Selenite Adsorption Mechanisms on Pure and Coated Montmorillonite: An EXAFS and XANES Spectroscopic Study

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ABSTRACT

Selenite (SeO_3^{2-}) is an oxyanion of environmental importance due to its toxicity to animals at higher concentrations, notably waterfowl and grazing animals. Sorption of SeO_3^{2-} with mineral phases typically controls the movement and bioaccessibility of SeO_3^{2-} in soils and sediments. Previous studies have successfully utilized synchrotron-based Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) spectroscopy to determine SeO_3^{2-} bonding mechanisms on Fe and Mn oxides, but the direct evidence of SeO_3^{2-} surface complexation mechanisms on important mineral phases such as Al hydroxide and aluminosilicate minerals is still lacking. In this study both EXAFS and XANES spectroscopy was conducted on aqueous SeO_3^{2-} solutions and on a variety of Al-bearing sorption samples at pH 4.5. The sorbents chosen were a hydroxyalumino-silicate (HAS) polymer, a hydroxyaluminosilicate (HYA) polymer, montmorillonite, and both HYA and HAS coated montmorillonite. For SeO_3^{2-} sorption on montmorillonite, only bidentate binuclear inner-sphere complexation was observed. For the hydroxyaluminosilicate and hydroxyaluminosilicate polymers, a mixture of outer-sphere and bidentate binuclear inner-sphere was observed. When montmorillonite was coated with either HYA or HAS polymers then adsorption behavior was intermediate between that of the mineral and the pure polymer. Since temperate soils often contain aluminum-hydroxy and aluminosilicate-coated minerals rather than discrete Al hydroxide minerals and pristine clay surfaces, the adsorption mechanisms observed on these coated surfaces are more realistic of the natural environment than sorption on pure minerals.

SeLENIUM is a common metalloid in the soil environment due to dissolution of Se-bearing minerals and to anthropogenic sources such as wastewater from coal burning power plants. Selenium is also a micronutrient required for human and animal health. Selenocysteine is important because it is a component of glutathione peroxidase, an enzyme that catalyzes the removal of toxic peroxides that are commonly formed during aerobic metabolic processes (Lehninger et al., 1993). Therefore Se uptake by forages is linked to proper health in grazing animals. However, if soil Se levels are too high, then it tends to accumulate in forages and toxicity effects are often observed in grazing animals (Rosenfeld and Beath, 1964). Selenium toxicity is also commonly encountered in aquatic ecosystems, as Se has a smaller range between deficiency and toxicity than any other element in aquatic systems (Chapman, 1999). Bioaccumulation is often responsible for Se toxicity to waterfowl, as Se levels increase from low concentrations in the water itself to extremely high levels in plants and fish. In waterfowl, Se is both embryotoxic and teratogenic in high concentrations (Hoffman, 2002).

Soil Se undergoes a variety of redox reactions, and can be found in oxidation states ranging from -2 (selenide) to +6 (selenate) (Shriver et al., 1994) with the form found in the environment being dependent on soil redox status (Huang and Fuji, 1996). One important intermediate form of selenium in soils and surface waters is SeO_3^{2-}. Selenium in SeO_3^{2-} has an oxidation state of +4, and SeO_3^{2-} is a weak diprotic acid that can exist as H_2SeO_3, HSeO_3^-, or SeO_3^{2-} depending on solution pH (pK_a = 2.64 and pK_a = 8.4) (Shriver et al., 1994). Selenite is considered to be one of the more toxic forms of Se, and as such its chemistry in the soil environment has been researched quite extensively. Sorption processes are extremely important for SeO_3^{2-} in soils, as adsorption between SeO_3^{2-} and soil mineral phases is often quite strong, and sorption complexes can also explain the slow reduction of oxidized Se forms in the presence of soils (Neal and Sposito, 1991). Sorption of SeO_3^{2-} is also an important reaction step in the reduction of SeO_3^{2-} to elemental Se in the presence of green rusts (Myneni et al., 1997).

Several researchers have studied the sorption of SeO_3^{2-} on inorganic soil components. Hingston and coworkers (Hingston et al., 1971, 1974) found that SeO_3^{2-} adsorption on Fe and Al oxides is pH dependent but does not vary with ionic strength. Additionally, they observed that the majority of SeO_3^{2-} was irreversibly bound to the oxide surface. They concluded that SeO_3^{2-} reacts to form covalent chemical bonds with metal oxide surfaces. Zhang and Sparks (Zhang and Sparks, 1990) utilized a pressure jump chemical relaxation technique and observed that the reaction between SeO_3^{2-} and goethite consisted of two reaction steps. The fast step was attributed to outer-sphere complex formation, and the subsequent slower step was assigned to formation of an inner-sphere surface complex. Several scientists have used spectroscopic techniques to determine precisely how SeO_3^{2-} bonds on mineral surfaces. Hayes and coworkers (Hayes et al., 1987) used EXAFS spectroscopy to determine bonding mechanisms of SeO_3^{2-} and SeO_3^{2-} on goethite. They determined that SeO_3^{2-} forms inner-surface complexes with goethite, and that these complexes are bidentate binuclear (bridging two adjacent Fe octahedral). Manceau...
and Charlet (Manceau and Charlet, 1994) published results from EXAFS studies of SeO$_3^{2-}$ adsorbed on hydrous ferric oxide. They also found bonding mechanisms consistent with a bidentate binuclear bonding mechanism, although a bidentate mononuclear SeO$_3^{2-}$ surface complex was also observed. This second, shorter Se-Fe distance was not observed on more crystalline Fe oxides such as goethite. More recently, Foster and coworkers studied SeO$_3^{2-}$ sorption on Mn oxides. (Foster et al., 2003) They observed that SeO$_3^{2-}$ forms both bidentate mononuclear (Se-Mn 3.07 Å) and monodentate surface complexes (Se-Mn 3.49 Å) on hydrous Mn oxides. MnSeO$_3$/H$_2$O precipitation could not completely be ruled out in this study, but if it does occur then the precipitate is extremely disordered and amorphous. Only one researcher has reported Se EXAFS data for SeO$_3^{2-}$ adsorbed on an Al oxide (Boyle-Wight et al., 2002b). Their study was conducted on γ-Al$_2$O$_3$ at pH 7.5 in the presence or absence of Co$^{2+}$. The researchers concluded that SeO$_3^{2-}$ formed inner-sphere complexes based on macroscopic data (Boyle-Wight et al., 2002a), but they were not able to conclusively observe these complexes with EXAFS. They attributed this to Al being an extremely weak backscatter. However, there do appear to be some second shell contributions present in the radial structure functions (RSFs) of their SeO$_3^{2-}$ samples (Fig. 4b of Boyle-Wight et al., 2002b). This highlights the need for additional studies of SeO$_3^{2-}$ reactivity with aluminum-bearing mineral phases.

