Selenite retention by nanocrystalline magnetite: Role of adsorption, reduction and dissolution/co-precipitation processes

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Abstract

We studied selenite ($\text{SeO}_3^{2-}$) retention by magnetite ($\text{Fe}^{II}\text{Fe}^{III}_2\text{O}_4$) using both surface complexation modeling and X-ray absorption spectroscopy (XAS) to characterize the processes of adsorption, reduction, and dissolution/co-precipitation. The experimental sorption results for magnetite were compared to those of goethite ($\text{Fe}^{II}\text{OOH}$) under similar conditions. Selenite sorption was investigated under both oxic and anoxic conditions and as a function of pH, ionic strength, solid-to-liquid ratio and Se concentration. Sorption onto both oxides was independent of ionic strength and decreased as pH increased, as expected for anion sorption; however, the shape of the sorption edges was different. The goethite sorption data could be modeled assuming the formation of an inner-sphere complex with iron oxide surface sites (SOH). In contrast, the magnetite sorption data at low pH could be modeled only when the dissolution of magnetite, the formation of aqueous iron–selenite species, and the subsequent surface complexation of these species were implemented. The precipitation of ferric selenite was the predominant retention process at higher selenite concentrations (>1 \times 10^{-4} \text{ M}) and pH < 5, which was in agreement with the XAS results. Sorption behavior onto magnetite was similar under oxic and anoxic conditions. Under anoxic conditions, we did not observe the reduction of selenite. Possible reasons for the absence of reduction are discussed. In conclusion, we show that under acidic reaction conditions, selenite retention by magnetite is largely influenced by dissolution and co-precipitation processes.

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1. INTRODUCTION

The mobility of selenium in the environment has been of interest for decades. Although selenium is an essential nutrient for humans, animals and plants, it is toxic at higher concentrations, with a narrow gap between toxic and beneficial concentrations (Lakin, 1972; Skorupa, 1998). It is therefore important to understand the processes controlling the distribution of selenium in soil and water.

The foremost processes controlling selenium mobility and bioavailability in the environment are adsorption onto geological materials and the formation of Se minerals (McNeal and Balistrieri, 1989). Selenium chemistry is quite complicated because its mobility strongly depends on both the redox state of the system and the factors influencing its speciation (e.g., pH, presence of organics and kinetics).

Selenium exists in four different oxidation states with very different chemical behaviors: selenide (Se^{−II}), elemental selenium (Se^{0}), selenite (Se^{IV}\text{O}_3^{2−}) and selenate (Se^{VI}\text{O}_4^{2−}). Metal selenides and elemental selenium have a very low solubility and are fairly immobile, but selenite and selenate (both oxoanions) are soluble and mobile. Selenium toxicity is also dependent on its chemical state, with selenite being more toxic than selenate, which is more toxic than selenide.

Oxoanions, in general, are of concern in the context of radioactive waste repositories because of their limited
adsorption onto geologic materials (Duc et al., 2003). 79Se, present in spent nuclear fuel and high-level radioactive waste, is an element of interest because of its long half-life, which is reported to be 4.8 × 10^5 or 1.1 × 10^6 years (Jiang et al., 1997; Magill et al., 2006).

As anion sorbents, Fe oxy-hydroxides are among the solid phases with the greatest adsorption capacity, especially for selenium. Many detailed studies exist on selenium adsorption onto the most common iron oxides in soil: goethite, hematite and amorphous ferrithydrate (Balestrieri and Chao, 1987; Duc et al., 2006; Hansmann and Anderson, 1985; Hayes et al., 1987; Manceau and Charlet, 1994; Parida et al., 1997; Peak and Sparks, 2002; Su and Suarez, 2000; Zhang and Sparks, 1990). Yet, far fewer studies exist on selenium sorption onto oxides containing Fe II, such as magnetite (Fe\(\text{III}O\cdot\text{Fe}^{\text{II}}\cdot\text{O}_3\)) (Martinez et al., 2006). Due to the presence of Fe II, magnetite may be capable of reducing selenium in a coupled redox reaction. In fact, this possibility has been recently confirmed (Scheinost and Charlet, 2008; Scheinost et al., 2008); however, selenium was not reduced by magnetite in another experiment (Loyo et al., 2008). The reason for this discrepancy is, up to now, not known.

Metal containers are the first physical barrier to radionuclide migration in radioactive waste repositories. In the moderate-to-strong reducing environment and neutral-alkaline conditions expected in these repositories, magnetite is the primary stable end product of oxide transformations (Cornell and Schwertmann, 1997). Therefore, a better understanding of radionuclide interactions with magnetite may allow the prediction of radionuclide migration within these waste systems.

We sought to explain the interactions between selenium and a very well characterized nanocrystalline magnetite (Missana et al., 2003a,c), accounting for both adsorption and the possible effects of selenium reduction at the magnetite surface.

To understand the underlying mechanisms of this radionuclide retention, we analyzed in parallel sorption results obtained with a well characterized goethite under similar conditions. Goethite and magnetite differ greatly in their behavior, not only inner-sphere complexation, but also oxide dissolution and co-precipitation processes, play a major role in selenium retention, while selenium reduction was not observed.

### 2. MATERIALS AND METHODS

All reagents were of analytical grade and used without further purification. The deionized water (MilliQ–Millipore system) used to prepare the electrolytes and suspensions was bubbled with N\(_2\) and boiled for at least 15 min to minimize CO\(_2\) contamination and then stored in an anoxic glove box. The atmosphere in the anoxic glove box was CO\(_2\)-free nitrogen (O\(_2\) < 1 ppm). All experiments were run at room temperature.

