Determination of Ni(II) and Th(IV) sorption mechanisms on clay mineral surfaces
a combined macroscopic, spectroscopic, and microscopic approach

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Determination of Ni(II) and Th(IV) Sorption Mechanisms on Clay Mineral Surfaces: A Combined Macroscopic, Spectroscopic, and Microscopic Approach

A dissertation submitted to the
Swiss Federal Institute of Technology Zürich

for the degree of
Doctor of Natural Sciences

presented by
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Abstract

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Abstract

The uptake mechanisms of Ni(II) and Th(IV) onto montmorillonite, a dioctahedral smectite, were investigated by combining wet chemistry methods with powder and polarized extended X-ray absorption fine structure (EXAFS and P-EXAFS) spectroscopy. At elevated pH and Ni concentrations the uptake of Ni on montmorillonite resulted in the formation of a Ni-phyllosilicate-like phase. These neoformed phyllosilicates were oriented with respect to montmorillonite layers. The neoformation of a phyllosilicate upon metal uptake on montmorillonite is documented here for the first time. It has important geochemical implications because this dioctahedral smectite is abundant in the environment. The resulting sequestration of sorbed trace metals in sparingly soluble phyllosilicate structure may prevent their migration. Transmission electron microscopy (TEM) was employed to observe neoformed Ni phyllosilicates directly with microscopic methods. The study revealed the presence of small clay like particles in the Ni treated montmorillonite. These particles contained a high amount of Ni and were very resistant to the electron beam. Such smectites were never observed in the untreated montmorillonite suggesting that they represent neoformed Ni phyllosilicates.

To find first evidence for the adsorption of Ni on layer edges of dioctahedral clays the uptake of Ni on montmorillonite was studied at near neutral pH and low Ni concentrations. The P-EXAFS study revealed the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets. Heavy metals binding to edge sites is therefore a possible sorption mechanism for dioctahedral smectites. Over a time period of one year no change in the uptake mechanism under the employed reaction conditions could be observed. Specifically the diffusion of Ni atoms into the montmorillonite structure could be excluded. It was observed that the structural order of the surface complexes was increasing with time. This finding could explain why even at trace element concentrations the observed release rate of Ni sorbed onto montmorillonite decreased with prolonged reaction time.

Finally, the uptake process of Th onto montmorillonite was studied at initial Th concentrations (pH 2 - 5) both under- and oversaturated with respect to amorphous Th (hydr)oxides. At low and intermediate surface coverage and in the whole pH range studied Th was bound to the montmorillonite surface by sharing double corners with Si tetrahedra. At higher pH and high surface loading the EXAFS spectrum resembled that of amorphous Th(OH)₄ suggesting the precipitation of a Th hydroxide. In contrast to Ni the formation of Th phyllosilicates is not occurring at higher metal concentrations.
Zusammenfassung

In dieser Doktorarbeit wurden makroskopische und kinetische Studien mit mikroskopischen und spektroskopischen Untersuchungen gekoppelt, um die Sorptionsmechanismen von Ni(II) und Th(IV) an Montmorillonit auf molekularer bzw. atomarer Ebene zu bestimmen.


Im letzten Kapitel dieser Doktorarbeit wurde das Sorptionsverhalten von Th an Montmorillonit untersucht. Die Studie wurde bei Th Konzentrationen durchgeführt, die bezüglich amorphen Th (hydr)oxiden sowohl übersättigt, wie auch untersättigt waren. Es zeigte sich, dass Th bei tiefen und mittleren Oberflächenbeladungen und im pH-Bereich von 2 - 5 eine spezifische Bindung mit der Montmorillonit-Oberfläche eingeht. Bei pH 5 und hoher Oberflächenbeladung fällt das Th in Form von amorphem Th(OH)$_4$ aus. Im Gegensatz zur Ni Studie konnten keine Hinweise für ein neugeformtes Th Phyllosilikat gefunden werden.
INTRODUCTION

1.1 Environmental relevance

Contamination of aqueous and terrestrial environments with heavy metals derived from industrial, municipal, and agricultural sources is of major concern worldwide. In natural environments heavy metals are usually present as trace elements, but anthropogenic input or deposition have in many cases strongly increased the metal concentrations and lead to accumulation that potentially effect environmental quality and human health (Salamons et al., 1995). Industries and governments are spending huge amounts of money determining what pollutants are present in contaminated soils and ground waters and implementing strategies to remediate or stabilize polluted sites.

