ADSORPTION MECHANISMS OF Zn ON HECTORITE AS A FUNCTION OF TIME, pH, AND IONIC STRENGTH

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ABSTRACT. The mechanisms of Zn uptake in dilute suspensions (~2 g L⁻¹) of hectorite were investigated by kinetics experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy on wet pastes and self-supporting films of Zn-sorbed hectorite. Kinetics experiments were performed at pH 4 and 6.5, in 0.3 and 0.01 M NaNO₃, and with a total Zn concentration of 100 μM.

In 0.01 M NaNO₃, significant amounts of Zn were sorbed within the first 5 min of reaction at both pHs. This rapid uptake is consistent with Zn adsorption on exchange sites located on hectorite basal planes. After this fast sorption, the amount of sorbed Zn slowly increased at pH 6.5 but decreased at pH 4. In 0.3 M NaNO₃, Zn uptake was less rapid within the first 5 min, and the amount of sorbed Zn subsequently increased at both pHs, with more Zn sorbing at the higher pH. This behavior is consistent with Zn adsorption on pH-dependent sites. The dissolution of hectorite was monitored during Zn sorption. In 0.3 M NaNO₃ at pH 6.5, initial Zn uptake was correlated with an excess release of Mg as compared to a hectorite suspension without added Zn. In contrast, Si release was inhibited initially by Zn addition. At pH 4, Zn addition did not affect the dissolution rate of hectorite.

At pH 6.5, polarized-EXAFS (P-EXAFS) spectra obtained on self-supporting films for the two ionic strengths at reaction times between 6 and 120 h show similar crystallochemical environments for Zn. Four atomic shells were identified: a nearest O shell at an interatomic distance $R_{\text{Zn-O}} = 2.06 \pm 0.01$ Å, a Mg shell at $R_{\text{Zn-Mg}} = 3.06-3.09 \pm 0.03$ Å, a Si shell at $R_{\text{Zn-Si}} = 3.23-3.26 \pm 0.03$ Å, and a next-nearest O shell at $R_{\text{Zn-O}} = 3.69-3.74 \pm 0.06$ Å. $R_{\text{Zn-Mg}}$ and $R_{\text{Zn-Si}}$ values are characteristic of edge-shared Zn and Mg octahedra and of corner-shared Zn octahedra and Si tetrahedra, respectively. The angular dependencies of the Zn-Mg and Zn-Si contributions indicated that Zn-Mg pairs were oriented parallel to the film plane, whereas Zn-Si pairs were not. These results indicate that inner-sphere (IS) Zn surface complexes formed at layer edges of hectorite platelets, in continuity to octahedral sheets. Magic-angle EXAFS spectra of wet pastes and self-supporting films obtained at pH 6.5 in 0.3 M NaNO₃ are similar, confirming the IS uptake mechanism operated under fully wet conditions at high ionic strength. In 0.01 M NaNO₃, a continuous evolution with increasing reaction time from predominantly outer-sphere (OS) to predominantly IS complexes was observed for wet pastes, suggesting that Zn initially sorbed as exchangeable OS complexes on interlayer sites, and then migrated to layer edges to form IS surface complexes. Based on previous work, Zn has a higher affinity than Co for the hectorite surface, in keeping with the higher stability of Zn phyllosilicates.

SYMBOLS

EXAFS = extended X-ray absorption fine structure
P-EXAFS = polarized extended X-ray absorption fine structure
FT = Fourier transform of the EXAFS spectrum
RSF = radial structure function
$\alpha$ = angle between the X-ray polarization vector and the phyllosilicate plane
$\beta_j$ = angle between the $c^*$ axis of the phyllosilicate layer and the vectors connecting the X-ray absorbing atom to backscattering atoms in the $j$ shell
$k$ = modulus of the wavevector in EXAFS spectroscopy
$\chi(k)$ = EXAFS function
$\chi_j^\alpha$ = EXAFS contribution of a $j$ shell at the $\alpha$ angle
\[ \chi_{iso}^{EXAFS} = \text{isotropic EXAFS contribution of a } j \text{ shell at the magic angle} \]

\[ N_{ij}^{EXAFS} = \text{apparent number of backscatterers in the } j \text{ shell at the } \alpha \text{ angle} \]

\[ N_{ij}^{opt} = \text{structural number of backscatterers in the } j \text{ shell} \]

\[ R_{Zn-j}^{EXAFS} = \text{EXAFS-derived interatomic distance between Zn absorber and backscattering atoms in the } j \text{ shell} \]

\[ \sigma = \text{Debye-Waller term in EXAFS spectroscopy} \]

\[ S_0^2 = \text{amplitude reduction factor in EXAFS spectroscopy} \]

\[ R_p = \text{reliability factor used to adjust model to sample EXAFS spectra} \]

ZnKer = Zn-containing kerolite
ZnKer300 = Zn-kerolite Zn\(_{2}\)Si\(_{4}\)O\(_{10}\)(OH)\(_2\)\cdot nH\(_2\)O
ZnKer070 = Zn-containing kerolite Zn\(_{0.7}\)Mg\(_{2.3}\)Si\(_{4}\)O\(_{10}\)(OH)\(_2\)\cdot nH\(_2\)O
ZnKer003 = Zn-containing kerolite Zn\(_{0.03}\)Mg\(_{2.97}\)Si\(_{4}\)O\(_{10}\)(OH)\(_2\)\cdot nH\(_2\)O

OS = outer sphere
IS = inner sphere
E linkage = edge-sharing linkage
C linkage = corner-sharing linkage
I = ionic strength
Zn\(_{aq}^{2+}\) = fully solvated Zn\(_{aq}^{2+}\) cation
[Zn]\(_{aq}\) = concentration of Zn in the supernatant
[Si]\(_{aq}\) = concentration of Si in the supernatant
[Mg]\(_{aq}\) = concentration of Mg in the supernatant
Zn\(_T\) = total Zn concentration in the suspension
Co\(_T\) = total Co concentration in the suspension

**INTRODUCTION**

At low concentration, Zn is a micronutrient (Stout, 1956; Reed and Martens, 1996). Because plants absorb Zn from soil solutions, adequate levels of dissolved Zn are essential for the optimal growth of crops (Reed and Martens, 1996). However, sewage sludge deposition, smelter emission, mine drainage, and industrial waste dispersion can raise Zn concentration to toxic levels in natural systems, causing leaf chlorosis and necrosis, plant death, and articular diseases to vertebrate organisms (O’Neill, 1993; Beyer and Storm, 1995; Reed and Martens, 1996). To satisfy both agricultural requirements and public health policies, it is important to understand the mechanisms regulating the solution concentration and bioavailability of Zn in soils.

The fate of Zn in natural systems is mainly controlled by reactions with both organic matter and mineral surfaces (Sposito, 1984; McBride, 1994). At low concentration and low pH, Zn is complexed by organic matter or held by clay minerals in an exchangeable form (McBride, 1994; Sarret, 1998). At higher concentration or at higher pH, the solution concentration of Zn is thought to be controlled by sorption on (hydr)oxide minerals (McBride, 1994) or by precipitation of Zn hydroxycarbonates (Schindler, 1991). Recently, structural association of Zn with clay minerals was observed in contaminated soils (Manceau and others, 2000c). The affinity of Zn for phyllosilicates observed in natural systems is consistent with the relatively low solubility of synthetic Zn-containing phyllosilicates (Decarreau, 1985; Manceau and others, 2000c). Thus, a detailed characterization of possible interactions between Zn and phyllosilicates such as smectites is needed.

Zn may be retained on smectites by various molecular mechanisms. Like many metal cations, Zn may adsorb as outer-sphere (OS) surface complexes on basal planes, balancing the structural layer charge (McBride, Pinnavaia, and Mortland, 1975; McBride, 1982; Papelis and Hayes, 1996; Muller and others, 1997). The exchangeability of such sorbed cations depends on their hydration enthalpies, the cationic composition of the solution, the smectite concentration, and the location and amount of the charge deficit in the layer structure (Laudelout, 1987; McBride, 1994). Metal cations can also sorb via a pH-dependent mechanism, as on (hydr)oxide mineral surfaces.
pH-dependent uptake is interpreted at the atomic scale by the formation of inner-sphere (IS) complexes on dangling oxygen bonds at the edges of smectite crystallites (Charlet and others, 1993; Zachara and Smith, 1994; Kraepiel, Keller, and Morel, 1999). The increase in pH and sorbate concentration can also lead to the formation of sorbate-containing precipitates (Ford and Sparks, 1998; Scheidegger and others, 1998).