#### 2.1. Oxide preparation and characterization

Magnetite was prepared using a synthesis method described in Cornell and Schwertmann (1997). Five hundred and sixty milliliters of a solution of 0.3 M FeSO\(_4\) was heated to 90 °C; 240 mL of a solution of 3.33 M in KOH and 0.27 M in KNO\(_3\) was slowly added; hydrazine, a strong reducing agent, was added to the suspension to prevent the formation of unwanted ferric oxides during the nucleation stage, and the suspension was bubbled with N\(_2\). The suspension was continually stirred at 90 °C for one hour and then the temperature was decreased to approximately 40 °C to continue the preparation in the glove box under anoxic conditions. The suspension containing a dark black solid was decanted and introduced into dialysis bags for washing. The dialysis bags were placed in a 1 L container filled with deionized, degassed water that was periodically changed to remove excess salts from the oxide suspension. This process was finished when the conductivity remained stable and below 10 \(\mu\)S/cm. The solid was then dried in the anoxic glove box under N\(_2\) atmosphere where it remained stored to avoid oxidation.

Goethite (\(\alpha\)-FeOOH) was prepared following a standard method (Cornell and Schwertmann, 1997). More detail on the goethite preparation can be found elsewhere (Missana et al., 2003b).

The structure of the solid samples was analyzed by transmission electron microscopy (TEM) and selected area diffraction patterns (SADP) using a Philips electron microscope operated at 80 kV. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were also used to characterize the Fe oxides.

#### 2.2. Preparation of the suspensions

The iron oxide suspensions were prepared in the anoxic glove box by adding 2 g/L of magnetite or goethite to an
electrolyte (NaClO₄) with different ionic strengths. The suspensions were placed in an ultrasonic bath for 1 h and then allowed to equilibrate for at least 1 day.

We previously reported (Missana et al., 2003a) the stability of the iron oxide in the electrolyte solutions by evaluating its degree of dissolution at different pH and contact times, in addition to its acid–base properties.

### 2.3. Sorption experiments: sorption edges and isotherms

Sorption experiments were carried out both in atmospheric and anoxic conditions. Experiments in anoxic conditions were carried out in the anoxic glove box with an N₂ atmosphere.

Suspensions of magnetite were prepared, as previously described, at different ionic strengths, in NaClO₄ (I = 1 x 10⁻¹, 1 x 10⁻² and 1 x 10⁻³ M). Sorption pH edges were established in the pH 2–11 range.

Three different aliquots of the suspension, at the selected pH, were introduced in 12.4 mL ultra-centrifuge tubes and ³⁵Se⁴⁺ was added to achieve a final concentration of 1 x 10⁻⁹–1 x 10⁻¹⁰ M.

After the radionuclide addition, the tubes were sealed, continuously stirred for 7 days and afterwards ultra-centrifuged (645,000g, 30 min). This centrifugation ensured the complete sedimentation of the colloids. After the solid was separated from the liquid, two aliquots of the supernatant from each tube were extracted to measure the final activity by gamma counting with a COBRA Packard gamma counter. The remaining solution was used to check the final pH.

Sorption isotherms were carried out at an ionic strength of 0.1 M and fixed pH, with Se⁴⁺ concentrations varying between 1 x 10⁻¹⁰ and 1 x 10⁻⁴ M. The highest selenium concentrations were achieved by adding sodium selenite (Na₂SeO₃, Merck). The separation and counting procedure was the same as that used for the sorption edges.

Finally, an additional sorption edge was performed at a high solid-to-liquid ratio (100 g/L), at high selenium concentration (0.01 M) and under anoxic conditions to approach the conditions used for XAS experiments.

Distribution ratios (R_D) were calculated with the following formula:

\[
R_D = \frac{C_i - C_f}{C_f} \frac{V}{m}
\]

where \(C_i\) and \(C_f\) are the initial and final Se concentrations in the liquid phase; \(V\) is the solution volume (mL); and \(m\) is the oxide mass (g).

In the modeling, when a species precipitates, the quantity of selenium in the solid is considered as “retained” and included in \(R_D\) calculations.

### 2.4. XAS measurements

The selenium sorption tests for XAS measurements were carried out under anoxic conditions and at three different pHs. Magnetite (100 g/L) was suspended in sodium selenite with a Se⁴⁺ concentration of around 5 x 10⁻² M. The samples were brought to the selected pH and maintained under continuous stirring for 10 days; afterwards, the solid was separated from the liquid by centrifuging twice for 30 min at 25,000g. The magnetite was dried under an N₂ atmosphere and placed in special holders for XAS measurements. The samples were packed in the anoxic chamber before their shipment to the beamline. The details of the XAS samples (solid-to-liquid ratio, Se concentration (in mol L⁻¹) and pH) are given in Table 1.

Selenium-K-edge XANES and EXAFS spectra were collected at the Rossendorf Beamline at ESRF (Grenoble, France). The energy of the X-ray beam was tuned by a Si(1 1 1) double-crystal monochromator operating in channel-cut mode. Two platinum-coated Si mirrors before and after the monochromator were used to collimate the beam into the monochromator and to reject higher harmonics. A 13-element high purity germanium detector (Canberra), together with a digital signal processing unit, (XIA) was used to measure samples in fluorescence mode. Spectra were collected at 15 K using a closed cycle He cryostat with a large fluorescence exit window and a low vibration level (CryoVac). As was confirmed by comparing repetitive short (10 min) XANES scans, the cooling prevented photon-induced redox reactions of the samples. For energy calibration, a gold foil (K-edge at 11,919 eV) was chosen because of its greater inertness in comparison to Se. Data in the XANES region were collected in steps of 0.5 eV, with higher resolution than the resolution of the Si(1 1 1) crystal at the given vertical divergence (1.7 eV), and the broadening due to the core-hole lifetime (2.3 eV). A comparison of single scans of the same sample showed an accuracy of better than 0.5 eV. Dead time correction of the fluorescence signal, energy calibration and the averaging of single scans were performed with the software package SixPack. Normalization, transformation from energy into k space and subtraction of a spline background were performed with WinXAS using routine procedures (Ressler, 1998). The EXAFS data were fit with WinXAS using theoretical backscattering amplitudes and phase shifts calculated with FEFF 8.2 (Ankudinov and Rehr, 1997). This method provides a precision of ±0.01 Å for shell distances and a resolution of about ±0.1 Å for neighboring shells. The error of coordination numbers is ±25%.