While previous EXAFS studies have concentrated on Fe and Mn oxides, many different mineral phases composed of Al (e.g., aluminosilicates and aluminum oxides) are potentially important sorbents for SeO$_3^{2-}$ in soils. To further complicate matters, it is well known that soil minerals are often associated with both inorganic and organic coatings in natural systems. These conglomerate sorbent phases may have reactivity much different from their individual components. Previous research (Saha et al., 2004) used HYA and HAS coated montmorillonite as a model system to investigate the importance of coatings on SeO$_3^{2-}$ adsorption. It was found that these coatings greatly enhanced the sorption capacity of montmorillonite and affect adsorption rates as well.

The goal of this study was to utilize synchrotron-based XAS (both EXAFS and XANES spectroscopy) to elucidate the adsorption mechanisms of SeO$_3^{2-}$ on HYA and HAS polymers, HYA and HAS-coated montmorillonite, and pure montmorillonite sorbent phases at pH 4.5. This pH was chosen for XAS studies because previous researchers (Saha et al., 2004) have extensively studied the reaction kinetics and sorption behavior of SeO$_3^{2-}$ with these surfaces and inferred that different adsorption mechanisms are responsible for differences in macroscopic reactivity. The spectroscopic experiments conducted in this research are therefore useful to validate the kinetic models and thermodynamic results from previous laboratory experiments (Saha et al., 2004). EXAFS spectroscopy was chosen because it is a well-established method for probing oxyanion-bonding mechanisms on mineral surfaces, and it is expected that possible inner-sphere complexes will be easily differentiated in our samples based on Se-Al distance. A large amount of specific chemical information is also contained in the XANES region, and we believe that XANES analysis will also be useful in probing SeO$_3^{2-}$ adsorption mechanisms on our sorbents. For example, researchers have found that XANES spectroscopy can distinguish outer-sphere and inner-sphere complexation of As(III) on aluminum oxides (Araki et al., 2001), outer-sphere and inner-sphere bonding mechanisms of lead on montmorillonite (Strawn and Sparks, 1999), and can distinguish the protonation states of As(III) and As(V) in aqueous solutions (Myneni et al., 1999). The XANES technique can be used to obtain detailed information about precipitate geometry (including cluster size) in surface precipitates (Waychunas et al., 2003), and can determine the coordination of sulfate in Fe minerals (Myneni et al., 1997). Based on the above studies, if outer-sphere complexation is occurring simultaneously with inner-sphere complexation, then it should be visible in the XANES spectra.

**MATERIALS AND METHODS**

**Mineral Synthesis**

Hydroxyaluminum precipitate was prepared using a method based on that of Sims and Bingham (Sims and Bingham, 1968) for the synthesis of hydroxy-Fe precipitate. A 200-mL aliquot of 1.5 M AlCl$_3$ was placed in a 1-L beaker and neutralized slowly at a rate of 0.5 mL min$^{-1}$ with 2.0 M NaOH up to a OH/Al ratio of 2.7 under continuously stirred condition. A HAS precipitate was prepared following a method based on Su and Suarez (Su and Suarez, 1997) for the synthesis of allophone. A 100 mL of 3.0 M AlCl$_3$ solution was mixed well with 100 mL of 1.5 M Na$_2$SiO$_3$, and placed in a 1-L beaker. The resulting solution, containing a Si/Al molar ratio of 0.5, was then neutralized at the rate of 0.5 mL min$^{-1}$ with 2.0 M NaOH up to a OH/Al ratio of 2.7 under continuously stirred condition. The resulting precipitates were aged for 1 h, resuspended in 1 L of distilled water, centrifuged at 1000 x g, and the supernatant was discarded. The precipitates were then washed three times with 600 mL of 95% ethanal followed by washing with distilled water until the leachate did not form a precipitate with AgNO$_3$. The washed precipitates were kept as suspension in distilled water with a density of solid as 20 g L$^{-1}$ and used immediately for SeO$_3^{2-}$ adsorption experiments. Unused precipitate was freeze-dried and analyzed for physical and chemical properties.