Cation exchange, layer edge adsorption, and sorbate precipitation are usually differentiated by the dependence on pH and ionic strength and by the reversibility of cation uptake. However, the dependence of sorption/desorption kinetics on pH and on ionic strength and the competition between distinct uptake mechanisms are generally overlooked in macroscopic studies (Scheidegger and others, 1998). Conversely, the environment of sorbed cations on clay minerals can be studied at the molecular level by extended X-ray absorption fine structure (EXAFS) spectroscopy (Scheidegger and others, 1998; Schlegel and others, 1999). Yet, the extent of the reciprocal space explored by EXAFS (generally \(\Delta k \leq 14 \text{ Å}^{-1}\)) precludes discrimination of close atomic shells (Teo, 1986) and results in large uncertainty in structural parameters (interatomic distances, nature and number of atomic neighbors) obtained from analysis of overlapping EXAFS contributions (Stern, 1988; Manceau and others, 1999). The overlap of EXAFS waves typically occurs in phyllosilicates, where X-ray absorbing atoms in the octahedral sheet are surrounded by neighboring cations at \(R \sim 3.00\) to \(3.12\ \text{Å}\) in the octahedral sheet and \(R \sim 3.20\) to \(3.30\ \text{Å}\) in tetrahedral sheets (Manceau, 1990). Still, these distinct shells can be singled out by polarized EXAFS (P-EXAFS) spectroscopy (Manceau and others, 1988, 1990; fig. 1). The contribution of cations in the tetrahedral sheets is minimized when the experimental angle \(\alpha\) between the X-ray electric field vector and the phyllosilicate plane equals \(0^\circ\) (parallel orientation) and enhanced when \(\alpha = 90^\circ\) (normal orientation), whereas the opposite angular dependence is observed for the contribution of cations in the octahedral sheet. P-EXAFS was recently applied to the crystal chemistry of oxidized and reduced nontronite (Manceau and others, 2000a, b) and to the sorption mechanism of Co on hectorite (Schlegel and others, 1999). These studies showed that P-EXAFS on smectite self-supporting films enables the characterization of the structural environments of cations sorbed on or occluded in smectites with an enhanced precision as compared to powder EXAFS.
This study is aimed at determining the mechanism(s) of Zn uptake in suspensions of hectorite, expanding the approach successfully applied to the study of Co sorption on hectorite. Hectorite is a trioctahedral magnesium smectite, and therefore its reactivity and dissolution chemistry may differ somewhat from that of soil smectites, which are essentially aluminous. Yet, recent results suggest that the sorption mechanisms observed in this study are also applicable to aluminium smectites (Dähn and others, 2000). The effects of pH and ionic strength on Zn uptake were studied by batch kinetics experiments, as these two parameters can have competitive effects on sorption (Fig. 2); chemical results were interpreted in terms of cation exchange and specific sorption reactions. The molecular environments of Zn sorbed at pH 6.5 and at high and low ionic strength were determined by P-EXAFS spectroscopy on films of Zn-sorbed hectorite. A new method, magic-angle EXAFS (MA-EXAFS) spectroscopy on wet pastes, was applied in this study to follow in-situ the changes in Zn crystallochemical environments. Finally, EXAFS-derived structural models were used to interpret mechanistically macroscopic data.

**EXPERIMENTAL**

**Hectorite Purification and Characterization**

Details on the purification and properties of hectorite \((Na_{0.40}(Mg_{2.65}Li_{0.35})(Si_{3.95}Al_{0.05})O_{10}(OH)_{2})\) can be found elsewhere (Schlegel and others, 1999). Briefly, hectorite purchased from the Source Clay Repository of the Clay Minerals Society (SHCa-1) was dispersed in deionized water. The < 2 μm fraction was extracted by sedimentation techniques, Na-exchanged, and treated to remove carbonate minerals, ferric and manganese oxides, and organic matter. Dialysis against deionized water was then performed until no Cl\(^-\) anions could be detected (AgNO\(_3\) test). The final 2 wt percent stock suspension was stored at 4°C in the dark prior to use. The cation exchange capacity (CEC) measured by Cs exchange (Anderson and Sposito, 1991) was 840 meq kg\(^{-1}\), and the specific surface area measured by BET was 114 m\(^{2}\) g\(^{-1}\).
Zn Sorption Experiments

Schlegel, Charlet, and Manceau (1999) and Schlegel and others (1999) gave details on the protocol of cation sorption. All solutions were prepared with the appropriate amounts of NaNO$_3$ salt to maintain constant concentrations of NaNO$_3$ electrolyte throughout experiments. Sorption experiments were conducted at 25° ± 0.1°C in polyethylene vessels under an Ar atmosphere. During kinetic experiments, the pH of the suspension was continuously monitored (Metrohm combined electrode) and maintained at pH 4 or 6.5 (± 0.05) by software-controlled addition of acidic (0.1 M HNO$_3$) or CO$_2$-free basic (0.01 M NaOH) solutions, as needed. Hectorite concentrations in suspensions ([hect.]) were 1.95 g L$^{-1}$ (pH 6.5) and 2.2 g L$^{-1}$ (pH 4).

After a pre-equilibration time of 48 h at pH 6.5, or 3 h at pH 4, an aliquot of a 0.21 M Zn(NO$_3$)$_2$, 10$^{-3}$ M HNO$_3$ solution was added to the suspension to obtain a total Zn concentration $Zn_T = 100 \mu$M. The time of Zn addition is $t = 0$. The pH was then immediately readjusted and maintained at the target value. At given times ($0 < t \leq 120$ h), samples were withdrawn from the suspension, centrifuged, and filtered. Zn and Mg total concentrations in the filtered supernatant [Zn]$_{aq}$ and [Mg]$_{aq}$ were measured by inductively coupled plasma-atomic emission spectrometry, and total Si concentration, [Si]$_{aq}$, by spectrophotometry (Jeffery and others, 1978). In experiments conducted at pH 6.5, [Si]$_{aq}$ never exceeded 400 $\mu$M, hence silicic acid was assumed to remain predominantly in monomeric form (Stumm and Morgan, 1996). In contrast, [Si]$_{aq}$ at the end of experiments at pH 4 (1550-1700 $\mu$M) was close to the solubility of amorphous SiO$_2$ (~2000 $\mu$M; Stumm and Morgan, 1996), and polymerization of silicate species may have occurred in solution. Supersaturation with respect to quartz (solubility of 183 $\mu$M; Rimstidt, 1997) was observed for all experiments but was neglected owing to the slow crystallization rate of quartz at room temperature (Stumm and Morgan, 1996). In all experiments, more than 99.9 percent of Zn dissolved in the supernatant was present as Zn(aq)$^{2+}$ (Baes and Mesmer, 1976). Thus, the solution concentration of Zn(aq)$^{2+}$, [Zn(aq)$^{2+}$] was approximately equal to [Zn]$_{aq}$ within uncertainties. Likewise, the solution concentration of Mg(aq)$^{2+}$, [Mg(aq)$^{2+}$] ≈ [Mg]$_{aq}$.

Preparation of Sorption Samples for EXAFS

Suspensions of Zn-sorbed hectorite were prepared and reacted as described above. Samples for self-supporting films and wet pastes were withdrawn from reaction vessels simultaneously. Self-supporting films were obtained by slowly filtering 60-ml aliquots on a 0.05 $\mu$m Sartorius cellulose nitrate filter under an inert Ar atmosphere, dried, cut and stacked on a sample holder for fluorescence-yield P-EXAFS measurements, following a procedure detailed elsewhere (Schlegel and others, 1999). Wet pastes were obtained by centrifuging 30 ml of the clay suspension (15 min at 10,000 rpm) and removing the clear supernatant. Pastes were then loaded in Teflon sample holders and sealed with Kapton windows. Wet pastes prepared in 0.01 M NaNO$_3$ were measured approx 30 min after centrifugation, whereas those prepared in 0.3 M NaNO$_3$ had to be stored at 2°C for 15 days before EXAFS measurements owing to experimental limitations. An additional sample was prepared by dispersing hectorite in distilled water ([hect.] = 2 g L$^{-1}$) at pH 3.7, then spiking the suspension with a Zn solution to a final $Zn_T = 995 \mu$M, and finally centrifuging the suspension after 30 min of reaction time. These chemical conditions (pH 3.7, ionic strength of 0.0015 M) were chosen to favor the formation of OS Zn surface complexes on cation exchange sites. For all wet pastes, more than 95 percent of total Zn was sorbed on hectorite, hence the EXAFS signal from the Zn fraction present in the residual supernatant was negligible. Chemical conditions for samples studied by EXAFS are summarized in table 1.
Reference Compounds

A solvated Zn\(^{2+}\)\(_{\text{aq}}\) reference was obtained by dissolving Zn(NO\(_3\))\(_3\) in distilled water to a total Zn concentration of 0.1 M. This solution was acidified to pH 4 to prevent any polymerization. ZnKer minerals of formula Zn\(_x\)Mg\(_{3-x}\)Si\(_4\)O\(_{10}\)(OH)\(_2\)\(_n\)H\(_2\)O (\(x = 3: \text{ZnKer300}; x = 0.7: \text{ZnKer070}; x = 0.03: \text{ZnKer003}\)) were prepared by aging fresh (Zn, Mg, Si) precipitates of the desired elemental compositions at 75 °C for 15 days (Decarreau, 1985). The purity and crystallinity of these references were checked by X-ray diffraction, and unit-cell b parameters were calculated from the position of (060) diffraction peaks.