### 2.5. Modeling

The reactions at the oxide surface involve the amphoteric surface functional groups (SÖH). The pH-dependent charge is determined by the following protonation/deprotonation reactions:

<table>
<thead>
<tr>
<th>Sample</th>
<th>S (g L⁻¹)</th>
<th>[Se]</th>
<th>pH_in/pH_fin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se-A</td>
<td>103.5</td>
<td>0.0510</td>
<td>2.39/4.37</td>
</tr>
<tr>
<td>Se-B</td>
<td>101.3</td>
<td>0.0498</td>
<td>6.28/6.90</td>
</tr>
<tr>
<td>Se-C</td>
<td>101.6</td>
<td>0.0516</td>
<td>9.25/9.35</td>
</tr>
</tbody>
</table>

### Table 1
Characteristics of the magnetite samples analyzed by XAS. XAS samples were prepared, stored and packed under N₂ atmosphere. Contact time 10 days.
SOH₂⁺ ⇔ SOH + H⁺  \( K_{a1} \)  
SOH ⇔ SO⁻ + H⁺  \( K_{a2} \)  

where SOH₂⁺, SOH, and SO⁻ represent the positively charged, neutral and negatively charged surface sites, respectively. \( K_{a1} \) and \( K_{a2} \) are the intrinsic equilibrium acidity constants. The mass law equations corresponding to the reactions, (2) and (3), are as follows:

\[
K_{a1} = \frac{[\text{SOH}][\text{H}^+]}{[\text{SOH}_2^+]} \exp\left(\frac{-FP\Psi}{RT}\right) 
\]

\[
K_{a2} = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}]} \exp\left(\frac{-FP\Psi}{RT}\right) 
\]

where \([\cdot]\) represents the ion activity and () the ion concentrations. \( \Psi \) represents the surface potential; \( R \) the molar gas constant; \( T \) the absolute temperature (K); \( F \) the Faraday constant. Since the activity coefficients for all the surface species are assumed to be equal, the activities of these species can be substituted by their concentrations. The exponential represents the columbic term that accounts for the electrostatic effects (Dzombak and Morel, 1990). In this study a simple non-electrostatic (NE) approach was preferred; therefore, the electrostatic term was not accounted for.

Specific adsorption of anions at the surface functional groups can be described with reactions of the following type:

\[
\text{SOH}_2^+ + \text{A}^- \Leftrightarrow \text{SOH}_2\text{A} \ \ K_{aw} 
\]

Model calculations were done with CHESS code v 2.4 (van der Lee and De Windt, 2000) and the fits of the experimental curves were obtained with a step-wise trial and error procedure.

3. RESULTS AND DISCUSSION

3.1. Characterization of the oxides

Both magnetite and goethite prepared in our laboratory have been thoroughly characterized previously (Missana et al., 2003a,b,c). Phase identity, purity and morphology were confirmed by XRD, XPS, TEM and SEM analysis. In addition, the oxide batches used in the present work were analyzed with AFM (Fig. 1). Magnetite (Fig. 1, left) is formed by nanocrystals (50–200 nm) with well-defined edges.

As shown in Missana et al. (2003a,c), the peaks of the XRD spectrum of these nanocrystals fit very well with those expected for magnetite (Fe₃O₄). An additional mineral phase could not be detected. However, since the XRD spectrum of magnetite (Fe₃O₄) and that of its iso-structural form, Fe₂O₃ (maghemite), in which all or most of the Fe is in a trivalent state, are actually difficult to distinguish, XPS measurements were needed to verify the iron oxidation state in the solid. The XPS analysis confirmed that the oxide was magnetite with a FeII/FeIII ratio ranging from 0.33 to 0.67 and a mean value only slightly lower (0.47) than the expected stoichiometric ratio (0.5).

Goethite (Fig. 1, right) is formed by acicular crystals 1–2 \( \mu m \) long and a few tenths of a nanometer wide.

Even when the two minerals were prepared in different experimental batches, their microstructure and properties were always very similar.

The single point N₂-BET surface area of the nanocrystalline magnetite was 8.5 m²/g; that of the acicular goethite was 35 m²/g.

The acid/base properties of the oxides and the surface site density were determined with potentiometric acid/base titrations as detailed in Missana et al. (2003a,b). The oxide/NaClO₄ suspensions (2 g/L) were titrated in polyethylene vessels and in the anoxic glove box to exclude CO₂ from the system. The acid and base used to change the pH were NaOH and HCl 0.1 mol/L, and the acid/base additions were made about every 2–3 min (fast titrations). No significant hysteresis between acid and base titration curves was observed using this “fast titration” procedure. The acidity constants were determined by the best fit of titration data for both oxides using either a DDL model (Missana et al., 2003a,b) or a non-electrostatic (NE) model (Missana et al., 2003b; Duro et al., 2004). Both approaches repro-
duced the titration curves very well. Table 2 summarizes the principal properties of both oxides.