Interfacial processes, such as sorption, precipitation and dissolution markedly affect the mobility, speciation and bioavailability of heavy metal contaminants in the environment. It is therefore important to determine the mechanism and the mineral phase responsible for the fate of contaminants in soils and aquatic systems. Among the naturally occurring mineral phases are clay minerals the ones that can severely retard the release of metals into the geosphere by uptake processes or the formation of new phases. They possess a large specific area and a high structural charge (up to 1000 meq per kg). These characteristics are ideal for the use as geochemical barriers in nuclear waste repositories or landfills for hazardous chemicals.

Most uptake studies of metals in clay systems have been performed using a macroscopic approach (batch equilibrium studies). The focus of many of these studies has been on the determination of distribution coefficients, the use of adsorption isotherms, empirical and semi-empirical equations (e.g., Freundlich, Langmuir), and surface complexation models to describe the sorption reactions of heavy metals. Surface complexation models employ an array of adjustable parameters to fit experimental data, and it has been shown that often sorption data will equally well fit a number of these models (e.g., Westall and Hohl, 1980). Another major disadvantage of most surface complexation models (and equilibrium-based models in general), is that processes such as precipitation and diffusion are not accounted for. One must realize that equilibrium-based models simply describe macroscopic data and do not definitively prove a reaction mechanism. For these reasons there has been a significant effort in combining macroscopic studies with spectroscopic and microscopic techniques which allow accurate speciation and which can provide molecular-level information fundamental for understanding mechanisms in natural systems. The approach of combining macroscopic studies with spectroscopic and microscopic techniques has created a new multidisciplinary field in environmental science, i.e. molecular environmental science.
Extended X-ray absorption fine structure (EXAFS) spectroscopy has been one of the most widely used molecular techniques employed in molecular environmental science to gain structural information at the mineral/water interface. EXAFS is a powerful, element-specific in-situ technique that can be used to determine the local structure (bond distance, number and type of near neighbors) around a sorbing element, even when the element is at low concentration levels (a few ppm, depending on the element and the matrix). EXAFS requires intense x-rays, and these are generated by electrons/positrons that circulate in a storage ring of a synchrotron facility at energies of 1 to 6 GeV in paths curved by magnetic fields. There are several reviews on EXAFS relevant to environmental science such as Brown (1990), Charlet and Manceau (1993), Schulze and Bertsch (1995), Fendorf (1999) and Manceau et al. (1999).

While EXAFS provides local chemical information up to ~5 Å around the X-ray absorber, it normally does not resolve the spatial distribution of an element within mineral particles. Such information can be obtained by microscopic methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are well established methods for acquiring both chemical and micromorphological data on soils and soil materials. TEM can provide spatial resolution of surface alterations and the amorphous nature or degree of crystallinity of sorbed species. It can also be combined with electron dispersive spectroscopy (EDS) for elemental analysis. In the last two decades several books and review articles on microcharacterization of soils using electron microscopy have been published. Good overviews are found in the books edited by Smart & Tovey (1981), Bullock & Murphy (1983), and Douglas (1990), and in the review articles by Whalley (1985), Allen (1993), and Chen (1994).

1.2 Objectives of this study

The objective of this thesis was to determine the uptake mechanisms of Ni and Th on montmorillonite using macroscopic, kinetic, microscopic and spectroscopic investigations. X-ray absorption spectroscopy (XAS) was used to study the effect of reaction conditions (pH, ionic strength, initial metal concentration, and reaction time) on the structural coordination environment of Ni and Th sorbed onto montmorillonite. Transmission electron microscopy (TEM) was used to investigate whether any surface alterations or precipitates could be detected after the montmorillonite had been in contact with the Ni over time. The TEM measurements were combined with electron dispersive spectroscopy (EDS) to determine local elemental distribution.