EXAFS Data Collection and Reduction

Zn K-edge EXAFS spectra (\(\chi(k)\)) of Zn-sorbed hectorite films and pastes and of ZnKer070 and ZnKer003 references were recorded at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on the BM32 CRG/IF station. Clay films were mounted on a goniometer and EXAFS spectra were recorded at \(\alpha = 0^\circ, 35^\circ, 55^\circ,\) and \(80^\circ\) in fluorescence detection mode with a 30 element array Ge detector. EXAFS spectra for wet pastes and reference powders were recorded at the magic angle (\(\alpha = 35^\circ\)). At this angle textural effects are cancelled and, therefore, \(\chi^{35^\circ}(k)\) is identical to the spectrum for a perfectly isotropic powder (\(\chi^{iso}(k);\) Manceau and others, 1990). Recording conditions for sorption samples are summarized in table 1. MA-EXAFS spectra of Zn\(^{2+}\)\(_{\text{aq}}\) and ZnKer300 references were recorded in transmission mode at the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE, Orsay, France) on the D42 station. Measurements were performed with gas ionization chambers filled with an air-helium mixture adjusted to attenuate the beam intensity by \(\sim 20\) percent before and \(\sim 50\) percent after the sample entry.

EXAFS data were reduced with the SEDEM software (Aberdam, 1998). As a preliminary step, absorption spectra were given the shape of the Stobbe function, which is a quantum-mechanically derived formula for atomic absorption at the K-edge. Fourier transformation was performed on \(k^2\chi(k)\) between 2 and 10 Å\(^{-1}\) using a Kaiser apodization window (Manceau and Combes, 1988), resulting in a radial structure

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>[hectorite] (g L(^{-1}))</th>
<th>Zn(_r) (µM)</th>
<th>pH</th>
<th>Ionic strength (M)</th>
<th>Reaction time (h)</th>
<th>Sample type</th>
<th>EXAFS acquisition</th>
</tr>
</thead>
<tbody>
<tr>
<td>#H001_30min_WP</td>
<td>2.0</td>
<td>995</td>
<td>3.7</td>
<td>0.0015</td>
<td>0.5</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
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<tr>
<td>#H01_5min_WP</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.01</td>
<td>0.08</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
</tr>
<tr>
<td>#H01_6h_WP</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.01</td>
<td>6</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
</tr>
<tr>
<td>#H01_6h_SSF</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.01</td>
<td>6</td>
<td>self-supporting film</td>
<td>P-EXAFS(^pp)</td>
</tr>
<tr>
<td>#H01_96h_WP</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.01</td>
<td>96</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
</tr>
<tr>
<td>#H01_96h_SSF</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.01</td>
<td>96</td>
<td>self-supporting film</td>
<td>P-EXAFS(^pp)</td>
</tr>
<tr>
<td>#H30_6h_WP</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.3</td>
<td>6</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
</tr>
<tr>
<td>#H30_6h_SSF</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.3</td>
<td>6</td>
<td>self-supporting film</td>
<td>P-EXAFS(^pp)</td>
</tr>
<tr>
<td>#H30_120h_WP</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.3</td>
<td>120</td>
<td>wet paste</td>
<td>MA-EXAFS(^b)</td>
</tr>
<tr>
<td>#H30_120h_SSF</td>
<td>1.95</td>
<td>100</td>
<td>6.5</td>
<td>0.3</td>
<td>120</td>
<td>self-supporting film</td>
<td>P-EXAFS(^pp)</td>
</tr>
</tbody>
</table>

\(\dagger\) Measurements performed at the magic angle (\(\alpha = 35^\circ\)).

\(\dagger\dagger\) Measurements performed at \(\alpha = 0^\circ, 35^\circ, 55^\circ,\) and \(80^\circ\).
function (RSF) in the distance space. RSF peaks are located at apparent absorber-backscatterer distances \((R + \Delta R)\), which differ from interatomic structural distances \((R)\) by \(\Delta R \sim -0.3-0.4\ \text{Å}\ \) (Teo, 1986). RSF structural peaks of interest were windowed and Fourier back-transformed in \(k\) space by using a software package implemented by D. Bonnin (ESPCI, Paris). \(R\) values and the numbers of atomic neighbors \((N)\) were determined by least-squares fitting \(k^2\)-weighted Fourier-filtered experimental contributions \((\chi_{\exp}(k))\) with theoretical phase and amplitude functions calculated with FEFF7.02 (Rehr, Albers, and Zabinsky, 1992) and using talc and Zn-doped hectorite as model structures for \(\text{Zn-O}, \text{Zn-Mg}\), and \(\text{Zn-Si}\) pairs (Oberlin and Mering, 1966; Kadi-Hanifi and Mering, 1972; Rayner and Brown, 1973). A \(k^2\)-weighting scheme was chosen to give the same importance to contributions from light atoms (for example, \(\text{O}\); amplitude maxima of EXAFS waves at low \(k\)), and heavier atoms (\(\text{Mg, Si, Zn}\); amplitude maxima at higher \(k\)). The amplitude reduction factor \(S_0^2\) was set to 0.85 (O’Day and others, 1994; Manceau, Chateigner, and Gates, 1998). The goodness of the fit between experimental \(\chi_{\exp}(k)\) and model \(\chi_{\text{calc}}(k)\) was quantified by the reliability factor \(R_p\), defined as

\[
R_p = \frac{\sum_k (k^2 \cdot \chi_{\text{calc}}(k) - k^2 \cdot \chi_{\exp}(k))^2}{\sum_k (k^2 \cdot \chi_{\exp}(k))^2}.
\]

RESULTS AND INTERPRETATION

Chemistry

Kinetics of Zn sorption.—Distinct trends in the kinetics of Zn uptake by hectorite occurred with pH and ionic strength (fig. 3A and B). In 0.01 M \(\text{NaNO}_3\), 72 percent (pH 4) and 82 percent (pH 6.5) of \(\text{Zn}_T\) were sorbed within the first 5 min of reaction time. The initial uptake was less rapid at higher ionic strength. This sorption behavior is typical of a cation exchange mechanism (Tang and Sparks, 1993). Following this fast reaction step, uptake still went on at pH 6.5 but at a slower rate (fig. 3A). In contrast, at pH 4 Zn slowly desorbed after the fast initial uptake (fig. 3B). Sorption behavior at pH 4 was not previously investigated for the \(\text{Co/hectorite}\) system (Schlegel and others, 1999). In 0.3 M \(\text{NaNO}_3\), the kinetics of Zn uptake at pH 6.5 and pH 4 were slower than in 0.01 M \(\text{NaNO}_3\). After 48 h, nearly 100 percent of \(\text{Zn}_T\) (51.3 \(\mu\text{M g}^{-1}\)) was sorbed at pH 6.5 (fig. 3A) and only 35 percent at pH 4 (fig. 3B). Increased uptake at higher pH is typical of a pH-dependent sorption mechanism.

At pH 6.5, identical amounts of base (37 \(\mu\text{mol NaOH per g hectorite}\) were added at both ionic strengths to prevent a pH decrease after Zn addition. The amount of acid in the Zn spikes (0.24 \(\mu\text{mol HNO}_3\) per g hectorite) was too low to account for the measured excess of protons. This release of protons is characteristic of a pH-dependent sorption and, therefore, suggests that this sorption mechanism also occurs at low ionic strength and pH 6.5 after the fast initial cation exchange.