### 3.2. Batch sorption experiments

#### 3.2.1. Kinetics

The optimum contact time for subsequent tests was determined by studying the kinetics of selenite sorption onto the oxides. The evolution of $R_D$ as a function of contact time is shown in Fig. 2 and was obtained at an ionic strength of $1 \times 10^{-3}$ M in NaClO$_4$ and pH 4.5. Under those experimental conditions, sorption was more than one order of magnitude higher for goethite than for magnetite. This finding is in agreement with the differences of surface area and initial Se concentrations. Sorption equilibrium was reached within hours in the case of goethite, whereas constant $R_D$ values were obtained after approximately 2 days for magnetite. However, to ensure sorption equilibrium, most experiments were carried out with a contact time of at least 7 days.

#### 3.2.2. Sorption edges and isotherms

Sorption edges were carried out under different experimental conditions to determine the effects of pH and ionic strength ($I$) on selenite sorption onto the oxides. Additionally, we tried evaluating the possible role of reduction processes in selenium retention in our system by performing sorption tests under both oxic and anoxic conditions.

Fig. 3 shows selenite sorption edges on magnetite (Fig. 3a) and goethite (Fig. 3b) at different ionic strengths ($0.1, 0.01$ and $0.001$ M in NaClO$_4$) and under oxic and anoxic conditions. The selenium concentration was $[\text{Se}] = 1 \times 10^{-9}$ M; the solid-to-liquid ratio was $S = 2$ g/L; and the contact time was 15 days.

In both oxides, $R_D$ values decreased with increasing pH as expected for anions, while the sorption did not depend significantly on ionic strength. This finding is in line with previous studies of selenite sorption on goethite (Hayes et al., 1987; Su and Suarez, 2000) showing sorption to be independent of ionic strength. The sorption independence of ionic strength is in agreement with the formation of inner-sphere complexes of selenite with the oxide surface.

In the case of magnetite, however, the shape of the curve was not exactly that observed for other oxides (Duc et al., 2006; Hayes et al., 1987; Su and Suarez, 2000), showing a high sorption peak at the lowest pH and a plateau region at pH 6–9.

The sorption curve obtained for magnetite under anoxic condition ($[\text{Se}] = 8 \times 10^{-10}$ M, $S = 1$ g/L and 22 days contact time, stars in Fig. 3b) did not deviate from those obtained under oxic conditions.

For goethite, the $R_D$ values obtained under anoxic conditions ($[\text{Se}] = 4 \times 10^{-10}$ M, $S = 0.2$ g/L and 24 days contact time) were also very similar to those obtained under oxic conditions, with an observable increase in sorption detected at acidic pH.

In general, the higher $R_D$ values for goethite than for magnetite (2 orders of magnitude in the range of pH 4–11) agree well with the higher surface area of goethite (Table 2). The major difference between goethite and magnetite seems to be the significant sharp increase of retention at lower pH for magnetite.

Fig. 4 shows the sorption isotherms obtained for magnetite (Fig. 4a) and goethite (Fig. 4b). Results are expressed as the logarithm of the dissolved selenium concentration at equilibrium ($\text{Se}_{eq}$) in mol L$^{-1}$ vs. the logarithm of the concentration of the adsorbed selenium ($\text{Se}_{ad}$) in mol/g. Linear sorption (slope of the log–log plot $\approx 1$) can be observed

<table>
<thead>
<tr>
<th>Species</th>
<th>Composition</th>
<th>Log K</th>
<th>Species</th>
<th>Composition</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface acidity, DDL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$^-$</td>
<td>1 SOH, $\cdot$ H$^+$</td>
<td>$-9.10$</td>
<td>SO$^-$</td>
<td>1 SOH, $\cdot$ H$^+$</td>
<td>$-10.00$</td>
</tr>
<tr>
<td>SOH$_2^+$</td>
<td>1 SOH, 1 H$^+$</td>
<td>$5.10$</td>
<td>SOH$_2^+$</td>
<td>1 SOH, 1 H$^+$</td>
<td>$7.20$</td>
</tr>
<tr>
<td>Magnetite (Duro et al., 2004)</td>
<td></td>
<td></td>
<td>Goethite (Missana et al., 2003b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$^-$</td>
<td>1 SOH, $\cdot$ H$^+$</td>
<td>$-9.79$</td>
<td>SO$^-$</td>
<td>1 SOH, $\cdot$ H$^+$</td>
<td>$-10.50$</td>
</tr>
<tr>
<td>SOH$_2^+$</td>
<td>1 SOH, 1 H$^+$</td>
<td>$4.11$</td>
<td>SOH$_2^+$</td>
<td>1 SOH, 1 H$^+$</td>
<td>$5.00$</td>
</tr>
</tbody>
</table>

Fig. 2. Kinetics of selenite sorption onto (○) goethite and (●) magnetite at pH 4.5. $[\text{Se}] = 4 \times 10^{-8}$ M (magnetite) and $1 \times 10^{-9}$ M (goethite).
across several orders of magnitude of selenite concentration for both oxides. The sorption isotherms do not give any evidence of multiple sorption sites. Langmuir-type behavior is observed and saturation of sorption sites started for Se equilibrium concentrations in solutions higher than $10^{-2} \times 10^{-1} \times 10^{-3} M$.

3.2.3. Sorption edges on magnetite at high solid-to-liquid ratio

Additional sorption experiments under anoxic conditions were carried out with magnetite at high selenite concentrations and solid-to-liquid ratio, approaching the conditions used for the XAS samples. The sorption edges obtained in these conditions are shown in Fig. 5a. $R_D$ values are quite small and, as we previously mentioned in the sorption isotherm description, little dependence on the pH was experimentally observed. In these conditions, the percentage of sorbed selenite ranged from 20% to 60%. This information was useful for optimizing the conditions for XAS measurements.

The sorption results obtained for goethite (Figs. 3b and 4b) are similar to those found by other authors, both qualitatively and quantitatively, but the sorption behavior of magnetite as a function of pH (Fig. 3a) is not fully comparable to that observed for other oxides, including goethite; therefore, it is important to understand the possible reasons for this behavior.