Montmorillonite (Mt), hydroxyaluminum-coated montmorillonite (HYA-Mt), and hydroxyaluminosilicate-coated montmorillonite (HAS-Mt) were prepared and characterized in a previous study (Saha et al., 2004). Surface area and point of zero salt effect (PZSE) measurements for all sorbents used in this study were previously reported by Saha and coworkers (2004) and are compiled in Table 1. PZSE for the montmorillonite were not experimentally determined, but is typically below 3. It is important to note that PZSE is not necessarily equal to the point of zero charge (PZC) of mineral surfaces, and instead is the point at which titrations conducted at different ionic strength cross one another. Researchers have shown that the PZC may differ from the experimentally determined PZSE, but both PZC and PZSE follow the same trends. Literature PZC values for pure aluminum hydroxide minerals range from 8.5 to 9.5 (Sparks 1995), which is consistent with the experimentally determined PZSE results of Saha and coworkers (2004). Based on experimentally determined PZSE values, at pH 4.5 one sorbent used in this...
study (Mt) will be negatively charged, two sorbents (HYA-Mt and HAS-Mt) are close to neutral/have a small surface charge, and the remaining sorbents (HYA and HAS) will be strongly positively charged. Previous researchers have shown that outer-sphere complexion of other oxyanions such as arsenite (Arai et al., 2001; Goldberg and Johnston, 2001) and SeO$_3^{2-}$ (Peak and Sparks, 2002; Wijnja and Schulthess, 2000) is common when solution pH is below the PZC of metal oxides as is the case for the pure HYA and HAS samples. It is also known that inner-sphere complexion of oxyanions can result in a surface complex with an overall negative charge. This leads to a decreased PZC, and may be important in the HAS and HYA-coated samples which have PZSE near the experimental pH of 4.5.

**Aqueous Samples**

Solutions containing 50 mM total SeO$_3^2-$ (as Na$_2$SeO$_3$) at pH 1.10, 3.52, 5.52, 8.50, and 11.02 were prepared in a glovebox under a nitrogen atmosphere to exclude oxygen from the samples. An oxygen-free environment was necessary to obtain spectra free of SeO$_3^{2-}$ oxidation at alkaline pH. Initially, 5 mL of 100 mM SeO$_3^{2-}$ solution pH was adjusted to the desired pH with either 1 M HCl or 1 M NaOH then enough deionized water (18.2 MΩ Barnstead Diamond NanoPure) was added to produce a 10-mL final volume. These samples were placed in a centrifuge tube, sealed with parafilm, placed into a nitrogen-filled ziploc bag, and shipped to the Advanced Photon Source (Chicago, IL). Samples were analyzed in transmission mode by placing the sealed tube in the path of the beam.

**Table 1. Characteristics of sorbents used in this study.**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Surface Area, m$^2$ g$^{-1}$</th>
<th>PZSE†</th>
<th>External</th>
<th>Internal</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>ND‡‡</td>
<td>72§§</td>
<td>529§</td>
<td>601§</td>
<td></td>
</tr>
<tr>
<td>Hydroxylaluminum (HYA)</td>
<td>9.38§§</td>
<td>122.6§</td>
<td>122.6§</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxylaluminaulate (HAS)</td>
<td>8.52§§</td>
<td>193.7§</td>
<td>193.7§</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HYA-Mt</td>
<td>4.75§§</td>
<td>128§§</td>
<td>322§§</td>
<td>450§§</td>
<td></td>
</tr>
<tr>
<td>HAS-Mt</td>
<td>4.4§§</td>
<td>108§§</td>
<td>379§§</td>
<td>487§§</td>
<td></td>
</tr>
</tbody>
</table>

† Point of zero salt effect.
‡ Not determined.
§§ Cited from Saha et al. (2004).

**Adsorption Sample Preparation**

A 1 g L$^{-1}$ suspension of sorbent was placed in 0.01 M NaNO$_3$, adjusted to pH 4.5, equilibrated overnight, and then Na$_2$SeO$_3$ was added from a freshly prepared 1 mM stock solution to reach a final concentration of 25 μM SeO$_3^{2-}$. Sample pH was readjusted to pH 4.5 after SeO$_3^{2-}$ addition and again if necessary as the reaction proceeded. After a 48-h reaction time, the suspensions were centrifuged at 1000 × g and the supernatants were analyzed with flame Atomic Absorption Spectrophotometry (AAS). HYA-Mt, HAS-Mt, Mt, and pure HYA and HAS adsorption studies were done open to the atmosphere at pH 4.5 as part of a separate research project (Saha et al., 2004). However, dissolved carbon dioxide concentrations in solutions at pH 4.5 are extremely low, and no oxidation of SeO$_3^{2-}$ was observed in the XANES spectrum of any samples. Selenite sorption amounts (expressed as μmol m$^{-2}$) for all samples are included along with reaction conditions in Table 2. One complication with this surface coverage/surface loading calculation arises from uncertainty in what portion of the mineral surface is actually available for reaction with SeO$_3^{2-}$.

**X-Ray Absorption Spectroscopy**

EXAFS spectra were collected at the Se K-edge (12.658 keV) at the PNC-CAT Bending Magnet beamline (20-BM) at the Cornell High Energy X-ray Source. The EXAFS data were collected in transmission mode with a sealed tube in the path of the beam.

**Table 2. Structural parameters of selenite in solution and sorbed on mineral surfaces.**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Loading</th>
<th>Reaction Conditions</th>
<th>First shell Se-O</th>
<th>Second shell Al-Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>HYA</td>
<td>0.77</td>
<td>pH 4.5, 1−0.01</td>
<td>S$^{\ddagger}$</td>
<td>R$_{\ddagger}$$^\ddagger$ N$^{\ddagger}$</td>
</tr>
<tr>
<td>HAS</td>
<td>0.34</td>
<td>pH 4.5, 1−0.01</td>
<td>0.86 10.78 1.70</td>
<td>2.92 0.001</td>
</tr>
<tr>
<td>Mt</td>
<td>0.01</td>
<td>pH 4.5, 1−0.01</td>
<td>0.86 10.34 1.70</td>
<td>2.78 0.001</td>
</tr>
<tr>
<td>HYA-Mt</td>
<td>0.06</td>
<td>pH 4.5, 1−0.01</td>
<td>0.86 11.21 1.70</td>
<td>2.5 0.002</td>
</tr>
<tr>
<td>HAS-Mt</td>
<td>0.002</td>
<td>pH 4.5, 1−0.01</td>
<td>0.86 10.37 1.70</td>
<td>2.67 0.003</td>
</tr>
</tbody>
</table>