Impact of Zn addition on hectorite stability.—The influence of Zn sorption on hectorite dissolution at pH 6.5 was assessed by following Mg and Si release rates before and after Zn addition (fig. 4A and B). In 0.3 M \(\text{NaNO}_3\) and at \(t \leq 0\), the ratio of Mg (0.56 \(\pm\) 0.09 \(\mu\text{mol h}^{-1} \text{g}^{-1}\)) to Si (0.82 \(\pm\) 0.09 \(\mu\text{mol h}^{-1} \text{g}^{-1}\)) release rates (0.68 \(\pm\) 0.13) is close to the atomic Mg/Si ratio of hectorite (0.67), but the \([\text{Mg}]_{\text{aq}}/[\text{Si}]_{\text{aq}}\) ratio at \(t = 0\) is significantly higher (1.02 \(\pm\) 0.02). This initial excess of \([\text{Mg}]_{\text{aq}}\) was likely caused by a partial exchange of interlayer Na by Mg during the dialysis stage of the hectorite purification (Schlegel, Charlet, and Manceau, 1999). At \(t \leq 0\), lower \([\text{Mg}]_{\text{aq}}\) were found at low rather than at high ionic strength for similar \([\text{Si}]_{\text{aq}}\) (fig. 4: see data at pH 6.5 and \(t = -24\ \text{h}\)), owing to the probable readsorption of dissolved Mg on cation exchange sites of Na-hectorite. Higher Si release rates were observed at low ionic
strength (1.56 ± 0.09 μmol h⁻¹ g⁻¹ in 0.01 M NaNO₃ at t = 0), in agreement with the results of Kreit, Shainberg and Herbillon (1982).

A change in Mg and Si release rates at pH 6.5 in 0.3 M NaNO₃ occurred after Zn addition (fig. 4A). The Si release rate decreased from 0.82 ± 0.09 to 0.24 ± 0.09 and to 0.13 ± 0.03 μmol h⁻¹ g⁻¹ at t ≤ 0, 24 h, and 120 h, respectively. In contrast, the release rate of Mg abruptly increased from 0.56 ± 0.09 μmol h⁻¹ g⁻¹ at t ≤ 0 to 2.05 ± 0.4 μmol h⁻¹ g⁻¹ at t = 3 h. The excess Mg release at t > 0 can be calculated from the values of [Mg]ₐq measured and extrapolated from t ≤ 0. The Mg excess equals 24.2 ± 4 μmol g⁻¹ at t = 6 h and is of the same order, though lower than the amount of sorbed Zn (35.4 ± 1.5 μmol g⁻¹). Both Zn sorption and excess release of Mg occurred simultaneously. At t ≥ 6 h, the Mg release rate gradually decreased to 0.09 ± 0.04 μmol h⁻¹ g⁻¹ at t = 120 h, a value less than that at t = 0. In 0.01 M NaNO₃, a decrease in Si release rate (from 1.56 ± 0.09 μmol h⁻¹ g⁻¹ at t = 0 to 0.56 ± 0.09 μmol h⁻¹ g⁻¹ at t = 96 h) was observed, as for 0.3 M NaNO₃ (fig. 4B). However, there was no abrupt enhancement of Mg release after Zn addition. The high uncertainty on release rates...
Fig. 4. Kinetics of Mg (□) and Si (○) release in the supernatant before (t < 0) and after (t > 0) Zn addition. Zn = 100 μM for all experiments. [hect.] = 1.95 g L⁻¹ at pH 6.5 (A and B) and 2.2 g L⁻¹ at pH 4 (C and D). (A) pH 6.5, 0.3 M NaNO₃. (B) pH 6.5, 0.01 M NaNO₃. (C) pH 4, 0.3 M NaNO₃. (D) pH 4, 0.01 M NaNO₃. Experiments at pH 4 and 6.5 have different time and [Me]ₐq scales.
for Mg in 0.01 M NaNO₃ (0.12 ± 0.09 and 0.10 ± 0.09 µmol h⁻¹ g⁻¹ at t = 0 h and 96 h, respectively) hampers interpretation.

At pH 4 (fig. 4C and D), neither Mg nor Si dissolution rates changed significantly during Zn uptake, in contrast to pH 6.5. At t ≥ 24 h, Mg and Si dissolution rates in 0.3 M NaNO₃ (7.6 ± 0.1 and 11.1 ± 0.2 µmol h⁻¹ g⁻¹, respectively) are only slightly lower than those of pure hectorite (8.2 ± 0.5 and 12.2 ± 0.9 µmol h⁻¹ g⁻¹; data not shown). Therefore, Zn adsorption had little effect on the dissolution rate of hectorite. In 0.01 M NaNO₃, the release rates of Mg and Si at t ≥ 24 h (9.7 ± 0.2 and 16.4 ± 0.4 µmol h⁻¹ g⁻¹) were higher than in 0.3 M NaNO₃. A similar behavior was observed for Si at pH 6.5. The ratio of Mg to Si release rates is lower in 0.01 M NaNO₃ than in 0.3 M NaNO₃ (0.59 ± 0.02 and 0.68 ± 0.02, respectively), which is likely a consequence of the adsorption of dissolved Mg on cation exchange sites.

**EXAFS Spectroscopy**

*Reference compounds.*—The EXAFS spectrum for Zn₂⁺(aq) has a single wave frequency for k > 3 Å⁻¹, and its amplitude decreases monotonically with k (fig. 5). This spectral feature is consistent with the presence of a single ordered coordination sphere (that is, 6 H₂O) around Zn₂⁺(aq). In contrast, EXAFS spectra for clay minerals have several distinct frequencies (arrows in fig 5). Because these frequencies are absent in the spectrum for Zn₂⁺(aq), they cannot be attributed to multiple scattering (MS) paths within the first coordination sphere of Zn. Therefore they must result from the presence of higher atomic shells.

All Fourier transforms (FTs) for reference compounds display a first peak (labeled A) located near R + ΔR = 1.6 Å, attributed to the contribution from nearest oxygen atoms coordinated to Zn (fig. 6A). Two RSF peaks at R + ΔR = 2.9 and 3.8 Å can also be observed. They were shown to originate from MS paths within the first hydration sphere (Kuzmin, Obst, and Purans, 1997).

The RSFs for Zn-containing kerolites display maxima at R + ΔR = 2.7-2.9 (peak B) and 3.8 Å (peak C). Their high amplitudes compared to Zn₂⁺(aq) indicate that they correspond essentially to single scattering contributions beyond the first oxygen shell. Their structural origins in phyllosilicates were determined by combining P-EXAFS measurements and FEFF7.02 calculations (Manceau, Chateigner, and Gates, 1998). Peak B corresponds to the mixed contribution from the 6 nearest octahedral (Oct1) and 4 nearest tetrahedral (Tet1) cations, and of higher oxygen shells (table 2). Its amplitude depends on the Zn/(Zn + Mg) ratio in the octahedral sheet of ZnKer (fig. 6A). Not only does the amplitude vary, but imaginary parts of FTs for ZnKer003 and ZnKer300 are almost out-of-phase (fig. 6B), a consequence of the π-dephasing between EXAFS waves backscattered by Mg on the one hand and by transition elements such as Fe, Ni, and Zn, on the other hand (Manceau and Calas, 1986). This sensitivity of the imaginary part to relative proportions of Mg and Zn atoms in the Oct1 shell can be used to identify the nature of the predominant cationic backscatterer in Zn-sorbed hectorite. Peak C corresponds to the contribution from next-nearest Si cations (Tet2) and from higher oxygen shells (table 2; Manceau and others, 1999). It has a large amplitude in trioctahedral layer silicates, and neither its amplitude nor its imaginary part significantly change with the elemental composition of the clay (fig. 6B).

For all kerolites, an EXAFS-derived R_Zn-O value of 2.07 Å typical of oxygen-hexacoordinated Zn was obtained (table 3; Kuzmin, Obst, and Purans, 1997). The uncertainties on R_Zn-O and N_O were estimated to ± 0.01 Å and ± 0.5 respectively, by successively varying and fixing these structural parameters during the least-squares fit (Schlegel and others, 1999). The Fourier-filtered EXAFS contributions corresponding to peak B, χ_B(k), were fitted by assuming only cationic (Mg, Zn, Si) backscatterers, with numbers of octahedral cations fixed to N_zn = 6 and N_Mg = 0 for ZnKer300, N_Zn = 1.4
Fig. 5. $k^2$-weighted Zn K-edge EXAFS spectra for $\text{Zn}^{2+}_{(aq)}$, Zn-doped kerolite (ZnKer003), (Zn,Mg)-kerolite (ZnKer070), and Zn-kerolite (ZnKer300). All spectra were recorded at the magic angle to prevent texture effects.
Fig. 6(A) $k^2$-weighted Zn K-edge radial structure functions (RSFs) for $\text{Zn}^{2+}_\text{aq}$, ZnKer003, ZnKer070, and ZnKer300. (B) Moduli (RSFs) and imaginary parts of the $k^2$-weighted Fourier transforms for ZnKer003 and ZnKer300. Note the similarity of peaks C.
and $N_{Mg} = 4.6$ for ZnKer070, and $N_{Zn} = 0$ and $N_{Mg} = 6$ for ZnKer003, based on elemental compositions. Optimal spectral simulations were obtained ($0.002 \leq R_p \leq 0.032$) for $R_{Zn-Zn}^{EXAFS} = 3.10 \text{ Å}$ and $R_{Zn-Mg}^{EXAFS} = 3.07-3.08 \text{ Å}$ (table 4 and fig. 7), as compared to X-ray diffraction (b/3) values of 3.08 and 3.06 Å, respectively. The systematic

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Successive atomic shells surrounding Mg in hectorite</th>
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<tbody>
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<td>Shell</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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† Angle between $c^*$ and the vector binding Mg to the atoms in the shell.