Montmorillonite is a dioctahedral smectitic 2:1 clay mineral with substantial isomorphic substitution. The structure of smectites consists of an octahedral sheet attached to two tetrahedral sheets. Smectites are classified as dioctahedral or trioctahedral depending on the number of cation positions in the octahedral sheet that are occupied. If two of the three positions
are filled, then the clay is dioctahedral. If all three positions are filled, the clay mineral is
 trioctahedral. Chemically, the high surface reactivity of clay minerals is a direct consequence of
their lamellar and defective structure. The permanent negative structural charge is compensated
by adsorption of cations on basal planes. Cations sorbed onto these planes form outer-sphere
surface complexes and are easily exchanged with ions from solution. Besides cation exchange
properties, clay minerals also possess pH-dependent sorption properties. The pH-dependent
sorption was inferred to take place at layer edges, where truncation of the bulk structure leads to
the formation of dangling oxygen bonds. It has been proposed that cations sorbed onto these
planes form inner-sphere surface complexes (Sposito, 1984; McBride, 1994; Sparks, 1995).

The elements Ni(II) and Th(IV) have been selected because both heavy metals are of
environmental concern. Ni(II) represents a divalent transition metal cation. Concentrations of
total nickel in soils are normally <2 mmol/kg (Adriano, 1986; Uren, 1994). Anthropogenic input
(e.g. from tanneries, smelters or sewage sludge application, phosphate fertilizers, mining
activities, auto emissions and industrial and municipal wastes), however, can increase the total
nickel concentration in soils to >50 mmol/kg (Uren, 1994). The mechanisms controlling nickel
activity in natural environments are not well understood. Both adsorption and precipitation
phenomena onto oxides, clay minerals and organic matter have been reported as the governing
nickel uptake mechanisms.

Thorium is a naturally occurring, weakly radioactive element which is predominately
(>99%) present as thorium-232 (half-life 1.41 x 10^{10} years). It occurs in a single redox state
(+IV) and is therefore a suitable analogue for other tetravalent actinides. It is widely distributed
in small amounts in the Earth’s crust, being about as abundant as lead or molybdenum and three
times as abundant as uranium (Weast and Astle, 1983). Th is present in small amounts in rocks,
soils, surface- and ground waters, plants, and animals. For example, soils commonly contain an
average of about 6 ppm thorium (Weast and Astle, 1983). There are several natural Th minerals,
the most common being rare earth-thorium-phosphate minerals (e.g., monazite) and thorium
silicate minerals such as thorite and huttonite. Large quantities of waste arising from mining, oil
and gas extraction contain naturally occurring radioactive material such as uranium, thorium
and potassium (Paschoa, 1998). Furthermore, fly ashes from lignite power stations are often
contaminated with Th (Savanonda et al., 1985).

The most critical environmental aspect concerning Ni and Th is their safe disposal in
nuclear waste repositories. The flow of ground water through a repository can potentially result
in the release of radionuclides such as ^{59}\text{Ni}, ^{63}\text{Ni}, ^{226}\text{Th}, ^{229}\text{Th} and ^{230}\text{Th} with half-life times
between 2 and 75000 years from waste matrices into the environment. The release of
radionuclides can be considerably retarded due to interactions with clay minerals. For example,
dioctahedral aluminous clays are foreseen as a backfill material in the Swiss concept for a high
level radioactive waste repository (NAGRA, 1994). Thus, a detailed understanding of the sorption mechanisms of Ni and Th with montmorillonite is of great importance for the safety assessment of nuclear waste repositories.

### 1.3 Outline of the thesis

The Ph. D. thesis consists of four chapters which are in different stages of the publication process:


In the first chapter the uptake mechanism of Ni on montmorillonite at elevated pH and Ni concentrations was investigated by combining kinetics as determined in batch experiments with EXAFS spectroscopy. The study revealed the formation of Ni phyllosilicate phases with increasing reaction time. The neoformed Ni phyllosilicates were oriented with respect to montmorillonite layers. The question remained however open whether the neoformed phyllosilicate is structurally linked to the montmorillonite surface.