† Amplitude reduction factor.
‡ Energy shift; § Interatomic distance.
$^\ddagger$ Coordination number.
# Debye-Waller factor fit quality estimated accuracy.
†† ± 0.02Å.
‡‡ ± 20%.
§§ EXAFS collected in transmission mode.
Advanced Photon Source at Argonne National Laboratory. The electron storage ring was operating at 4.5 GeV and in top up mode (100 mA) for all experiments. The beamline was calibrated using a Pt foil placed in the path of the beam downfield from the sample chamber between \( I \) and \( I_{\text{ref}} \). Solution samples were analyzed in transmission mode to avoid self absorption effects while sorption samples were analyzed in fluorescence mode using a solid-state 13-element Ge detector (Canberra). Solution samples were analyzed at room temperature while a cryostat was utilized to lower sorption samples (analyzed as moist pastes) to 25 K to avoid any beam-induced oxidation over long scan times (up to 4 h for the most dilute samples). An aqueous SeO\(_3^{2-}\) sample at pH 9.8 was analyzed at both 25 K and 298 K to compare with the room temperature data and no significant differences were observed.

**XAS Data Analysis**

WinXAS version 2.3 (T. Ressler, 1997) was used for all data reduction and analysis. All scans were first checked for edge shifts, which were corrected if observed. Multiple scans (from 5 for solutions to 25 scans for the Mt sorption sample) were averaged and then background subtracted using a linear equation for the pre-edge region and a second-order polynomial for the post-edge region. After baseline correction, then every spectrum was normalized to an edge jump of 1.0. EXAFS fitting was done by comparing experimental spectra to theoretical single scattering paths for model compounds. ATOMS 3.0 (Ravel, 2001) was used to construct mineral phases from crystallographic data, and FEFF7 (Zabinsky et al., 1995) was then used to calculate theoretical single scattering paths. Fits were conducted in R space with the amplitude reduction factor \( S_0^2 \) fixed at 0.86 while coordination number, bond distance, Debye-Waller, and \( \epsilon_0 \) shift were all allowed to vary. Data was then also fit in k space to verify that optimized parameters were similar in both cases. Linear combination XANES (LC-XANES) fitting was conducted on samples using the methods recommended by WinXAS and aqueous and adsorbed SeO\(_3^{2-}\) reference spectra. The fitting with reference spectra was conducted in two runs: an initial run where \( E_0 \) was allowed to vary to optimize the relative contributions of all components, and then a second run where \( E_0 \) shift was fixed at 0.00.

**RESULTS AND DISCUSSION**

**EXAFS of Selenite Aqueous Solutions**

To investigate how protonation state may affect EXAFS spectra, solutions containing 50 mM Se were analyzed at three different pHs (1.1, 5.5, and 11.0) to produce solutions containing only H\(_2\)SeO\(_3\), HSeO\(_3\), or SeO\(_3^{2-}\). The k\(^3\)-weighted chi data and the RSFs obtained from performing a Fourier transformation on the chi data are shown in Fig. 1 (raw data denoted with solid lines). Structural parameters obtained from EXAFS fitting (fitted spectra are shown with open circles in Fig. 1) are tabulated in Table 2. In all protonation states, ~2.5 oxygen atoms surrounds the central Se atom at 1.70 ± 0.01 Å. This bond distance is in good agreement with previous studies (Hayes et al., 1987; Manceau and Charlet, 1994, etc.), and the coordination number differs from the true value of 3.0 by only 20% (the estimated error for the fitting routine). Interestingly, the amplitude of oscillations in the chi data and the intensity of the Se-O shell in the RSF decrease as SeO\(_3^{2-}\) becomes protonated (Fig. 1). This is most likely caused by a shift from three equivalent Se-O distances in SeO\(_3^{3-}\) (with bond delocalization) to single and double Se-O bonds in both biselenite and selenous acid. It was possible (data not shown) to fit the H\(_2\)SeO\(_3\) data with two separate Se-O distances (at 1.61 and 1.74 Å), but the \( r^2 \) was similar to the single shell fit that is presented in Fig. 1.

**EXAFS of Selenite Adsorbed on Mineral Samples**

Samples containing SeO\(_3^{2-}\) adsorbed on HYA and HAS polymers, Mt, and HYA-Mt or HAS-Mt polymers...
at pH 4.5 were analyzed with EXAFS to determine bonding mechanisms on these sorbents. The \( k^3 \)-weighted chi data and the Radial Structure Functions obtained from performing a Fourier transformation on the chi data are shown in Fig. 2 for all sorption samples (raw data denoted with solid lines). Structural parameters obtained from EXAFS fitting (fitted spectra are shown with circles in Fig. 2) are tabulated in Table 2. In all samples there are features (denoted by arrows in Fig. 2) in both the raw chi data and the Fourier transforms that suggest inner-sphere complexation of \( \text{SeO}_3^{2-} \). There are clearly some constructive and destructive interferences in the chi data that result in deviations from a single Se-O shell (as seen in the aqueous samples), and when a Fourier transform is performed then a second shell Se-Al contribution is observed between 3.16 and 3.22 Å in all samples. Fitting routines suggest that this Se-Al bond distance is shortest (3.16 Å) when SeO\(_3^{2-}\) is sorbed on montmorillonite, longest (3.22–3.24 Å) when SeO\(_3^{2-}\) is adsorbed on hydroxyaluminum and hydroxyaluminosilicate polymers, and of an intermediate distance (3.16–3.18 Å) on the polymer-coated montmorillonite samples. This bond distance is consistent with those calculated for bidentate binuclear (also termed bridging or corner sharing) SeO\(_3^{2-}\) complexes. While the change in bond distance with pure polymer sorbents is larger than the error associated with the fits (estimated at 0.02 Å), it is not significant enough to represent a change in bonding configuration from monodentate to bidentate. One would predict a monodentate complex to have a Se-Al distance of \(~3.42\) Å and a bidentate mononuclear (edge-sharing) complex is expected to have a Se-Al bond distance of \(~2.57\) Å. These numbers are based on simple geometrical calculations based on an Al-O distance of 1.72 Å [as calculated for octahedral Al(H\(_2\)O)\(_6\)\(^{2+}\)] and an Se-O distance of 1.70 Å (as observed with EXAFS in this study). Instead, it is more likely that there may be some slight deviation in bond lengths and coordination number for a bidentate binuclear bonding environment that is possible as the sorbent structure is changed.