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<th>Table 3</th>
<th>Quantitative EXAFS analysis of the first Zn-O coordination shell</th>
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<td>α</td>
<td>IFT range$^b$</td>
</tr>
<tr>
<td></td>
<td>(Å)</td>
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<tr>
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</tr>
<tr>
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$^b$ $R + ΔR$ intervals for inverse Fourier transforms (IFTs).

$^b$ The threshold energy $E_0$ was taken at the half-height of the absorption edge ($Δμ/2$).

† Value held fixed during the fitting procedure.
Table 4

Quantitative EXAFS analysis of higher coordination shells

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<th>Zn-Mg shell</th>
<th>Zn-Si shell</th>
<th>Zn-O3 shell</th>
<th>$\Delta E_0^{pp}$ (eV)</th>
<th>$R_\rho$</th>
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<td>4.6 $^\dagger$</td>
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<td>3.08 $^§$</td>
<td>6.0</td>
<td>0.10</td>
<td>3.20</td>
<td>4.0</td>
</tr>
</tbody>
</table>

References

P-EXAFS samples

| #H30_6hSSF | 0° | 2.3 - 3.5 | 3.06 | 2.4 | 0.10 | 3.25 $^\dagger$ | 1.9 | 0.11 $^\dagger$ | 3.72 | 4.6 | 0.10 | -2.5 | 0.025 |
|            | 80° | 2.2 - 3.4 | 3.25 | 4.4 | 0.11 | -2.5 $^\dagger$ | 0.008 |
| #H30_120hSSF | 0° | 2.3 - 3.5 | 3.08 | 2.2 | 0.10 | 3.26 $^\dagger$ | 1.4 | 0.10 $^\dagger$ | 3.74 | 3.4 | 0.10 | -2.5 | 0.045 |
|            | 80° | 2.2 - 3.4 | 3.26 | 4.5 | 0.10 | -2.5 $^\dagger$ | 0.005 |
| #H01_6hSSF | 0° | 2.3 - 3.5 | 3.09 | 2.4 | 0.11 | 3.23 $^\dagger$ | 0.8 | 0.11 $^\dagger$ | 3.69 | 4.7 | 0.10 | -1.6 | 0.011 |
|            | 80° | 2.2 - 3.4 | 3.23 | 3.8 | 0.11 | -1.6 $^\dagger$ | 0.011 |
| #H01_96hSSF | 0° | 2.3 - 3.5 | 3.06 | 2.7 | 0.10 | 3.26 $^\dagger$ | 1.2 | 0.10 $^\dagger$ | 3.71 | 3.8 | 0.10 | -1.4 | 0.007 |
|            | 80° | 2.2 - 3.4 | 3.26 | 3.5 | 0.10 | -1.4 | 0.015 |

$^b$ R + $\Delta R$ interval for the inverse Fourier transforms (IFTs).

$^\dagger$ Value held fixed during the fitting procedure.

$^§$ The crystallographic distance, calculated from the position of the (060) diffraction peak, is 3.06 Å.

$^\dagger$ The threshold energy $E_0$ was taken at the half-height of the absorption edge ($\Delta\mu/2$).
difference in distance likely originates from uncertainty in theoretical phase shift functions for these particular atomic pairs (Schlegel and others, 1999). $R_{Zn-Si}^{\text{EXAFS}}$ markedly decreases with increasing Mg/(Zn + Mg) ratio from 3.30 Å for ZnKer003 to 3.20 Å for ZnKer003 (table 4). This 0.10 Å reduction cannot be explained by a contraction of the unit cell, because $R_{Zn-Zn}^{\text{EXAFS}}$ and $R_{Zn-Mg}^{\text{EXAFS}}$ differ by only 0.03 Å in agreement with the difference of ionic radii between Zn and Mg (0.03 Å; Shannon, 1976). Instead, this shortening is not significant and results from the overlap of the $\chi_{\text{Si}}$ waves by the $\chi_{\text{Mg}}$ and $\chi_{\text{Zn}}$ waves, which increases the uncertainty on the EXAFS-derived Si shell distance to about ± 0.06 Å (Scheidegger and others, 1998). The uncertainty on $R_{Zn-Si}^{\text{EXAFS}}$ is lower in P-EXAFS (± 0.03 Å) because $\chi_{\text{Si}}$ is singled out in the perpendicular
of Zn on hectorite as a function of time, pH, and ionic strength

orientation (Manceau, Chateigner, and Gates, 1998). The uncertainties on $R_{\text{Zn-Mg}}^{\text{EXAFS}}$ and $R_{\text{Zn-Mg}}^{\text{EXAFS}}$ were evaluated to $\pm 0.03$ Å, and the uncertainties on $N_{\text{Zn}}$, $N_{\text{Mg}}$, and $N_{\text{Si}}$ to $\pm 0.5$.

$P$-EXAFS of self-supporting films.—Figure 8A shows $P$-EXAFS spectra at pH 6.5 in 0.3 M NaNO$_3$ and for a short contact time ($t = 6$ h; #H30_6h_SSF; table 1). Several frequencies are observed up to 7 Å$^{-1}$, suggesting the presence of several backscattering shells around Zn. The angular dependence of EXAFS spectra is clearly apparent from the variations in amplitude and position of EXAFS oscillations (for example, wave maxima near 5.2 Å$^{-1}$ and 5.9 Å$^{-1}$), and this polarization dependence indicates that the structural environment of sorbed Zn was anisotropic. Owing to the axisymmetrical symmetry of the self-supporting film (Schlegel and others, 1999), the polarization dependence of K-edge EXAFS spectra can be written:

$$
\chi^a = \chi^\parallel \cos^2 \alpha + \chi^\perp \sin^2 \alpha = \chi^\parallel + (\chi^\parallel - \chi^\perp) \cos^2 \alpha
$$

(2)

where $\chi^a$ is the P-EXAFS spectrum at any value, and $\chi^\parallel$ and $\chi^\perp$ are P-EXAFS spectra in the parallel ($\alpha = 0^\circ$) and perpendicular ($\alpha = 90^\circ$) orientations (fig. 1). A good linear correlation between $\chi^\parallel$ and $\cos^2 \alpha$ (equation 2) is visible for $35^\circ \leq \alpha \leq 80^\circ$ (fig. 8B and C), attesting to the good quality of the data and the reliability of the EXAFS normalization. However, $\chi^\parallel$ deviates significantly from regression lines (fig. 8B and C), due to the poorer quality of this particular spectral record (fig. 8A). The same amplitude problem was observed for all experimental $\chi^a$ and, consequently, $\chi^0$ were systematically recalculated from linear regressions of $\chi^a$ for $35^\circ \leq \alpha \leq 80^\circ$. Schlegel and others (1999) showed that experimental and recalculated $\chi^0$ have similar uncertainties. Experimental ($35^\circ \leq \alpha \leq 80^\circ$) and recalculated ($\alpha = 0^\circ$) P-EXAFS spectra for all self-supporting films are shown in figure 9. At given $\alpha$, only minor differences are observed from one sample to another, indicating similar crystallochemical environments of Zn in these samples. $\chi^{35\text{°}}$ (k) spectra do not resemble ZnKer300 (fig. 5), indicating that Zn-rich kerolite did not precipitate. Instead, strong spectral similarities between Zn-sorbed hectorite and Zn-doped kerolite (ZnKer070, ZnKer003) indicate that Zn is located, at least partly, in a phyllosilicate structural environment, as was previously observed for Co sorbed on hectorite (Schlegel and others, 1999).

