Å (Fig. 10). No first shell of a reduced species (Se(0) or lower) is visible. Hence Mössbauer spectrometry and EXAFS spectroscopy show a clear difference between the clay reaction product and the homogeneous FeSe(IV) precipitate. We can therefore conclude that homogeneous precipitation does not correspond to the reaction pathway observed for the Se(IV)–Fe(II)–clay system.

In order to reconcile the fact that half of the Fe atoms are present as Fe(III) in the poorly crystalline precipitate, while all Se atoms remain in a selenite-like local structure, we performed molecular dynamics calculations on bulk FeSeO₃(s) and on its solid/water interface, followed by an interpretation of the resulting structures by the previously described Bond Valence method. Since published Fe selenite structures contain only trivalent Fe (Giester and Wildner, 1991; Giester, 1996; Lefrant et al., 1996), we used the structure of Fe(II)SO₄ (Bugli and Carre, 1980) as starting point for our models after replacing S by Se.

The calculations on the bulk phase were based on the structure of one unit cell of FeSeO₃. The forces between ions were calculated at every step and minimized until convergence in energy was reached. The resulting Fe–O bond lengths are shown in Table 4. Only one position for Fe(II) resulted in a bond valence sum very close to the nominal valence of 2 of Fe in this structure. Modeling the bulk data with the parameter for Fe(III) resulted in a bond valence sum very close to the nominal valence of 2 of Fe in this structure. Therefore, the analysis confirms that Fe(II) is the most favorable oxidation state in the bulk structure. The geometry optimization of the bulk FeSeO₃ structure yields an average Se–O bond length of (dₑₑ–O) = 1.75 Å. This value is only slightly larger than the distance of 1.69 Å determined by EXAFS for the precipitate, while the starting structure based on S had a much smaller S–O distance of 1.54 Å, supporting the reliability of our modeling approach (Fig. 13).

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE (eV)</th>
<th>χ²(10⁶) a</th>
</tr>
</thead>
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### Table 4

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V₂⁺ = 1.9766 V⁺ = 2.1148 V⁺ = 2.85 V⁺ = 3.05

### 3.7. Homogeneous iron selenite precipitation

In order to ensure that the observed Se(IV) reduction and Se(0) precipitation is a clay–water interfacial reaction and did not proceed via homogeneous precipitation from solution, we investigated the formation and structure of Fe selenite. The solid was precipitated by mixing equal quantities of Fe(II) and Se(0) and aged for up to 5 days. The solution remained oversaturated with respect to the published solubility product of FeSeO₃ (Kₛₛ = 10⁻⁹.99, Seby et al., 2001). Other solids like Na₂Fe(SeO₃)₂, Fe₂(SeO₃)₂ or Fe₂(SeO₃)₃·6H₂O may precipitate as well, but to the best of our knowledge no solubility product has been published for these phases. X-ray diffraction patterns after various aging periods exhibit very broad bands (data not shown), corresponding to poor crystallinity, which prevented the phase identification by this method.

XANES spectra recorded at the Se K-edge show no reduction of selenium after a 1 h reaction time, and about 25% reduction after 4 h (shoulder at the low energy side in Fig. 9). The predominant oxidation state remains IV. The corresponding Mössbauer spectra (Fig. 8 and Table 2) show 50% Fe(III), whereas Fe(III) never exceeded 4% of total iron in the reacted clay systems. The EXAFS spectrum of the 4-h precipitate shows a selenite-like oxygen coordination sphere (1.9 O at 1.69 Å) and an additional backscattering shell fitted with 1.1 Fe atoms at a distance of 3.35 Å (Fig. 10). No first shell of a reduced species (Se(0) or lower) is visible. Hence Mössbauer spectrometry and EXAFS spectroscopy show a clear difference between the clay reaction product and the homogeneous FeSe(IV) precipitate. We can therefore conclude that homogeneous precipitation does not correspond to the reaction pathway observed for the Se(IV)–Fe(II)–clay system.

In order to reconcile the fact that half of the Fe atoms are present as Fe(III) in the poorly crystalline precipitate, while all Se atoms remain in a selenite-like local structure, we performed molecular dynamics calculations on bulk FeSeO₃(s) and on its solid/water interface, followed by an interpretation of the resulting structures by the previously described Bond Valence method. Since published Fe selenite structures contain only trivalent Fe (Giester and Wildner, 1991; Giester, 1996; Lefrant et al., 1996), we used the structure of Fe(II)SO₄ (Bugli and Carre, 1980) as starting point for our models after replacing S by Se.