For the pure polymer samples, it appears that the single Se-Al scattering path may not fully describe the second shell; the coordination number for both HYA (2.55) and HAS (2.80) samples is quite large and the width of the second shell of the Fourier transforms is consistent with a disordered bonding environment. This could be due to either a large static disorder in the bonding environment (meaning that a single type of surface complex has a large range of bond distances) or two distinct complexes with slightly different Se-Al distances in HYA and HAS samples. It is not possible to distinguish these possible explanations with the existing EXAFS data. In the coated montmorillonite samples this effect is less pronounced, coordination numbers decreases to 1.78 for HYA-Mt and 1.80 for HAS-Mt, and bond distances also shorten slightly to 3.16 Å (HYA-Mt) and 3.18 Å (HAS-Mt). In the pure montmorillonite adsorption sample, the Se-Al distance (3.16 Å) is significantly shorter than the interatomic Se-Al distances observed in any of the pure polymer samples (3.22–3.24 Å). When considered together, it appears that there is a bidentate binuclear complex forms on all surfaces, but that there is a slight difference in bonding environment depending on sorbent. This is reasonable given the nature of montmorillonite and the polymers. On montmorillonite, the only available Al groups for reac-

![Fig. 2. Se K-Edge EXAFS results for selenite adsorbed on a range of sorbents at pH 4.5 and 0.01 M I. Solid lines denote the raw data, and open squares are the fit to theoretical standards. Arrows denote spectral features consistent with Se-Al backscattering due to inner-sphere complexation.](image-url)
tion would occur at the fairly structured edge sites of the mineral. On the HYA and HAS polymers, however, essentially all of the Al on the surface of the polymer is available for reaction. Additionally, these polymers are of short-range order rather than crystalline. This results in longer bond distances and larger coordination number as SeO$_3^{2-}$ is essentially enveloped by the polymer. On polymer-coated montmorillonite surfaces, a portion of the polymer’s reactive surface is tied up by interaction with the planar tetrahedral sheet and with pillaring in the montmorillonite interlayer. When reacted with SeO$_3^{2-}$, these polymer-coated montmorillonite sorbents have Se-Al coordination numbers and bond distances somewhat intermediate between what is observed on a pure montmorillonite surface and on a pure polymer phase.

Some of the more qualitative differences in the EXAFS spectra also deserve discussion. One interesting observation in the raw chi data is that the amplitude of the montmorillonite sorption sample is much less than the other samples, and the amplitude of the coated montmorillonite samples is also somewhat decreased relative to the pure polymer sorption samples. This is also visible in the form of decreased Se-O shell height in the RSFs. This is very similar to the effects of protonation on aqueous SeO$_3^{2-}$. Although coordination numbers and Se-O distance was similar for all protonation states of aqueous SeO$_3^{2-}$, HSeO$_3$ had a decrease in EXAFS amplitude (in the chi data) and Se-O shell height (in the RSF). This may be a general effect that is caused by full localization of bonds to form a formal Se = O double bond and two formal Se-O single bonds. The fact that the amplitude of the chi data and the height of the Se-O shell in the RSFs are larger in the polymer-coated and pure polymer sorption samples implies that there may be some contributions to the spectra from SeO$_3^{2-}$ in a different coordination with more delocalized Se-O bonding. This could possibly be explained with the presence of some additional outer-sphere complexation, which occurs simultaneously with inner-sphere complex formation. However it is difficult to conclusively assign outer-sphere complex formation with EXAFS when inner-sphere complexes are also present. Previous researchers (Arai et al., 2001) have found that XANES spectroscopy is extremely useful tool in determining outer-sphere complexation in such systems, and for this reason XANES spectra of aqueous and adsorbed SeO$_3^{2-}$ were next examined in detail.

**XANES of Selenite in Aqueous Solutions**

By changing solution pH to produce H$_2$SeO$_3$, HSeO$_3^{-}$, and SeO$_3^{2-}$, it is possible to produce standards for XANES analysis that represent the full range of molecular symmetry possible for SeO$_3^{2-}$. When SeO$_3$ is protonated, either partially or fully, then there are changes in molecular structure that may affect symmetry. First of all, the proton may disrupt vertical mirror planes or it may be placed in a position that preserves them. This will change symmetry from $C_s$ to $C_1$. Second, bond delocalization may no longer occur, which would reduce symmetry of the structure further. Diagrams of molecular symmetry and Lewis structures for all protonation states of SeO$_3^{2-}$ are compiled in Fig. 3 to aid in the following discussion.

![Fig. 3. Relationship between protonation state, molecular symmetry, and bond delocalization for selenite species.](Image)
There has not been a rigorous assignment of symmetry for all protonation states of \( \text{SeO}_3^{2-} \) based on either molecular modeling or vibrational spectroscopy. However, Nakamoto (Nakamoto, 1997) includes \( \text{SeO}_3^{2-} \) in the discussion of pyramidal \( \text{XO}_3 \) molecules, and researchers (Wang and Zhang, 2002) have recently optimized the structure of \( \text{H}_2\text{SO}_3 \), \( \text{HSO}_3^- \), and \( \text{SO}_3^- \) using both theoretical modeling and experimental data. The optimization of \( \text{SO}_3^- \) is not directly applicable to \( \text{SeO}_3^{2-} \) because \( \text{SO}_3^- \) is trigonal planar unlike \( \text{SO}_3 \) or \( \text{SeO}_3^{2-} \), but the effects of protonation on bond delocalization are still relevant for \( \text{SeO}_3^{2-} \).