Polarized-RSFs (P-RSFs) exhibit several intense peaks at $R + \Delta R$ distances near 1.6 Å (peak A), 2.6-2.8 Å (peak B1), 3.2 (peak B2), and 3.8 Å (peak C) (fig. 10). The positions and imaginary parts of peak A coincide with those in ZnKer003, implying that Zn is hexacoordinated to oxygen atoms in sorption samples, as in the reference (fig. 11A). Quantitative analysis yielded $R_{\text{Zn-O}}^{\text{EXAFS}} = 2.06$ Å for all sorption samples and $\alpha$ values ($R_p \leq 0.009$; table 3). The position and imaginary parts of peak C in sorption samples also coincide with those in ZnKer003 (Tet2 shell, predominantly; table 2 and fig. 11A). The angular invariance of this peak (fig. 11B and C) indicates that Zn-Tet2 pairs are tilted by $\beta = 54.7^\circ$ with respect to e* (the "magic angle"; Manceau and others, 1988), that is, to a value close to $\beta_{\text{Tet2}}$ in phyllosilicate structures (table 2). This result strongly supports a phyllosilicate environment for sorbed Zn. The lower amplitude of peak C in sorption samples as compared to clay references (fig. 11A) may result either from an increase in structural disorder or a decrease in the number of next-nearest Si atoms. Peaks B1 and B2 have a strong angular dependence. For instance, the amplitude of peak B1 for #H30_6h_SSF decreases from $\alpha = 0^\circ$ to $\alpha = 35^\circ$ and then increases from $\alpha = 35^\circ$ to $\alpha = 80^\circ$, whereas its maximum shifts from $R + \Delta R = 2.8$ Å to 2.6 Å (fig. 10A). This dependence indicates the presence of at least two atomic shells having distinct inclinations relative to e* (Schlegel and others, 1999). The angular dependence of the contribution to the EXAFS spectrum from a j shell ($\chi_j^a$) can be written:

$$
\chi_j^a = \chi_j^{iso} \cdot \left[ 1 - \frac{(3 \cos^2 \beta_j - 1)(3 \cos^2 \alpha - 1)}{2} \right]
$$

(3)
From eq (3), the amplitude of $\chi_j^\alpha$ increases with increasing $\alpha$ for $\beta_j$ values lower than the magic angle ($54.7^\circ$) and decreases with increasing $\alpha$ for $\beta_j$ values higher than $54.7^\circ$. The apparent number of backscatterers in the $j$ shell as a function of $\alpha$ ($N_j^\alpha$) is (Manceau, Chateigner, and Gates, 1998)

$$N_j^\alpha = N_j^{iso} \cdot \left[ 1 - \frac{(3 \cos^2 \beta_j - 1)(3 \cos^2 \alpha - 1)}{2} \right]$$  \hspace{1cm} (4)

where $N_j^{iso}$ is the crystallographic value obtained in MA-EXAFS. These theoretical considerations can be exemplified by looking at the prochlorite case study (Manceau and others, 1988). This phyllosilicate contains divalent Fe dispersed in magnesium...
Fig. 9. $k^2$-weighted P-EXAFS spectra at $\alpha$ angles of 0°, 35°, 55°, and 80°. The 0° spectra were obtained by regression of experimental data at 35° $\leq \alpha \leq$ 80° and extrapolation to $\alpha = 0°$. (A) 0.3 M NaNO$_3$, reaction time t = 6 h; (B) 0.3 M NaNO$_3$, t = 120 h; (C) 0.01 M NaNO$_3$, t = 6 h; (D) 0.01 M NaNO$_3$, t = 96 h.
Fig. 10. Polarization dependent RSFs for Zn-sorbed hectorite at \( \alpha \) angles of 35°, 55°, 80° (experimental), and 0° (extrapolated). (A) 0.3 M NaNO\(_3\), \( t = 6 \) h; (B) 0.3 M NaNO\(_3\), \( t = 120 \) h; (C) 0.01 M NaNO\(_3\), \( t = 6 \) h; (D) 0.01 M NaNO\(_3\), \( t = 96 \) h. At \( \alpha = 0° \) in 0.01 M NaNO\(_3\), peaks B1 and B2 merge in a single peak B.
Fig. 11 (A) Comparison of Fourier transforms (FTs) at $\alpha = 35^\circ$ (magic angle) for #H30_6h_SSF and ZnKer003; (B, C) Angular dependence of moduli (RSFs) and imaginary parts of FTs for Zn sorbed hectorite in 0.3 M NaNO$_3$ (#H30_6h_SSF); (B) $\alpha = 0^\circ$ and $80^\circ$; (C) $\alpha = 0^\circ$ and $35^\circ$. Peak C is invariant with $\alpha$. 
sheets with ~75 percent of Fe located in the octahedral sheet of the TOT layer and ~25 percent of Fe located in the interlayer brucitic sheet (fig. 12A). Hence, Fe is surrounded, on average, by 6 in-plane Mg neighbors in TOT and brucitic octahedral sheets (β = 90°) at R ~ 3.05 Å and by 4*0.75 = 3 out-of-plane (Si, Al) neighbors in tetrahedral sheets (β ~ 33°) at R ~ 3.25 Å. Therefore, N_{Mg}^{35°} = 6 and N_{Si,Al}^{35°} = 3. From equation (4), N_{Si,Al}^{90°} = 1.4, N_{Si,Al}^{90°} = 6.3, N_{Mg}^{90°} = 9, and N_{Mg}^{90°} = 0. As divalent Fe and Zn have similar numbers of electrons and similar ionic radii (Shannon, 1976), their EXAFS signals are similar for comparable structural environments. Therefore, the similarity in the positions and imaginary parts of peaks B and C for prochlorite and Zn-sorbed hectorite at α = 90° (fig. 12B) offers evidence for the presence of nearest (Tet1) and next-nearest (Tet2) Si shells in sorption samples. In contrast, the amplitude, position, and imaginary part of peak B in prochlorite differ from those of peaks B1 and B2 in sorption samples at α = 0° (fig. 12C). The nature of in-plane nearest atomic neighbors was determined from the hectorite structure (table 2) and spectral simulations.

Fourier-filtered $X_{B1,B2}^{80°}$ for all sorption samples were successfully fitted (0.005 ≤ $R_g$ ≤ 0.015) with a Si shell of 3.5 to 4.5 atoms at R_{Zn-Si}^{EXAFS} = 3.23-3.26 Å (fig. 13; table 4). $X_{B1,B2}(k)$ could not be fitted with a combination of only Mg as Oct1 and Si as Tet1 shells. A third shell, corresponding to peak B2, had to be added. The fading of peak B2 at high α values indicates that this shell has a β value greater than 54°. A previous P-EXAFS study on nontronite, a ferric dioctahedral smectite, showed that the O3 shell at R ~ 3.7 Å significantly contributed to the EXAFS signal and had to be added to Oct1 + Tet1 contributions in the spectral simulation (Manceau, Chatteigner, and Gates, 1998). To decrease the degree of freedom of the spectral fit, the three-shell fits were performed by fixing $R_{Zn-Si}^{EXAFS}$ and $\sigma_{Si}$ to their values at α = 80°. Correct fits were obtained with $R_{Zn-Mg}^{EXAFS}$ and $R_{Zn-O3}^{EXAFS}$ values comparable (within uncertainty) to those in clay references (table 4; fig. 13). As in Schlegel and others (1999), no atomic pairs of sorbate cations were observed (that is, Zn-Zn in the present study).

Figure 10 shows that peaks B1,B2 almost cancel at α = 35°. From eq (3), $X_{B1,B2}^{35°}$ can be written

$$X_{B1,B2}^{35°} \approx 0.345 \times X_{B1,B2}^{80°} + 0.656 \times X_{B1,B2}^{90°}$$

(5)

Because $X_{B1,B2}^{90°}$ and $X_{B1,B2}^{80°}$ are out-of-phase in the [3.5-6 Å] k-range, with the amplitude of $X_{B1,B2}^{80°}$ being about twice as intense as that of $X_{B1,B2}^{90°}$ (fig. 14), equation (5) predicts that $X_{B1,B2}$ should almost cancel, as observed. The consequence of this wave extinction is that no stable fit could be obtained at the magic angle. However, N_{Mg}^{90°}, N_{Si}^{35°}, and N_{O3}^{35°} can be determined from values obtained at α = 0 and 80° by using eq (4) (table 5).