In the second chapter TEM was employed to observe and identify precipitates formed upon Ni uptake on montmorillonite at elevated pH and Ni concentration. The reaction conditions employed were similar to those used in chapter 1. In this TEM study raw
montmorillonite was used because smectite particles in the unconditioned material were more resistant to the electron beam than in the conditioned montmorillonite.

In the third chapter P-EXAFS was used to study the uptake of Ni on montmorillonite at lower pH and Ni concentrations compared to the first two studies. In this chapter first structural evidence for the adsorption of metal ion on the layer edges of a dioctahedral smectite is presented. The reaction was followed up to a reaction time of one year and the data indicate that Ni does not diffuse into the montmorillonite structure.

The goal of the last chapter was to investigate the uptake mechanisms of Th on montmorillonite using powder EXAFS and P-EXAFS. The uptake was studied at reaction conditions (pH 2-5) both under- and oversaturated with respect to Th-(hydr)oxides. The data suggest at low and intermediate surface loading the sorption of Th onto edge sites and at higher Th loading and pH the formation of an amorphous Th(OH)₄ like phase.

### 1.4 Short introduction to EXAFS and P-EXAFS

When X-rays impinge upon a sample they are elastically or inelastically scattered. X-rays not reflected from the surface are exponentially attenuated as a function of sample thickness (x) and the absorption coefficient $\mu(E)$ at a particular energy E.

$$I_t = I_0 e^{-\mu(E) x} \quad (1)$$

Or after rearrangement

$$\mu x = \ln \left( \frac{I_0}{I_t} \right) \quad (2)$$

where $I_0$ is the incident and $I_t$ the transmitted beam intensity. Measurements of the transmitted beam can be achieved by placing two detectors (usually ionization chambers) in the beam path; one before ($I_0$) and one after the sample ($I_t$). Measurements in transmission mode work well when the concentration of the X-ray absorber in the sample exceeds about 2 wt%. For more dilute samples the measurements must be based on the core-hole production by the impinging X-rays (fluorescence and Auger emission). Auger and fluorescence emission are inversely related; with increasing atomic number electron production decreases and x-ray production increases. Because of the short penetration depth of electrons the detection of Auger electrons is useful in surface studies. The disadvantage of Auger electron measurements is the requirement for vacuum conditions. For natural samples which usually contain water this requirement is problematic, but one can overcome this problem by measurements in bulk sensitive
fluorescence mode. Detectors used for fluorescence measurements are Stern-Heald-type
detectors (Lytle detector, The EXAFS Co.) and energy discriminating solid-state detectors.

In fluorescence mode the relationship between the intensity of the fluorescence signal \( I_f \) and the incident beam intensity \( I_0 \) can be expressed as:

\[
\mu \chi \approx \frac{I_f}{I_0}
\]

(3)

When the X-ray energy \( h\nu \) is equal or slightly larger than the binding energy \( E_0 \), a core
electron is emitted by photoelectric processes and a sharp increase in the absorption spectrum is
observed. Pre-edge features and the so-called ‘white-line’ of the absorption spectrum are due to
interatomic transitions into free bound states. The region \( E-E_0 < 50 \text{ eV} \) in the absorption
spectrum is called X-ray absorption near edge structure (XANES). The XANES region is
dominated by electron transitions and multiple-scattering events. XANES is mainly used to
extract information about the oxidation state based on the edge position and a comparison with
reference compounds. The region \( E-E_0 > 50 \text{ eV} \) in the absorption spectrum is called extended X-
ray absorption fine structure (EXAFS). In the EXAFS region multiple scattering can be
neglected in a first approximation. In this case the photoelectron can be regarded as a
photoelectron wave emanating from the absorbing atom with a wave number \( k \sim (E-E_0)^{1/2} \). This
photoelectron wave interacts with the inner electrons of the neighbor atoms and is elastically
scattered. Depending on the phase of the waves (in-going and out-going) this interaction results
in a constructive or destructive interference and a slight modification of the total absorption.
The interference causes that the absorption coefficient in the EXAFS region shows a series of
oscillations which may extend up to 2000 eV above the edge.