The possible reasons leading to this different behavior must be related to the different characteristics of both oxides. One explanation for the “higher than expected” retention in magnetite at pHs lower than 4 could be that the selenite reduction was triggered by the presence of Fe(II) at the magnetite surface. Under similar experimental conditions, the partial reduction of uranyl, triggered by adsorption, was previously observed (Missana et al., 2003c). The possible effect of selenite reduction was therefore analyzed with XANES (see below).

3.3. XAS measurements

Table 1 includes the list of magnetite samples dispersed in Na$_2$SeO$_3$ ($\sim$0.05 M) and analyzed with XAS. Three additional references were measured Se(0), Na$_2$SeO$_3$ and Fe$_2$(SeO$_3$)$_3$ (Giester, 1993).

Fig. 6 shows the Se-K-edge XANES spectra of the samples Se-A, Se-B and Se-C described in Table 1. All samples show only the strong white line peak at 12,663 eV typical for SeIV. Peaks or shoulders at 12,658 eV, indicative of Se0, are absent; hence, the reduced Se species, if present at all, constitutes <5% of the samples. This finding is a clear indication that selenium remains in oxidation state IV in our system and that sorption “anomalies” observed are...
not the consequence of selenite reduction at the magnetite surface and the subsequent precipitation of elemental selenium or of iron selenides (Scheinost and Charlet, 2008).

There are, however, significant differences, especially in the post-edge region between 12,670 and 12,680 eV (see black line in Fig. 6). Sample Se-A has a strong upward beat at 12,673 eV, which becomes increasingly weaker and shifts towards higher energy from Se-B to Se-C. Sample Se-A shares this feature with a solid, ferric selenite, while Se-C is similar to Se IV-sorbed goethite.

Fig. 7 shows the Se-K-edge EXAFS spectra and corresponding Fourier transform magnitude of Se IV-reacted magnetite samples (Table 1) in comparison with ferric selenite and Se IV-sorbed goethite. The Se-K-edge EXAFS spectra are dominated by the oscillation from Se to O backscattering, giving a strong peak at around 1.2 Å (uncorrected for phase shift) (Fig. 7). This peak can be fitted by three oxygen atoms at 1.70 Å (Table 3). Note that a strong localization of the Se–O double bond leading to one shorter and two longer Se–O distances is far below the resolution of EXAFS (about 1.3 Å at the given k-range from 2 to 14.5 Å⁻¹). However, the Debye–Waller factor (σ²) of samples Se-B and Se-C is significantly larger than that of Se-A, suggesting a stronger localization and hence stronger splitting of the three Se–O bond distances, similar to the goethite sample. In contrast, smaller Debye–Waller factors of Se-A and ferric selenite suggest a stronger delocalization of the double bond and hence a greater uniformity of the bond lengths.

All spectra show relatively strong second shell contributions, but at different distances. While the Fourier transform of Se-A has a maximum at 3 Å (uncorrected for phase shift), sample Se-C shows a maximum at a shorter distance of about 2.5 Å, and Se-B has weaker maxima at both positions, suggesting a transitional speciation. This was confirmed by principal component analysis, which suggested that only two components are necessary to reproduce all three spectra (not shown). The longer shell could be fitted with Fe atoms at 3.29–3.43 Å distance from Se, representing a corner-sharing arrangement between the SeO₃ trigonal pyramids and the Fe(O,OH)₆ octahedra, while the shorter shell with Fe atoms at 2.91–2.97 Å suggest an edge-sharing arrangement.

For Se-C, the Se–Fe coordination number of one, together with the distance of 2.91 Å, suggests the formation of an edge-sharing sorption complex at the surface of magnetite. However, the spectrum of Se IV-sorbed goethite, with an Se–Fe coordination number of two and a distance of 3.35 Å is in line with a double corner-sharing sorption complex.

In contrast to these two inner-sphere sorption complexes with a relatively high degree of static disorder, which prevents identification of atom neighbors beyond 3.5 Å, the
fit data of Se-A show a Se shell at 4.19 Å. Furthermore, the second shell contains three Fe atoms. These data may be interpreted in two different ways. First, we can test the hypothesis that this local arrangement corresponds to the solid state structure of a precipitate. In fact, the XANES and EXAFS spectra, as well as the EXAFS fit data, show substantial similarities with a ferric selenite precipitate (Figs. 6 and 7, Table 3). The spectrum of this precipitate was fitted with about three Fe atoms at a distance of 3.30. This distance and coordination number fits well with the structure of Fe$_2$(SeO$_3$)$_3$·3H$_2$O with three Fe atoms at 3.25–3.33 Å (Giester and Pertlik, 1994). The lack of backscattering from Se atoms at larger distances (e.g., 2 Se at 3.98 and 2 Se at 4.35 Å) may suggest an amorphous or nanoparticulate nature of the investigated precipitate. The fit data of Se-A, however, show a weak Se shell at an average distance of 4.19 Å, supporting that the sorption product of Se-A is, in fact, a ferric selenite.

### Table 3
Se-A EXAFS fit results ($S_0^2 = 0.9$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coordination shell</th>
<th>Further shells</th>
<th>$\Delta E_0$ (eV)</th>
<th>$\chi^2_{\text{res}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN$^a$</td>
<td>$R^b$ (Å)</td>
<td>$\sigma^2$ (Å$^2$)</td>
<td>CN</td>
</tr>
<tr>
<td>Se-A magnetite</td>
<td>2.8 O</td>
<td>1.70</td>
<td>0.0012</td>
<td>3.1 Fe</td>
</tr>
<tr>
<td></td>
<td>1.5 Se</td>
<td>4.19</td>
<td>0.0065</td>
<td>0.9 Fe</td>
</tr>
<tr>
<td></td>
<td>1.2 Fe</td>
<td>3.42</td>
<td>0.0084</td>
<td>1.0 Fe</td>
</tr>
<tr>
<td>Se-B magnetite</td>
<td>2.9 O</td>
<td>1.70</td>
<td>0.0026</td>
<td>1.8 Fe</td>
</tr>
<tr>
<td></td>
<td>2.6 O</td>
<td>1.70</td>
<td>0.0020</td>
<td>0.5 O</td>
</tr>
<tr>
<td></td>
<td>3.1 O</td>
<td>1.70</td>
<td>0.0015</td>
<td>2.9 Fe</td>
</tr>
</tbody>
</table>

$^a$ CN: coordination number, error ±25%.