The calculations on the bulk phase were based on the structure of one unit cell of FeSeO₃. The forces between ions were calculated at every step and minimized until convergence in energy was reached. The resulting Fe–O bond lengths are shown in Table 4. Only one position for Fe(II) was found with this method; the result was confirmed by Mulliken Population Analyses with DMol3 (Accelrys Software Inc.). The bond valence sum for the bulk Fe(II) ions is very close to the nominal valence of 2 of Fe in this structure. Modeling the bulk data with the parameter for Fe(III) resulted in a bond valence sum very close to the nominal valence of 2 of Fe in this structure. Therefore, the analysis confirms that Fe(II) is the most favorable oxidation state in the bulk structure. The geometry optimization of the bulk FeSeO₃ structure yields an average Se–O bond length of (dₑₑ–O) = 1.75 Å. This value is only slightly larger than the distance of 1.69 Å determined by EXAFS for the precipitate, while the starting structure based on S had a much smaller S–O distance of 1.54 Å, supporting the reliability of our modeling approach (Fig. 13).
In the next step, we modeled the FeSeO$_3$/water interface. We used the (001) face of FeSeO$_3$ in a box of $12 \times 12 \times 25$ Å, where the upper half was filled with water molecules. Due to the periodic conditions of the box in the simulation, two FeSeO$_3$/water interfaces were simulated, one at the middle of the box and one at the bottom (Fig. 13). A first step of 1 ps accounts for the thermal equilibration at 300 K and a second step of 1.5 ps accounts for the collection of the structural data. The temperature was set constant to 300 K. The Fe atoms closer to the surface ($<3$ Å from the interface) have a mean Fe–O distance of $d_{Fe-O}$ (Table 4). This mean value is significantly smaller that the corresponding value for bulk FeSeO$_3$ ($d_{Fe-O}$ (bulk) = 2.15 Å). Such a contraction could suggest an oxidation of Fe(II) to Fe(III).

The Fe–O bond lengths at the surface of FeSeO$_3$ in contact with water were again analyzed with the bond-valence approach. The bond valence for Fe is $V_{3+} = 3.05$, slightly oversaturated but very close to the nominal valence of 3+. In contrast, the bond-valence sum assuming a valence of 2+ is over saturated ($V_{2+} = 2.85$). Consequently, our modeling approach predicts an oxidation of Fe(II) to Fe(III).

The Mössbauer data shows a contribution of 50% of Fe(II) and 50% of Fe(III). Assuming that the Fe(III) signal is from the iron atoms at the surface, and the Fe(II) is from iron atoms within the bulk structure, one can estimate an average particle size of about 2 nm for the FeSeO$_3$ precipitate. This small particle size is further confirmed by the EXAFS-derived Se–Fe coordination number of 1.1 in comparison to the expected coordination number of 4 in the bulk structure. In conclusion, the EXAFS and Mössbauer data of the selenite precipitate is consistent with the formation of a nanoparticulate precipitate, where surface Fe atoms are oxidized, while the Se atoms remain in tetrahedral O coordination typical for selenite and hence do not show a clear trend towards a reduced oxidation state.

### 3.8. Quantitative kinetics and mechanism of Se(IV) reduction

Prior to the addition of Se(IV), the Fe(II)–clay suspensions were equilibrated at pH 6, with most Fe sorbed as divalent outer-sphere species, while 4–6% of Fe was stabilized as trivalent inner-sphere species by specific sorption (Figs. 4 and 7). At time zero, 0.05 mmol L$^{-1}$ of Se(IV) was added. The pH increased to values above 7 and then decreased again during the course of the experiment (Fig. 5, bottom). In spite of these pH shifts, the concentration of adsorbed selenium remained remarkably constant (Fig. 5, middle). Our surface complexation computations predicted-based on the Boult et al. data (1998), a selenium surface concentration of 0.8 mmol kg$^{-1}$, a value that compares well with the measured concentration of 1.25 mmol kg$^{-1}$ (Fig. 7). The measured amount of sorbed Fe (13–14%) also compares well with the predicted amount (17%) (Fig. 6).