The EXAFS function \( \chi(k) \) is defined as the relative difference between the measured
absorption \( \mu(k) \) and the atomic absorption \( \mu_0(k) \):

\[
\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}
\]

(4)

In order to obtain an easy applicable EXAFS formalism one assumes that the radius of
the absorber \( r_i \) is regarded much smaller than the distance between the absorber \( i \) and the jth
shell (\( r_i << R_j \)). In that case the outgoing photoelectron can be considered as a plane wave at the
location of the backscattering atom. This leads to the single-scattering, plane-wave EXAFS
equation for a given atomic pair \( (ij) \) and at the K-edge of the X-ray absorber \( i \) (Stern and Heald,
1983):
\[ \chi_{ij}(k, \theta) = \sum_{j=1}^{N_{\text{cryst}}} 3 \left( \cos^2 \theta_j \right) \chi_{ij}^{\text{iso}}(k) \]  

where \( \theta_j \) is the angle between the electric field vector \( \mathbf{e} \) and the vector \( \mathbf{R}_{ij} \) that connects the absorbing atom \( i \) to the backscattering atom \( j \). \( \chi_{ij}^{\text{iso}} \) represents the isotropic contribution of the \( j \) shell and \( N_{\text{cryst}} \) stands for the crystallographic number of atoms in the \( j \) shell. For a completely random powder, there is no angular variation and \( \chi(k) \) reduces to:

\[ \chi_{ij}(k) = \sum_{j} \chi_{ij}^{\text{iso}}(k) \]  

with

\[ \chi_{ij}^{\text{iso}}(k) = \sum_{j} A_j(k) \cdot N_j \cdot \sin \left[ 2kR_{ij} + \delta_j(k) \right] \]  

The effective backscattering Amplitude \( A_j \) is defined as

\[ A_j(k) = \frac{S_0^2 e^{-2\sigma_j^2}}{kR_{ij}^2} \cdot F_j(k) \cdot e^{-2k^2\sigma_j^2} \]  

with

- \( N_j \): number of atoms in the \( j \)th shell
- \( R_{ij} \): mean distance between the absorber \( i \) and the \( j \)th shell
- \( F_j(k) \): the magnitude of the backscattering amplitude of the \( j \)th neighbor atom
- \( \delta_j(k) \): the phase shift due to the atomic potentials
- \( \lambda \): mean free path of the photoelectron due to the finite core hole lifetime,
- \( \sigma_j^2 \): relative mean square disorder parameter between the absorber \( i \) and an atom in the \( j \)th shell
- \( S_0^2 \): the amplitude reduction factor in coordination shell \( j \)

\[ k = \frac{2m(E - E_0)}{\hbar^2} = \frac{\hbar}{2\pi} \]  

\( E_0 \): threshold energy of the absorption process

The first term in equation (8) describes the damping, the second the scattering power and the third the disorder of the system.
\( \chi(k) \) can be obtained by series of data reduction steps of the absorption spectra. First, the background of the absorption spectra is usually be removed by fitting the pre-edge region by a low-order polynomial. The fitted polynomial is extrapolated beyond the edge and subtracted from the spectra. This step isolates the contribution of a particular absorption edge from the total absorption. Following background subtraction, the absorption intensity is normalized to a unit jump height by dividing the data through the edge jump at the absorption edge. To define the edge energy \( E_0 \), normally the inflection point (maximum in the first derivative) in the edge region is chosen. After converting the spectra from energy to \( k \) space the contribution of the atomic absorption (the absorption which would occur for a single atom) needs to be removed. A spline function is often used to model the atomic-like absorption; subtracting of the spline function leaves only contributions arising from the coordination environment of the adsorber, which is the \( \chi(k) \) function.

Fourier transformation (FT) of \( \chi(k) \) yields a spectrum in real space. This has the advantage that peaks in real space correspond to individual coordination shells, i.e. the real part of the FT gives a radial structure function (RSF). Generally phase shifts are not incorporated into the FT and thus the peaks in the FT spectrum correspond to atomic distances uncorrected for phase shifts \( \phi \). Furthermore the FT allows to isolate various shells by a backtransformation of selected FT peaks. Fourier transformation and Fourier-filtering of the experimental \( \chi(k) \) was first introduced by Sayers et al. (1971) into the EXAFS data analysis. FT is defined as:

\[
\text{FT}(r) = \frac{1}{\sqrt{2\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} k^n \chi(k)e^{2i\phi k} dk
\]

(9)

The weight factor \( k^n \) can be used to compensate for the decay in amplitude of the spectrum with increasing \( k \) values or to emphasize a particular part of the EXAFS spectrum. The structural parameters are obtained in the last step of data analysis by a fit of either experimental or theoretical phase and amplitude functions to the \( \chi(k) \) function, the FT function or the Fourier filtered \( \chi(k) \) function.