$^b$ $R$: radial distance, error ±0.01 Å.

$^c$ $\sigma^2$: Debye–Waller factor, error ±0.0005 Å$^2$. 

---

Fig. 7. Se-K-edge EXAFS spectra and corresponding Fourier transform magnitude of Se$^{IV}$-reacted magnetite samples (Se-A, Se-B and Se-C) in comparison to ferric selenite (top) and to Se$^{IV}$-sorbed goethite (bottom).
A second alternative explanation would be the formation of a sorption complex at the ditrigonal oxygen “cavities” of the magnetite \{111\} faces, which are normally occupied by tetrahedrally coordinated Fe\(^{3+}\). Formation of such highly ordered sorption complexes with next-neighbor coordination numbers of three and higher have been previously observed at the ditrigonal cavities of gibbsite (Yamaguchi et al., 2002) and for As and Sb sorption to magnetite (Kirsch et al., 2008; Wang et al., 2008). However, in this case, one would expect to see additional Fe neighbors at distances >4 Å, while a stable fit of sample Se-A could be achieved with Se at 4.19 Å, but not with Fe. Therefore, we can discard this possibility of a sorption complex and maintain that the observed reaction product is a ferric selenite precipitate. This interpretation is further supported by the acidic pH of this sample, where enough Fe should have been released from the magnetite surface to allow a co-precipitation with Se.

XANES indicated that selenium remained in oxidation state IV; therefore, in our systems, the differences observed between selenite sorption in magnetite and goethite cannot be attributed to selenite reduction. The absence of any selenite reduction is in obvious contrast to a previous experiment, where a complete reduction of selenite by nanocrystalline magnetite at pH 5.3 was observed after 24 h reaction time (Scheinost and Charlet, 2008; Scheinost et al., 2008).

A possible explanation of the observed difference lies in the different reaction conditions. In Scheinost et al. (2008), a lower solid-to-liquid ration (31 g/L), a smaller mean particle diameter (10 nm) with a higher surface area (100 m\(^2\)/g) and a smaller initial Se concentration (10\(^\text{-}^{-5}\) M) were used, resulting in a theoretical surface loading of 0.3 \(\mu\)mol/m\(^2\). In the current experiment, the theoretical surface loading (assuming 100% sorption) is 59 \(\mu\)mol/m\(^2\), two orders of magnitude higher. Since electron transfer from Fe\((\text{II})\) to Se\((\text{IV})\) is strongly favored by heterogeneous surface reaction, while reduction is restricted in solution (Charlet et al., 2007; Scheinost and Charlet, 2008), the lack of reduction in the current system is most likely due to the inhibited surface reaction because of the much smaller available surface area per selenite anion. The smaller surface area of the magnetite used here might be one of the reasons why reduction is not observed in our system.

In contrast, the “sorption” samples (Figs. 3 and 4) were prepared with a much smaller selenium loading; hence, selenite reduction would be possible. Although we were not able to collect EXAFS data because of the low total Se concentration, we assume that reduction also did not occur in these samples.

### 3.4. Redox and dissolution behavior of magnetite

Different magnetite suspensions from those used for sorption experiments (2 g/L in NaClO\(_4\)) were prepared at different pH. One series was maintained under oxic conditions and the other under anoxic conditions. The Eh and the pH of these suspensions were measured at different contact times (from 1 to 62 days). Fig. 8 shows the theoretical predominance Eh–pH diagram for selenium. Superimposed onto this theoretical diagram are the experimental values of Eh and pH, measured, in both series of samples (Fig. 8a, oxic conditions; Fig. 8b, anoxic conditions). The experimental Eh–pH data are mostly in the range of selenite predominance above the Se\(^0\) stability region, even after 2 months of reaction time.

This finding was an additional result strengthening the hypothesis that reduction did not occur in “sorption” samples. However, as show in Fig. 8, under anoxic conditions the Eh progressively decreased with time, showing that kinetics certainly play a role in this system.

The reason for the absence of selenite reduction in “sorption” samples is more difficult to explain, but we speculate that two factors may have contributed. First, the larger particle size of magnetite (and low surface area) may generally reduce the reactivity, thereby slowing down reduction kinetics. Second, the oxidizing nature of the inert electrolyte selected to fix the ionic strength (NaClO\(_4\)) in sorption edges and isotherms may hinder or slow the selenite reduction in our system. In Scheinost and Charlet (2008) and Scheinost et al. (2008), for example, the contact electrolyte was CaCl\(_2\).

An additional, remarkable difference previously observed between the magnetite and goethite was their dissolution behavior. Laboratory experiments were performed
on these oxides, in the conditions of sorption studies, to evaluate the kinetics of their dissolution at different pH (Missana et al., 2003a,b).

The increase of Fe content over time (0–3 months) was measured to understand the degree of their stability in the time frame of sorption experiments. Goethite dissolution was negligible, with aqueous Fe of a few ppb after several weeks even at very acidic pH.

Fig. 9 shows the aqueous Fe dissolved from magnetite (2 g/L) as a function of pH and different contact times.