The normalized speciation at each time step, as derived by ITFA from the XANES spectra (see above) is shown in the top part of Fig. 5. Table 5 gives the raw result of ITFA, demonstrating the reliability of the reconstruction with the sum of both species never exceeding ±10%. About 40% of Se(IV) is reduced within 6 h and about 75% is reduced within 1 month. According to these relatively slow reaction kinetics, the reduction of Se(IV) to Se(0) is controlled by a time-limiting step, i.e. by the initial reducing capacity of the Fe-sorbed clay. Although a new hypothetical species appears in the Mössbauer spectra, this species, tentatively attributed to a Se(IV)–Fe(II)–clay ternary complex, may not represent the activated complex for the Se reduction step, as its concentration remains comparatively high.

After 5 days only half of the initial Se(IV) is reduced to Se$^0$. This corresponds to an amount of 2.5 mmol kg$^{-1}$ (or 50 µmol L$^{-1}$) Fe oxidized to Fe(III). This value agrees well with the one predicted by the surface complexation model in the absence of Se and with the one measured by Mössbauer spectroscopy in the presence of Se ($<2$ mmol kg$^{-1}$, Fig. 7). This means that once the sorbed Fe(II) is oxidized, Fe(III) occupies all high affinity sites and the Fe oxidation reaction is stopped without regeneration of the redox reactive sites. However, the electrons produced by the reaction and presumably stored as sorbed H$_2$ species are available for the reaction with an oxidized ion such as Se(IV). The phenomenon that the reduction of Se(IV) is slow, although the oxidation of Fe(II) has already been completed, might suggest that the Se(IV) reduction is limited by the diffusion of Se(IV) to the newly formed reducing sites, or it might be

### Table 5

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<th>$t$ (h)</th>
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<th>Sum</th>
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<tr>
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</tr>
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</table>
limited by the diffusion of surface H₂ to Se-sorbing sites. The overall reduction mechanism could then be written as:

\[ 4S \equiv 3\,(O^-)\_3\,Fe^{3+}\,(OH^-)\_2\cdots\,(H_2)\_0,5 + HSeO_3^- \]
\[ \rightleftharpoons 3S \equiv 3\,(O^-)\_3\,Fe^{3+}\,(OH^-)\_2 + S \]
\[ \equiv 3\,(O^-)\_3\,Fe^{3+}\,(OH^-)\_3 + Se^0 + 2H_2O \]

The amount of protons released in solution (Fig. 5) is roughly two orders of magnitude smaller than the amount of selenium reduced. Due to the uncertainty on the proton mass balance of the overall reaction (which includes Se reduction, proton sorption on edges and particle dissolution), the stoichiometry of the above reaction must be considered cautiously.

3.9. Environmental relevance

In suboxic natural environments (hydromorphic soils, anaerobic groundwater systems, and engineered systems (zero-valent iron permeable reactive barriers, and radioactive waste repository sites), aqueous Fe(II) is ubiquitous. In carbonate-rich, sulfide-poor superficial waters, the Fe³⁺ concentration is controlled by siderite (FeCO₃(s)), green rust and Fe-rich calcite and varies between 10⁻⁴ and 10⁻²⁵ mol L⁻¹ depending on pH and PCO₂ (Criaud and Fouillac, 1986a,b; Emerson, 1976; Postma, 1982). In more anoxic conditions, for example, in organic-rich sulfide-rich environments, Fe³⁺ concentration is controlled by FeS₂ (where 1 < x < 2; mackinawite for x = 1 and pyrite for x = 2) and varies between 10⁻⁵ and 10⁻³ mol L⁻¹ (Berger, 1971; Emerson et al., 1980; Balzer, 1982; Bott, 2002; Davison et al., 1999; Wolthers et al., 2005; Gaucher et al., 2006). In low-P_CO₂, low-P_H₂S environments, Fe(II) solubility is controlled by the precipitation of Fe(OH)₂ₙₙ, Fe₂O₄ (magnetite), green rust, or Fe₃PO₄(s). In the presence of steel, for example in near-field engineered barriers, Fe(II) concentrations typically lie between 10⁻⁶ and 3 × 10⁻⁷ M (Naftz et al., 2000). The dissolved Fe²⁺ concentration used in the present work (5 × 10⁻⁴ mol L⁻¹) is hence representative of such environments.