Infrared and Raman spectroscopy verify that \( \text{SeO}_3^{2-} \) has \( C_3v \) symmetry, meaning that all three oxygens are interchangeable (Nakamoto, 1997). In other words, the bonding described by a \( \text{Se} = \text{O} \) double bond in Lewis structures is actually fully delocalized (hence the three resonance structures drawn in Fig. 3). This is also the case in the molecular modeling of \( \text{SO}_3^- \), which is reported as having \( D_{3h} \) symmetry (Wang and Zhang, 2002).

In contrast, \( \text{H}_2\text{SeO}_3 \) represents another extreme in symmetry. When the structure of \( \text{H}_2\text{SeO}_3 \) (analogous to \( \text{H}_2\text{SeO}_3 \)) was optimized (Wang and Zhang, 2002), it was found to possess \( C_3 \) symmetry, meaning that there is one \( \text{Se} = \text{O} \) localized double bond and two \( \text{Se}-\text{OH} \) bonds with protons arranged so that there is a reflection plane in the molecule.

Biselenite (\( \text{HSeO}_3 \)) is somewhat more difficult to assess, since it is possible that it may or may not have bond delocalization among the two bare oxygen atoms, and the single proton may or may not lie in the mirror plane. Wang and Zhang (Wang and Zhang, 2002) reported an optimized \( C_i \) symmetry for the \( \text{HOSO}_2 \) molecule, but they do not mention whether this is due to lack of delocalization or if it is caused by proton position in the molecule. One would expect that since \( \text{SO}_3^- \) and \( \text{SeO}_3^{2-} \) exhibit bond delocalization, \( \text{HSeO}_3^- \) would as well.

Given the above information about symmetry, XANES spectra of aqueous \( \text{SeO}_3^{2-} \) species may now be more rigorously interpreted. Transmission mode XANES spectra of 50 mM \( \text{SeO}_3^{2-} \) solutions adjusted with acid or base were collected and presented in Fig. 4a. An enlargement of the 12.66- to 12.69-keV range of these samples is also shown in Fig. 4b to highlight differences in the XANES region. The two most important observations that can be made from the XANES spectra of aqueous \( \text{SeO}_3^{2-} \) solutions are: (1) \( \text{H}_2\text{SeO}_3 \) has features that are different in position and shape from the other samples and (2) The position of peaks in \( \text{HSeO}_3^- \) and \( \text{SeO}_3^{2-} \) is fairly similar but the intensity of the features is different. These observations are completely consistent with the symmetry discussion above if there is bond delocalization in the unprotonated oxygens of \( \text{HSeO}_3^- \). In this case, both \( \text{HSeO}_3^- \) and \( \text{SeO}_3^{2-} \) would have shared pi electron density and intermediate Se-O bond lengths. Such delocalization cannot occur with \( \text{H}_2\text{SeO}_3 \), and distinct long (single bond) and short (double bond) Se-O distances must occur in this molecule. One important consequence of this interpretation of the data is that molecules with different symmetry (\( \text{SeO}_3^{2-} \) is \( C_{3v} \) while \( \text{HSeO}_3^- \) is \( C_3 \) or \( C_i \)) have similar spectra and not molecules with the same symmetry (both \( \text{H}_2\text{SeO}_3 \) and \( \text{HSeO}_3^- \) are either \( C_i \) or \( C_3 \) depending on the position of protons). This suggests that bond delocalization is the dominant force in affecting...
XANES spectra of SeO$_3^{2-}$. This is not too surprising since the Se-O bond lengths in the first coordination shell will certainly affect the geometry of the molecule, and therefore the intensity and position of multiple scattering effects in the XANES spectra.

**LC-XANES of Aqueous Solutions**

Aqueous samples were also analyzed that contained two SeO$_3^{2-}$ protonation states (pH 3.3 and 8.5). These spectra were fit with a linear combination approach using WinXAS 2.3 and the H$_2$SeO$_3$, HSeO$_3^-$, and SeO$_3^{2-}$ solutions as standards. Error in LC analysis was estimated at 3% by comparing the fit of all individual scans to the fit results for the overall averaged spectrum. Results are shown in Fig. 5. The pH 3.3 spectrum could be fit with a mixture of 82% HSeO$_3^-$ and 18% H$_2$SeO$_3$, and the pH 8.5 spectrum could be fit with a mixture of 44% HSeO$_3^-$ and 56% SeO$_3^{2-}$. These distributions are in agreement (within 0.5%) with the expected speciation of SeO$_3^{2-}$ using published pK$_a$ values of 2.63 and 8.4.

Using those pK$_a$s, the Henderson–Hasselbalch equation predicts 82.4% HSeO$_3^-$ and 17.6% H$_2$SeO$_3$ for the pH 3.3 sample and 55.7% SeO$_3^{2-}$ and 44.3% HSeO$_3^-$ for the pH 8.5 sample. This excellent agreement between solution speciation models and LC-XANES fitting suggests that changes in the XANES spectra as a result of Se-O bond delocalization are fairly quantitative in nature.