For more details about EXAFS theory and data analysis there are several reviews and books on EXAFS such as Sayers et al. (1971), Teo (1986), Sayers and Bunker (1988) and Stern (1988).

Application of EXAFS to the uptake mechanism of metal ions on clay minerals has severe limitations. In most cases, the reciprocal space explored by EXAFS is relatively limited (at best \( \Delta k = 14 \, \text{Å}^{-1} \)), which prevents the discrimination of atomic shells separated by less than 0.10 - 0.15 \( \text{Å} \) (Teo, 1986). This is typically the case in phyllosilicates. In montmorillonite, for
example, X-ray absorbing atoms of the octahedral sheet are surrounded by neighboring atoms
from the octahedral and tetrahedral sheets at R ~ 3.00 - 3.10 Å and R ~ 3.13 - 3.28 Å,
respectively. This local structure results in a strong overlap of scattering contributions from the
octahedral and tetrahedral cations, making any definitive structural interpretation of powder
EXAFS data for phyllosilicates difficult (Manceau, 1990). Manceau and co-workers showed
that this limitation can be overcome by polarized-EXAFS (P-EXAFS) spectroscopy. X-ray
synchrotron radiation is more than 95% linearly polarized in the central part of the horizontal
plane, and the degree of polarization is further enhanced by a Lorentz polarization effect in the
monochromatic process (Hazemann et al., 1992). Consequently, for noncubic compounds it is
possible to obtain angularly-resolved structural information by orienting an anisotropic sample
in the electric field vector (ε) of the X-ray beam. Initially P-EXAFS measurements on minerals
were performed on single crystals e.g. Manceau et al. (1988), but Manceau et al. (1998 and
1999) demonstrated that this technique can be extended to fine-grained layered minerals, such
as smectites. Its application requires strongly textured samples with a high degree of preferred
orientation. In the case of smectites, preparing self-supporting films, in which individual
platelets have their ab basal planes preferentially aligned parallel to the film surface, is
relatively easy.

In a self-supporting film individual clay platelets have their a and b axes randomly
distributed around the normal to the film plane and consequently θ varies from one crystallite
to another. Therefore it is necessary to introduce in equation (5) angles which are independent
of the orientation of layers in the film plane. Utilizing the axisymmetrical symmetry of self-
supporting films and assuming that individual platelets have their (001) basal plane perfectly
aligned parallel to the film plane one can write (Manceau et al., 1988)

\[
\langle \cos^2 \theta \rangle = \cos^2 \beta \sin^2 \alpha + (\sin^2 \beta \cos^2 \alpha) / 2 \tag{10}
\]

Where α is the angle between ε and the layer plane and β is the angle between \( \mathbf{R}_i \) and
the layer normal. Then

\[
X_{ij}^{\text{iso}}(k, \alpha) = \frac{N_{i\alpha}^{\text{exafs}}}{N_{\text{crystal}}^{\text{exafs}}} X_{ij}^{\text{iso}}(k) \tag{11}
\]

with the apparent coordination number (\( N_{i\alpha}^{\text{exafs}} \))
\[ \frac{N_{\text{exaf}}^{\text{exaf}}} {N_{\text{cryst}}^{\text{cryst}}} = 1 - \frac{1}{2} \left( 3 \cos^2 \beta - 1 \right) \left( 3 \cos^2 \alpha - 2 \right) \] (12)

Equation (11) can be simplified for two “magic angles”: \( N_{\text{exaf}} = N_{\text{cryst}} \) for \( \alpha = 35.3^\circ \), regardless of the value of \( \beta \), and for \( \beta = 54.7^\circ \), regardless of the value of \( \alpha \).