3.5. Modeling of batch sorption data

All the parameters needed for the modeling (surface area, sorption site density and acidity constants) were previously experimentally determined (Table 2), thus, the only additional parameters needed to fit the experimental data were the surface complexation constants.

The thermodynamic constants for selenium used for the modeling were taken from (Seby et al., 1998, 2001), the most significant for our work being summarized in Table 4. The parameters used to fit the experimental sorption curves with the selected model are also included in Table 4.

Since the sorption isotherms showed linear sorption, and for sake of simplicity, only one sorption site (SOH) was considered. Initially, the formation of inner-sphere selenite....

<table>
<thead>
<tr>
<th>Species Composition</th>
<th>Log K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSeO₃⁻</td>
<td>1 H⁺, 1 SeO₃²⁻</td>
<td>8.54</td>
</tr>
<tr>
<td>Fe₂(SeO₃)₃·6H₂O (cr)</td>
<td>3 SeO₃²⁻, 2 Fe³⁺, 6H₂O</td>
<td>41.58</td>
</tr>
<tr>
<td>FeSeO₃⁺</td>
<td>1 Fe³⁺, 1 SeO₃²⁻</td>
<td>11.15</td>
</tr>
<tr>
<td>FeHSeO₃²⁺</td>
<td>1 Fe³⁺, 1 SeO₃²⁻, 1 H⁺</td>
<td>12.90</td>
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</table>

<table>
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<tr>
<th>Species Composition</th>
<th>Log K (NEM)</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Goethite (Model 1 and Model 2)</td>
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<td></td>
</tr>
<tr>
<td>Surface complexation SOH and selenite</td>
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<td></td>
</tr>
<tr>
<td>S–SeO₃⁻</td>
<td>1 SOH, 1H⁺, 1 SeO₃²⁻</td>
<td>13.60 ± 0.10</td>
</tr>
<tr>
<td>S–HSeO₃</td>
<td>1 SOH, 2H⁺, 1 SeO₃²⁻</td>
<td>19.10 ± 0.10</td>
</tr>
<tr>
<td>Species Composition</td>
<td>Log K (NEM/DDL)</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Magnetite (Model 1 and Model 2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface complexation SOH and selenite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S–SeO₃⁻</td>
<td>1 SOH, 1H⁺, 1 SeO₃²⁻</td>
<td>12.15 ± 0.10/11.6 ± 0.15</td>
</tr>
<tr>
<td>S–HSeO₃</td>
<td>1 SOH, 2H⁺, 1 SeO₃²⁻</td>
<td>16.60 ± 0.10/16.65 ± 0.25</td>
</tr>
<tr>
<td>Species Composition</td>
<td>Log K (NEM/DDL)</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>-----------</td>
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<tr>
<td>Magnetite (Model 3)</td>
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<tr>
<td>Surface complexation SOH and selenite and surface complexation SOH and Fe–Se species</td>
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</tr>
<tr>
<td>S–SeO₃⁻</td>
<td>1 SOH, 1H⁺, 1 SeO₃²⁻</td>
<td>12.15 ± 0.10/11.6 ± 0.15</td>
</tr>
<tr>
<td>S–HSeO₃</td>
<td>1 SOH, 2H⁺, 1 SeO₃²⁻</td>
<td>16.60 ± 0.10/16.65 ± 0.25</td>
</tr>
<tr>
<td>S–FeSeO₃⁺</td>
<td>1 SOH, 1 Fe³⁺, 1 SeO₃²⁻</td>
<td>17.40 ± 0.20/17.50 ± 0.15</td>
</tr>
<tr>
<td>S–FeHSeO₃²⁺</td>
<td>1 SOH, 1 Fe³⁺, 1 SeO₃²⁻</td>
<td>17.40 ± 0.20/17.50 ± 0.15</td>
</tr>
</tbody>
</table>
complexes with the SOH sites, as previously suggested by several authors (Duc et al., 2006; Dzombak and Morel, 1990; Goldberg, 1985), was postulated and the oxide dissolution was not allowed (Model 1). NE approach was used.

In Model 1, the two major species, HSeO$_3$\(^{2-}\) and SeO$_3$\(^{2-}\), were supposed to react with the iron oxide surface site, SOH, forming monodentate inner-sphere complexes. The surface complexation constants $K_1^i$ and $K_2^i$ depend on the following reactions:

$$\text{SOH} + 2\text{H}^+ + \text{SeO}_3^{2-} \Leftrightarrow \text{S-} \text{HSeO}_3 + \text{H}_2\text{O} \quad K_1^i$$

$$\text{SOH} + \text{H}^+ + \text{SeO}_3^{2-} \Leftrightarrow \text{S-SeO}_3 + \text{H}_2\text{O} \quad K_2^i$$

Model 1 was fit to the goethite data without further assumptions. The theoretical curve of selenite sorption onto goethite calculated with Model 1 parameters is shown superimposed to the experimental points in Fig. 3b (sorption edges) and Fig. 4b (sorption isotherm) as a continuous line. In the case of goethite, this very simple model predicted the sorption behavior as a function of pH, radionuclide concentration and ionic strength, reliably (Fig. 3b).

When we tried to fit the magnetite sorption data with the same model (dotted line in Fig. 3a) we could reasonably predict the experimental data for pH values above 5, but the fit was not acceptable at pH values below 5. Thus, in Model 2, we allowed the dissolution of both goethite and magnetite without changing any other parameters. The kinetics of oxides dissolution were not taken into account. In the case of goethite, the modeled curves of Model 1 or Model 2 were indistinguishable, in agreement with the expected small dissolution of goethite.