**XANES of Selenite Adsorbed on Mineral Samples**

XANES spectra of SeO$_3^{2-}$ adsorbed on a variety of mineral soil components are shown in Fig. 6. The spectra of HSeO$_3^-$ (aq) and H$_2$SeO$_3$(aq) are also included for reference. HSeO$_3^-$ is the dominant solution species at pH 4.5. XANES spectra of all sorption samples contain features that are clearly different from HSeO$_3^-$, which suggests that some inner-sphere complexation is occurring. This is in good agreement with the EXAFS studies. However, while the EXAFS spectra all had generally similar features, the XANES spectra for different sorbents show some important differences. In particular,
the XANES spectrum of SeO$_3^{2-}$ sorbed on montmorillonite has a well-defined 12.67 keV peak in the XANES region (noted by the arrow in Fig. 6a) that is similar in both energy and shape to H$_2$SeO$_3$(aq). As discussed previously, H$_2$SeO$_3$ has a fully localized double bond and two Se-O-H bonds. The fact that adsorbed SeO$_3^{2-}$ has features in similar positions therefore suggests that it has similar coordination chemistry and is most likely bound as a bidentate complex. This is also consistent with the EXAFS fit results for the montmorillonite sample. It has also been observed that SeO$_3^{2-}$ adsorbed on FeOOH via a bidentate binuclear inner-sphere complexation mechanism has a similar XANES spectrum over all pH range (data not shown). One other type of surface complex would result in a fully localized Se = O bond: monodentate adsorption of HSeO$_3$ would produce a monodentate biselenite complex with one of selenite’s oxygens coordinated to Al, one to a proton, and the third present as the double-bonded O. As mentioned in the EXAFS analysis section, this complex would produce a Se-Al bond distance of $\sim$3.4 Å, which was not observed in any of the sorption samples. Instead, the EXAFS data showed evidence for the bidentate binuclear SeO$_3^{2-}$ species. Based on that, the monodentate biselenite species can be ruled out.

It could also be possible that the XANES spectrum of Mt resembles aqueous H$_2$SeO$_3$ because H$_2$SeO$_3$ adsorption into the interlayer of the mineral occurs. This has been proposed by previous researchers (Saha et al., 2004), who predicted that H$_2$SeO$_3$ will be preferentially adsorbed in the interlayer of montmorillonite because HSeO$_3$ and SeO$_3^{2-}$ are repelled by the negatively charged interlayer. The mechanism of this reaction is unknown, but conceivably could involve hydrogen bonding between H$_2$SeO$_3$ and O from silica tetrahedral layers of the interlayer space. Once H$_2$SeO$_3$ diffuses to the interlayer space, a ligand exchange reaction would also be possible. While the relative importance of interlayer H$_2$SeO$_3$ to the overall XANES spectrum is difficult to assess, the XANES do seem to suggest that such complexation cannot be disregarded.

The important changes in XANES features for SeO$_3^{2-}$ adsorbed on HYA, HYA-Mt, and Mt are enlarged in Fig. 6b for clarity; HAS, HAS-Mt, and Mt spectra show the same trends. The broadening and weakening of the 12.67 keV XANES feature to a varying extent in the HYA, HAS, HYA-Mt, and HAS-Mt samples suggests that a fraction of the SeO$_3^{2-}$ is in a surface complex that retains the molecular structure of SeO$_3^{2-}$ in solution (note the similarity to the HSeO$_3$ spectrum). The two
possible sources of such a bonding environment are the presence of unbound (entrailed) or weakly bound biselenite in these samples. Since the entrained solution SeO$_3^{2-}$ levels were <3% of the total Se signal in all samples, weakly bound SeO$_3^{2-}$ is the most likely source of these spectral features. This also makes sense given the nature of HYA and HAS polymers. Aluminum hydroxide is strongly positively charged at pH 4.5 and so outer-sphere complexation is possible. It has previously been shown that arsenite forms both outer-sphere and inner-sphere complexes on aluminum hydroxide below the mineral's PZC (Arai et al., 2001) (Goldberg and Johnston, 2001), so this type of bonding mechanism is certainly not unprecedented for HYA samples. Since aluminosilicates have a lower PZC than aluminum hydroxides, one would expect relatively more inner-sphere complexes and relatively less outer-sphere complexes on HAS. When the XANES data are examined then it can indeed be observed that the features of HAS are somewhat sharper and better defined than those of HYA. Montmorillonite, on the other hand, has a permanent negative charge from isomorphic substitution. This negative surface charge would make outer-sphere complexation of negatively charged oxyanions quite unlikely. When HYA or HAS polymers are used to pillar the montmorillonite interlayer and coat the planar sites of the smectite then the resulting colloid has intermediate surface behavior. Some of the positive surface charge of the polymers is neutralized by the association with the negatively charged mineral surface, which results in an overall PZSE of pH 4.4 to 4.7 for the polymer-coated montmorillonite sorbents (Saha et al., 2004). Based on that fact alone, one would expect (and can observe) a relatively small amount of outer-sphere complexation in the polymer-coated mineral samples compared to the pure polymers (Fig. 6).

When the EXAFS results and XANES results are considered together, a fairly complete picture of SeO$_3^{2-}$ adsorption on HYA, HAS, and montmorillonite becomes clear. The proposed bonding mechanisms (consistent with both techniques) are summarized in Fig. 7. These bonding mechanisms are also completely consistent with the kinetics experiments previously conducted by Saha and coworkers (Saha et al., 2004). In those experiments, they used a fast and a slow reaction to model the kinetics of SeO$_3^{2-}$ adsorption on pure and coated montmorillonite. They determined that activation energy for SeO$_3^{2-}$ adsorption on montmorillonite was much greater than the energy of activation for SeO$_3^{2-}$ adsorption on either HYA or HAS coated montmorillonite. This was the case on Mt, HYA-Mt, and HAS-Mt for both the fast reaction (39, 11, and 19 kJ mol$^{-1}$, respectively) and the slow reaction (33, 32, and 27 kJ mol$^{-1}$, respectively) (Saha et al., 2004). This decrease in activation energy was attributed to the presence of positively charged Al-OH$_2^+$ functional groups on both HYA and HAS polymers at pH 4.5. These minimize repulsion between the negatively charged biselenite and montmorillonite (Saha et al., 2004). The observation (from XAS) of outer-sphere complex formation on the polymers and the polymer-coated clay is also consistent with the observed decrease in activation energy. Saha and coworkers (Saha et al., 2004) also observed that the rates of reaction were significantly increased on the HYA and HAS coated clay sorbents. This is also consistent with the presence of outer-sphere complexes, which are known (via many pressure-jump chemical relaxation experiments) to have rates of formation that are more rapid than those of inner-sphere complex formation on mineral surfaces.