**MA-EXAFS of wet pastes.**—Figure 15 compares MA-EXAFS spectra of the wet pastes of Zn-sorbed hectorite. At pH 3.7 in 0.0015 M NaNO$_3$ and t = 30 min (#001_30min_WP), the EXAFS spectrum is nearly identical to that of Zn$_{aq}$ (fig. 16A), again indicating that Zn formed OS surface complexes at low ionic strength and pH. At pH 6.5 in 0.01 M NaNO$_3$, the spectrum for short reaction time (t = 5 min; #H01_5min_WP) resembles those for #H001_30min_WP and Zn$_{aq}$, indicating the presence of OS surface complexes. A spectral evolution then occurs with increasing sorption time, and EXAFS spectra from t = 6 h (#H01_6h_WP) to 96 h (H01_96h_WP) increasingly resemble those of the self-supporting films. At pH 6.5 in 0.3 M NaNO$_3$, only little spectral evolution is observed from t = 6 h to 120 h (fig. 15) and MA-EXAFS spectra resemble those of the self-supporting films (fig. 16B).
Fig. 12(A) Schematic structure of prochlorite. TOT phyllosilicate layers alternate with brucitic octahedral sheets (O). Fe(II) atoms are distributed in the two types of octahedral sheets. (B and C) Comparison of moduli and imaginary parts of FTs for Zn-sorbed hectorite (#H30_6h_SSF, Zn K-edge) and Fe(II) dispersed in Mg-rich prochlorite (Fe K-edge) at $\alpha = 90^\circ$ (B) and $0^\circ$ (C).
Fig. 13. Comparison between experimental and simulated Fourier-filtered EXAFS contributions of peaks B1,B2 for Zn-sorbed hectorite at $\alpha = 0^\circ$ ($\chi'_{B1,B2}(k)$) and $80^\circ$ ($\chi'_{B1,B2}(k)$). (A) 0.3 M NaNO$_3$, $t = 6$ h; (B) 0.3 M NaNO$_3$, $t = 120$ h; (C) 0.01 M NaNO$_3$, $t = 6$ h; (D) 0.01 M NaNO$_3$, $t = 96$ h.
DISCUSSION

Structural Environment of Zn in Self-supporting Films and Wet Pastes

P-EXAFS results indicate that sorbed Zn octahedra are surrounded by in-plane Mg and out-of-plane Si atoms. $R_{Zn-Mg}^{EXAFS}$ and $R_{Zn-Si}^{EXAFS}$ distances match those in ZnKer and are characteristic of edge-sharing (E) linkages with Mg octahedra and corner-sharing (C) linkages with Si tetrahedra. The detection of the Tet2 shell further indicates that neighboring Si tetrahedra are polymerized in a tetrahedral framework, as in a phyllosilicate structure. In addition, the angular dependence of EXAFS spectra provides strong evidence for the physical association of Zn atoms with the clay sorbent and indicates that the Mg, Si (Tet1 + Tet2) and O3 shells belong to hectorite. This whole set of results demonstrates that Zn octahedra are located in structural continuity with the hectorite octahedral sheet, as was demonstrated before for Co (Schlegel and others, 1999). Because EXAFS is not sensitive to Li, the actual number of nearest octahedral cations sharing edges with Zn octahedra ($N_{oct}$) is probably higher than $N_{Mg}^{35°}$. Assuming a random distribution of Li within the hectorite octahedral sheet, $N_{oct} \approx N_{Mg}^{35°} * 3 / 2.65$ (table 5). $N_{oct} \approx 1.7-2.0$ (±0.8), which is significantly lower than

<table>
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<tr>
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<th>$N_{Mg}^{35°}$</th>
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<th>$N_{Si}^{35°}$</th>
<th>$N_{O3}^{35°}$</th>
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</tr>
<tr>
<td>#H30_120h_SSF</td>
<td>1.5</td>
<td>1.7</td>
<td>2.4</td>
<td>2.3</td>
</tr>
<tr>
<td>#H01_6h_SSF</td>
<td>1.6</td>
<td>1.8</td>
<td>1.8</td>
<td>3.1</td>
</tr>
<tr>
<td>#H01_96h_SSF</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Calculated as $N_{int} = N_{Mg}^{35°} * 3 / 2.65$. 

Fig. 14. Comparison of $\chi^{2}(k)$ for #H30_6h_SSF (0.3 M NaNO₃, t = 6 h) at $\alpha = 0°$, 35°, and 80°. Note the extinction of $\chi^{2}(k)$ for $3 \leq k \leq 7 \, \text{Å}^{-1}$. 

Table 5

Calculated number of neighboring atoms at 35° for self-supporting films
Fig. 15. $k^2$-weighted magic-angle EXAFS spectra for wet pastes of hectorite reacted with Zn under various ionic strength and reaction time conditions. Sorption conditions are listed in table 1.
the expected number for Zn in octahedral sheets ($N_{\text{oct}} = 6$). As for Co under similar sorption conditions (Schlegel and others, 1999), only the formation of IS Zn complexes at the edges of hectorite platelets complies with both the clay-like environment and the low number of neighboring sorbent cations. The structure of these surface complexes depends on the morphology of the hectorite layer edges. Hectorite platelets are generally lath-shaped, and their {001} basal faces are bounded by {010}, {110}, and {100} edge faces (Oberlin and Mering, 1966). Several types of Zn surface complexes, each having a distinct number of nearest sorbent cations, can form on a given edge face (fig. 17A-C). Experimental $N_{\text{oct}}$ and $N_{\text{Si}35}^*$ values for each film sample
(table 5) can be accounted for by assuming adequate combinations of distinct surface complexes (Schlegel and others, 1999).

At pH 6.5 in 0.3 M NaNO₃, the similarity between MA-EXAFS spectra collected for self-supporting films and wet pastes points to the presence of IS complexes at high

Fig. 17. Possible structures of mononuclear Zn surface complexes on the edges of hectorite platelets. (A) [010] layer edges; (B) [110] layer edges; (C) [100] layer edges. Zn octahedra are located in structural continuity with the (Mg, Li) octahedral sheet.
ionic strength, even under fully wet conditions. In contrast, the spectral evolution observed for wet pastes at pH 6.5 in 0.01 M NaNO₃ indicates that IS complexes progressively replace OS complexes with increasing reaction time. This point is addressed below.

**Zn Uptake at High Ionic Strength**
Excess Mg release upon Zn sorption onto hectorite at pH 6.5 in 0.3 M NaNO₃ is similar to the excess Mg release upon Co sorption on hectorite for identical pH and ionic strength conditions (Schlegel, Charlet, and Manceau, 1999). This Mg release cannot be assigned to partial dissolution of hectorite and parallel precipitation of (Zn, Mg)-kerolite, owing to the absence of evidence for Zn-Zn pairs in the EXAFS spectra. Also, exchange of Mg by Zn on interlayer sites is unlikely because cation exchange is inhibited at high ionic strength. A third hypothesis is that, prior to Zn addition, Mg forms edge surface complexes. As chemical conditions favor hectorite dissolution, these surface complexes would have a low stability and Mg would dynamically adsorb and desorb. The net accumulation of Mg in solution at the beginning of Zn uptake would result from the replacement of Mg surface complexes by IS Zn complexes of higher stability. These IS Zn complexes then passivate layer edges and inhibit the dissolution of hectorite, thus explaining the measured decrease in Si and Mg release rates (fig. 4A and B).

**Cation Exchange and Zn Uptake at Low Ionic Strength and pH 6.5**
EXAFS results for fully wet samples indicate that the proportion of Zn IS over OS complexes increases with reaction time at pH 6.5 in 0.01 M NaNO₃. These structural results confirm a sorption mechanism previously inferred for Co from kinetics measurements and EXAFS spectroscopy on self-supporting films (Schlegel, Charlet, and Manceau, 1999): initial fast Zn sorption by cation exchange followed by Zn fixation on edge sites. To better link spectroscopic and macroscopic observations, the time-dependent amount of exchangeable Zn can be estimated from chemical data. For this purpose, the initial adsorption of Zn in 0.01 M NaNO₃ can be described by the exchange reaction

\[
2 \ XNa + Zn^{2+}_{(aq)} \leftrightarrow X_2Zn + 2 \ Na^{+}_{(aq)} \quad (6)
\]

where X⁻ refers to one mole of exchange sites. This reaction is known to reach equilibrium within minutes (Tang and Sparks, 1993). Therefore, exchangeable Zn \((X_2Zn)\) is believed to be always near or at equilibrium with \([Zn^{2+}_{(aq)}] \ (\sim [Zn]_{aq})\) whatever the reaction time. This equilibrium can be written in the Vanselow convention (Sposito, 1981; Charlet and others, 1993)

\[
K^c_{Na-Zn} = \frac{(X_2Zn)[Na^{+}_{(aq)}]^2}{(XNa)^2[Zn^{2+}_{aq}]^2} \quad (7)
\]

where \((X_2Zn)\) and \((XNa)\) are the molar fractions of exchangeable cations and \(K^c_{Na-Zn}\) is a conditional selectivity coefficient, which includes activity coefficients for cations in the supernatant and the exchanger phases and therefore depends on both exchanger and solution compositions (McBride, 1994). Molar fractions are calculated from the molar concentrations of Zn and Na adsorbed on exchange sites (respectively \([X_2Zn]\) and \([XNa]\)) as