From a thermodynamic point of view, magnetite is not stable at pHs lower than 3, and the model considers higher dissolution than that experimentally observed. In Fig. 9 the experimental values of aqueous Fe at different contact times are compared with the theoretical prediction of the solid dissolution. At pH 4 the model predicts 0.03% of the magnetite dissolution (still in agreement with the experiments), but a pH 2 the model predicts an almost complete dissolution of magnetite, which was not observed within the time frame of our experiments. For this reason, such a strong decrease in $R_D$ values is predicted by Model 2 (dot line, Fig. 3a).

An increase in $R_D$ values was experimentally observed, indicating that additional mechanisms affect selenite retention. The aqueous Fe ions coming from the solid dissolution may also directly react with the selenite. In Rai et al. (1995), an extremely strong interaction between aqueous Fe$^{3+}$ and SeO$_3^{2-}$ is reported, leading to the formation of aqueous Fe–Se species as FeSeO$_3$\(^{4-}\) and FeHSeO$_3$\(^{2+}\) (Table 4).

To explain the selenite retention behavior on magnetite at acidic pH we considered a third model. In Model 3, we allowed the dissolution of magnetite, leading to the formation of the two above-mentioned Fe–Se species, and additionally hypothesized that these species formed inner-sphere surface complexes with magnetite by the following reactions:

$$\text{SOH} + \text{FeSeO}_3^{4-} \Leftrightarrow \text{S-FeSeO}_4 + \text{H}^+ \quad K_3^i$$

$$\text{SOH} + \text{FeHSeO}_3^{2+} \Leftrightarrow \text{S-FeHSeO}_3^{3+} + \text{H}^+ \quad K_4^i$$

Fig. 10. Comparison between electrostatic (dot line) and non-electrostatic (continuous line) model in the range in which sorption to magnetite is dominated by inner-sphere complexation with Se.

The inner-sphere complexation reactions used in Model 1 and Model 2 were not changed. The theoretical curve corresponding to Model 3, with the surface complexation of these Fe–Se aqueous species, is included in Fig. 3a as a (red)\(^1\) continuous line. The simulation was carried out considering the values of dissolved iron calculated by the code, which is in agreement with the experiments from pH 4 to 11. To confirm the validity of the model at lower pH, when the code overpredicts magnetite dissolution, we performed punctual calculations disabling the “dissolution” option and using the values of iron experimentally found in solution after one month of contact time (Fig. 9 for pH 4 and 3). The calculated log $R_D$ is included in the Figure as a solid circle.

Regarding the preference for a non-electrostatic model, at the beginning, both approaches were tested. The same problems discussed for simulating the data at pH lower than 4 were observed also with the DDL approach. The comparison between the DDL and NE approaches was therefore carried out in the pH region where sorption is dominated by the inner-sphere complexation (pH 4–11). The values of Log $K$ for complexation reactions obtained with the DDL model are also included in Table 4.

Fig. 10 shows the experimental $R_D$ data obtained for magnetite in this region, and the best fit obtained using the NE and the DDL (calculated for $I = 0.1$ M) approaches. As can be seen in the Figure, the simulation performed by an electrostatic or non-electrostatic model provided very similar $\chi^2$. In principle, both could have been accepted, however, when the data are expressed in a logarithmic scale, it is clear that a better fit is obtained with the NE approach (Fig. 3a, dashed line), and for this reason it was selected.

NE Model 3 provided a very good fit of the experimental results for magnetite, for trace selenium concentrations, and also of the sorption isotherms, as shown in Fig. 4a, over a wide range of selenium concentrations.

At higher selenium concentration ($>1 \times 10^{-4}$ M), the precipitation of the ferric selenite Fe$_3$(SeO$_3$)$_2$·6H$_2$O (cr) is indicated by the model.

\(^1\) For interpretation of the references to color in this text, the reader is referred to the web version of this article.
Finally, the sorption edges obtained at high Se concentration and solid-to-liquid ratio (Fig. 5a) were modeled. Also in this case, Model 1 (dotted line) showed sorption independent of pH from pH 2 to 10 and the model clearly under predicts the retention at acidic pH. The behavior of sorption data is also better reproduced by Model 3, including the sorption of Fe–Se phases and precipitation of ferric selenite.

Finally, we tried to observe the possible effects when including the redox reactions in the calculations (Fig. 5b). It is very interesting to note that when magnetite dissolves at these high selenium concentrations, the formation of the crystalline specie Fe₂(SeO₃)₃·6H₂O in the acidic pH region is still thermodynamically favored even if redox reactions are allowed and the reduction of Se⁴⁺ to Se⁰ is present.

In fact, in spite of the predicted Se⁰ precipitation, the Rₒ increase is still mostly attributable to the formation of the iron selenite solid phase (Fig. 5a and b, dashed lines). Quantitatively, selenium retention by magnetite is not greatly influenced by the inclusion of redox reactions.

4. CONCLUSIONS

The retention features of selenite on iron oxide magnetite are not directly comparable with other oxides. The selenite retention onto goethite can be modeled over the entire pH range, assuming only the formation of inner-sphere complexes between the solid surface and selenite. The same mechanism explains selenite retention by magnetite only in the neutral-to-alkaline range. However, at acidic pH, selenite retention is dominated by significant dissolution of magnetite, the presence of Se–Fe aqueous species, and the co-precipitation of Se⁴⁺–Fe species. All these processes could be adequately modeled.

The XANES analysis did not show selenite reduction occurring in our experimental conditions, in contrast to that observed in previous works. A minor change of conditions (e.g., higher surface loading or perchlorate instead of nitrate) seems to have a relatively strong influence on Se reduction. In fact, magnetite seems to be a rather “soft” reducer compared to green rust (Myneni et al., 1997) and mackinawite (Kirsch et al., 2008), possibly because electron transfer in magnetite can happen only along the sheets where octahedrally coordinated FêII and FeIII alternate, but not across the sheets containing tetrahedrally coordinated FeIII centers.

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