**LC-XANES of Selenite Adsorbed on Polymer-Coated Montmorillonite**

To estimate the relative distribution of SeO$_3^{2-}$ on the components of polymer-coated clays, LC-XANES fitting was conducted on the polymer-coated samples from Fig. 6 using the pure polymers and the montmorillonite spectra as standards. The results are shown in Fig. 8. Error in LC analysis was estimated at 5% by comparing the fit of individual scans to fit results for the overall averaged spectrum. It was observed that ~54% of the adsorbed SeO$_3^{2-}$ on HYA-Mt was bound to the montmorillonite surface, while on HAS-Mt approximately 42% was bound to the clay mineral phase. The most likely explanation for this difference in sorption is the difference in surface area for the two-coated sorbents. HAS-coated Mt has 487 m$^2$ g$^{-1}$ surface area while HYA has only 450 m$^2$ g$^{-1}$; PZSE for the two coated clays in both cases is similar: 4.7 for HYA and 4.4 for HAS (Saha et al., 2004). The surface area differences suggest that in the HAS-Mt sample there is relatively more polymer available for reaction with SeO$_3^{2-}$ than in the case of the HYA-Mt. It was reported by Saha and coworkers that more Al (1.21 mol Al$^{3+}$ kg$^{-1}$ Mt) for HAS versus 1.16 mol Al$^{3+}$ kg$^{-1}$ Mt for HYA-Mt) sorbed on Mt from HAS solutions than HYA solutions during the sorbent synthesis.

There is an important assumption made in the choice of standards used in the above analysis. Because there is both outer-sphere and inner-sphere adsorption in the HYA and HAS samples, using these mixed bonding environment samples as standards assumes that the sorption mechanisms on the polymers is unchanged by interaction with montmorillonite. It is also possible that the interaction with the Mt surface could change the ratio of outer-sphere to inner-sphere on the polymer coating. However, one would expect that if these polymer-Mt interactions were dramatically different for the HAS and HYA samples then it would be reflected in the PZSE of the coated minerals. Instead, the PZSE values are quite similar (4.7 for HYA-Mt and 4.4 for HAS-Mt). In view of

![Fig. 7. Selenite adsorption mechanisms for pH 4.5 samples consistent with EXAFS and XANES spectroscopy.](image-url)
their PZSE values (Saha et al., 2004), HAS-Mt should form slightly more inner-sphere complexes and slightly fewer outer-sphere complexes compared with HYA-Mt. This surface charge effect coupled with the increased total amount of polymer on the HAS-Mt sample (via surface area and via mol $\text{Al}^{3+}$ adsorbed) is consistent with the data presented in Figs. 6 and 8.

**Larger Significance of this Study**

From an environmental standpoint, these results are the first to clearly demonstrate the mechanism of $\text{SeO}_3^{2-}$ adsorption on aluminum-bearing mineral phases. On montmorillonite, only bidentate binuclear inner-sphere complexation was observed. For the hydroxyaluminum and hydroxyaluminosilicate polymers, a mixture of outer-sphere and bidentate binuclear inner-sphere was observed. When montmorillonite was coated with either HYA or HAS polymers then adsorption behavior was intermediate between that of the mineral and the pure polymer. The adsorption behavior of these polymer-coated minerals is especially important to natural systems. Temperate soils often contain aluminum-hydroxide minerals and pristine clay surfaces. More XAS studies are planned for contaminant sorption on more realistic and complicated sorbents such as organic and inorganic polymer coated clay minerals.

The finding (from XANES) that outer-sphere complexes form on the HAS, HYA, HYA-Mt, and HAS-Mt samples but not on pure Mt is consistent with the macroscopic kinetics experiments previously conducted by Saha and coworkers (Saha et al., 2004). They determined that activation energy for $\text{SeO}_3^{2-}$ adsorption on montmorillonite was much greater than the energy of activation on HYA-Mt or HAS-Mt. They also observed that reaction rates were more rapid on HYA-Mt and HAS-Mt, which is also consistent with the presence of outer-sphere complexes. This effect on kinetics parameters demonstrates that shifts in complexation from outer-sphere to inner-sphere can have a large effect on macroscopic adsorption experiments, and therefore on larger-scale transport of $\text{SeO}_3^{2-}$ in the environment.

The XAS results also show that it is possible to infer bonding mechanisms of $\text{SeO}_3^{2-}$ on mineral phases reliably with XANES as well as with EXAFS spectroscopy. The EXAFS results also suggest that it may be possible to infer the presence of outer-sphere oxyanion complexation...
in samples where inner-sphere complexes are also present by the amplitude of the EXAFS spectra and the height and shape of the first (Me-O) shell in RSFs. However, XANES spectra remain more conclusive and reliable for observing outer-sphere complex formation. The interpretation of Se XANES data relies on changes in molecular geometry and Se-O bond delocalization that occur as \( \text{SeO}_3^2^- \) changes protonation state in solution or forms inner-sphere complexes on surfaces.

Careful use of XANES spectral features in determination of bonding configuration can extend the utility of X-ray absorption spectroscopy in environmental samples for two reasons. First is the fact that concentrations in natural samples are often too low for EXAFS spectroscopy to be conducted. Additionally, many synchrotron-based studies now utilized microprobe beamlines where XANES spectroscopy is far more practical to conduct than is EXAFS.

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