Selenium is an essential trace element, which becomes toxic when present at high concentration. The maximum Se sorption capacity in China and California soils is 13–600 µg Se per kg soil (Tan et al., 1994; White and Dubrovsky, 1994). Within the experimental conditions used in the present work (the maximum montmorillonite Se sorption capacity is 79 µg Se per g of clay; Fig. 3), the results obtained demonstrate that solubility in anoxic iron rich waters would be controlled by abiotically precipitated Se(0). The low solubility of Se(0), 3 × 10⁻⁹ mol/L (Bruggeman et al., 2005), would substantially reduce selenium mobility and toxicity. Over the past few decades, researchers have focused mainly on naturally occurring selenium, which is responsible for severe dietary toxicity-related diseases (Kesterson Reservoir, CA). It was noticed that anoxic deep waters in seleniferous areas of California, North West India and China had in fact very low concentrations of selenium (White et al., 1991; White and Dubrovsky, 1994; Dhillon and Dhillon, 2003). These low water concentrations were attributed to microbiological activity, as it is well known that cells reduce selenium to Se(0) as a detoxification pathway. The present work demonstrates how that, in the presence of the common phyllosilicate, montmorillonite and Fe²⁺(aq), the reduction might be a totally abiotic process.

Recently, selenium has received renewed attention (e.g., Bruggeman et al., 2005) due to its presence as a fission product in high-level nuclear waste, where it exists as non-stable isotopes, e.g., ⁷⁹Se (1.1 million years half-life; http://www.nucleide.org/DDEP_WG/Nuclides/Se-79_com.pdf). In fact, recent nuclear waste disposal safety evaluations have demonstrated that anionic ⁷⁹Se, ¹²⁹I, ³⁶Cl and ⁹⁹Tc radionuclides might contribute most to the ultimate dose released during the next million years, as these anions were assumed to freely diffuse through clay confinement barriers (Toulhouat, 2002; Andra, 2005; SKB, 2006). The assessment to what extent ⁷⁹Se is a critical radionuclide at high-level radioactive waste disposal sites depends on its actual speciation and mobility under storage conditions. Until now, little data concerning the behavior of Se in geochemically reducing conditions has been published, mainly due to a lack of appropriate investigation techniques. By a combination of several spectroscopic techniques and extreme care to maintain anoxic conditions during sample preparation, storage, transport and measurements, we were able to tackle this problem. Our results suggest that the contribution of ⁷⁹Se to the risk of radioactive disposal sites could be smaller than previously assumed. This, however, has to be confirmed by experiments based on engineered barriers.

4. CONCLUSIONS

Selenite adsorption on clay edges in the presence of aqueous Fe²⁺ results in the formation of Se(0) nanoparticles. This is a kinetically controlled process, as demonstrated by the slow transition of the XANES selenite signal to a Se(0) signal. A requirement for the observed heterogeneous reaction is that both iron and selenium are co-adsorbed at edge sites of clay; thus, the reaction is limited by the density of edge surface sites and the amount of sorbed iron. When all the iron present on the edges is consumed, the reaction stops. This surface-induced reductive precipitation mechanism profoundly influences the retention of selenium. Selenium sorption is minimal at high pH and decreases to zero when the positive charge of the edge sorption sites also decreases to zero. Although this site specific sorption has often been assumed to be negligible if compared with the large amount of cations exchangeably sorbed to the pH-independent sites of montmorillonite and other similar clay minerals, the observed Se reduction demonstrates that such a quantitatively small process may control to a large extent the sequestration of Se in natural or engineered suboxic environments.

Homogeneous precipitation of Fe(II) and Se(IV) leads to 2-nm particles with part of the Fe being oxidized at the water interface, while selenium is only slightly reduced. Therefore, substantial Se reduction may occur only at a pH range, where both Fe and Se ions sorb to the mineral edges, i.e. below pH 7. Under these conditions, Se precipitates as stable, insoluble metallic clusters on the edge surface of smectite minerals,
suggesting that reductive precipitation may be an effective and relatively irreversible process that can abiotically regulate Se concentrations in reducing environments. Other forms of Fe(II) such as siderite, green rust or mackinawite may lead to the reductive precipitation of Se(0) as well. Furthermore, the influence of other geochemical parameters, such as $P_{CO_2}$, $PE$ or $H_2$, should be investigated in the future in order to determine the long-term stability of Se in various reductive environments.

ACKNOWLEDGMENTS

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