\[
(X_2Zn) = \frac{[X_2Zn]}{\sum_j [X_mM_j]} \quad (8)
\]
and

\[(X_{Na}) = \frac{[X_{Na}]}{\sum [X_{m}M_{j}]} \tag{9}\]

where the summation runs over all \(M_{j}^{m+}\) cations that can sorb on exchange sites. In the present system, \(M_{j} = Na, Zn, Mg,\) and \(Li. Thus [X_{mj}M_{j}]] must be known to calculate exchangeable \(Zn\) as a function of \([Zn]_{aq}\). Solution Na is approximately constant, and \([X_{Na}]\) can be calculated from the difference between the total concentration of exchange sites and \([XLi] + 2 [X_{2}Zn] + 2 [X_{2}Mg]\). \([XLi]\) can be neglected, because \(Li\) is known to have a lower affinity for exchange sites than Na (McBride, 1994), and the sum of exchangeable and dissolved \(Li\) concentrations never exceeded 100 \(\mu M\), two orders of magnitude lower than \([Na]_{aq}\). \([X_{2}Mg]\) cannot be neglected and, in addition, is not constant because \([Mg]_{aq}\) increases with reaction time. Exchangeable Mg is calculated from \([Mg]_{aq}\) by using equations similar to eqs (7-9) and taking \(K_{Na-Mg} = 0.34 \pm 0.06\) (Schlegel, Charlet, and Manceau, 1999). \(K_{Na-Zn} = 0.41 \pm 0.06\) was obtained from chemical data at \(pH 4\) in 0.01 M \(NaNO_{3}\) at \(t = 5 \text{ min}\) by assuming that all sorbed \(Zn\) cations are retained in an exchangeable form. Because specific sorption occurs even at \(pH\) as low as 4, as evident in figure 4B, the calculated \(K_{Na-Zn}\) value actually represents an upper limit for the real selectivity coefficient. Finally, the time-dependent amount of exchangeable \(Zn\) and \(Mg\) at \(pH 6.5\) in 0.01 M \(NaNO_{3}\) was obtained by solving the set of equations for \(Na-Zn\) and \(Na-Mg\) exchanges at each kinetic point using experimental values of \([Na]_{aq}, [Zn]_{aq}, [Mg]_{aq}\).

Figure 18A shows that the fraction of \(Zn_{T}\) sorbed on exchange sites steadily decreased with increasing reaction time from 70 to 4 percent of \(Zn_{T}\) between 5 min and 96 h, whereas the total amount of sorbed \(Zn\) increased from \(\sim 80\) to nearly 100 percent of \(Zn_{T}\) over the same period. The waning proportion of \(Zn\) OS complexes agrees with EXAFS results on wet pastes, and allows us to determine a mechanism of \(Zn\) sorption on hectorite which parallels that of Co under the same chemical conditions (\(pH 6.5\) in 0.01 M \(NaNO_{3}\); Schlegel, Charlet, and Manceau, 1999). Initially, solution \(Zn\) rapidly adsorbed as OS complexes on exchange sites. Then, \(Zn\) IS complexes formed at layer edges, either by diffusion of \(Zn\) from basal surfaces or by direct sorption of solution \(Zn\) to edge sites. Because direct specific sorption is slower than cation exchange, it caused a steady decrease of \([Zn]_{aq}\), which was immediately balanced by rapid release of \(Zn\) from exchange sites to solution. After 96 h of sorption, the proportion of \(Zn\) retained on exchange sites (4 percent) was well below the detection limit of EXAFS (estimated to be \(\sim 20\) percent). Therefore, OS complexes remaining at the end of sorption experiments were overlooked in the analysis of wet pastes and self-supporting films.

As noted above, \(Zn\) transfer from exchange sites to edge sites may occur either by \(Zn\) release into solution and then readsorption on edges or by lateral diffusion on the basal planes. The first mechanism is expected to occur easily because cation exchange is rapid; however the sorption rate to edge sites should then be similar to that observed in 0.3 M \(NaNO_{3}\), when the exchange mechanism is inhibited. In contrast, rapid diffusion on basal planes may result in larger sorption rates to edge sites, unless this rate is controlled by reactions at the layer edge rather than sorbate diffusion toward platelet edges. The comparison of edge sorption kinetics in 0.3 and 0.01 M \(NaNO_{3}\) (fig. 18B) shows that sorption rates are comparable at the two ionic strengths, which suggests either that sorption rate is controlled by surface reactions at the layer edge or that basal plane diffusion is negligible with respect to solution transfer of \(Zn\).

The agreement between chemical calculations and MA-EXAFS results on wet pastes suggests that a fraction of the predominant IS complexes observed on the
of Zn on hectorite as a function of time, pH, and ionic strength

In contrast to the study of the Co/hectorite system, low-pH data were collected for Zn/hectorite in order to macroscopically characterize the pH dependency of edge sorption, as well as to understand the sorption behavior of Zn under acidic conditions. At pH 4 in 0.01 M NaNO₃, Zn initially sorbed by cation exchange, but in contrast to pH 6.5, the amount of sorbed Zn subsequently decreased with increasing reaction time (fig. 4B). The fraction of exchangeable Zn, calculated with the same set of equations as for pH 6.5, always represents more than 87 percent of sorbed Zn, indicating that long-term Zn sorption is mainly controlled by cation exchange of Zn for Na and Mg.

The amount of exchangeable Mg calculated from the exchange model increases from 77 μmol g⁻¹ at t = 5 min (that is, (X₂Mg) ≈ 0.11) to about 270 μmol g⁻¹ at t = 48 h.
((X_{2}\text{Mg}) \approx 0.51), due to the increase of [Mg]_{aq} released by the fast dissolution of hectorite at pH 4. The increase of exchangeable Mg reduces the number of exchange sites accessible to Zn, thus accounting for the observed Zn desorption.

### Comparison Between Co and Zn Sorption on Hectorite

The sorption mechanism of Zn on hectorite at pH 6.5 is qualitatively similar to Co (Schlegel, Charlet, and Manceau, 1999; Schlegel and others, 1999). Both cations form IS surface complexes on hectorite edges at high ionic strength, and OS and then IS complexes at low ionic strength. This is consistent with the high affinity of both cations for the magnesium trioctahedral clay structure (Decarreau, 1985). More generally, the other divalent cations from the first raw transition series (Ni^{2+}, Fe^{2+}, \ldots) are expected to behave similarly. However, for identical chemical conditions (that is, pH 6.5 in 0.3 M NaNO_{3}, \text{[hect.]} = 1.95 \text{ g L}^{-1} and total sorbent concentrations ZnT or CoT = 100 \mu M), more Zn was always sorbed than Co (72 percent of CoT versus 100 percent of ZnT at t = 120 h; fig. 19). The higher affinity of Zn for hectorite edge sites is consistent with the higher stability (lower Gibbs free energy of formation) of Zn-kerolite compared to Co-kerolite (Decarreau, 1985).

### CONCLUDING REMARKS

Successful identification of the sorption mechanisms of Zn on hectorite is due to a combination of four factors: (1) the detailed characterization of the complete chemistry of the sorbate-sorbent system, including the role of parameters such as ionic strength and reaction time, (2) the preparation of appropriate Zn structural references mimicking the possible sorbate structural environments, (3) the application of P-EXAFS to the determination of the spatial orientation of nearest atomic neighbors around sorbed Zn, and (4) the application of MA-EXAFS to the determination of Zn local structure under fully wet conditions. This last analysis was not performed in our previous study of the Co/hectorite system.

The present study highlights the importance of pH, ionic strength, and sorbate-smectite contact time on the fate of Zn in clayey soils. Under low ionic strength conditions, Zn can be temporarily held in an exchangeable form by smectite particles and thereafter released, owing to the fast reversibility of the cation exchange chemical reaction. Released Zn can migrate to plant roots, be sorbed on high energy surface

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**Fig. 19.** Comparison between kinetics of Zn (○) and Co (△) sorption on hectorite at pH 6.5 in 0.3 M NaNO_{3}, and for total Zn and Co concentrations of 100 \mu M. [hect.] = 1.95 \text{ g L}^{-1}. 

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sites, such as those at clay edges and on (oxyhydr)oxide mineral surfaces, or be incorporated into neoformed solids, such as Zn-containing phyllosilicates. Clearly, the uptake of trace elements by soil constituents is a time-dependent process and the study of natural samples usually provides only a crystal-chemical snapshot. Kinetics studies at macroscopic and microscopic scales are required to improve transfer models of trace elements in natural systems.

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