Assuming that individual clay platelets have their (001) basal plane perfectly aligned parallel to the film plane equation (12) describes the apparent coordination number \( (N_{\text{exaf}}^{\text{exaf}}) \) obtained in a P-EXAFS experiment. In P-EXAFS experiments with smectite films, the contribution of cations from the tetrahedral sheets (Al, Si) is minimized by orienting the layer \( ab \) plane parallel to \( \varepsilon \) and, conversely, the contribution of cations from the octahedral sheet (Al and Mg in montmorillonite) is extinguished in the perpendicular orientation of \( \varepsilon \). The higher the texture strength, the greater is the anisotropy of EXAFS spectra. It is therefore important to know the misalignment of clay particles for the P-EXAFS analysis. This information can be obtained by determine the orientation distribution (OD) of crystallites. The OD is measured by diffraction on a classical goniometer. For more details on texture analysis see Bunge and Esling (1982) and Manceau et al. (1998).
1.5 References


CHAPTER 2
NEOFORMATION OF NI PHYLLLOSILICATE UPON NI UPTAKE ON MONTMORILLONITE. A KINETICS STUDY BY POWDER AND POLARIZED EXAFS
Abstract

Wet chemistry kinetics and powder and polarized extended X-ray absorption fine structure (EXAFS and P-EXAFS) spectroscopy were combined to investigate the mechanism of Ni uptake on montmorillonite, at pH 8, high ionic strength (0.2 M Ca(NO₃)₂), initial Ni concentration of 660 μM, and solid concentration of 5.3 g/L. About 20 % of Ni sorbed within the first 24 h, thereafter the Ni uptake rate slowed down and 12 % of the initial Ni concentration remained in solution after 206 days of reaction time. Powder EXAFS spectra collected on wet pastes at 1, 14, 90 and 206 days showed the presence of Ni-Ni pairs at ~3.08 Å in an amount which gradually increased with time. Results were interpreted by the nucleation of a Ni phase having either an α-Ni-hydroxide or a Ni-phyllosilicate-like local structure. This alternative was left by recording P-EXAFS spectra of a highly textured self-supporting montmorillonite film prepared in the same conditions as the wet samples and equilibrated for 14 days. The orientation distribution of the c axes of individual clay particles off the film plane, as measured by quantitative texture analysis, was 32.8° FWHM (full width at half maximum), and this value was used to correct the effective numbers of Ni and Si nearest neighbors determined by P-EXAFS from texture effect. Ni atoms were found to be surrounded by 2.6 ± 0.5 Ni atoms at 3.08 Å in the in-plane direction, and by 4.2 ± 0.5 Si atoms at 3.26 Å in the out-of-plane direction. These structural parameters, but also the orientation and angular dependence of the Ni and Si shells strongly supported the formation of a Ni phyllosilicate having its layers parallel to the montmorillonite layers. The neoformation of a phyllosilicate upon metal uptake on montmorillonite, documented herein for the first time, has important geochemical implications because this dioctahedral smectite is abundant in the environment and that the resulting sequestration of sorbed trace metals in sparingly soluble phyllosilicate structure may durably decrease their migration.
2.1 Introduction

Smectites are widespread phyllosilicates in weathered continental formations and sediments. They possess a large specific area and a high structural charge (up to 1000 meq per kg) imparting them with important sorptive properties. Therefore, these minerals play a key role in the fate and mobility of contaminants in natural systems, and they are of special interest in nuclear waste management. They are major components of sedimentary rock formations, which are being considered as potential locations for nuclear waste repositories. Furthermore, it is planned that bentonite, a mixture of phyllosilicates consisting predominantly of the smectite montmorillonite, is used as a back-fill material in the near field for high level nuclear waste. Montmorillonite is available in large quantities in all parts of the world and is widely used in industry for the stabilization of molding-sand, cosmetics and the preparation of drilling muds.

From a structural standpoint, montmorillonite is a 2:1 phyllosilicate, and therefore possesses two tetrahedral sheets apart from the octahedral sheet (Fig. 1) (Güven, 1988). The generic half-cell chemical formula of montmorillonite is 
\[(\text{Si}_{4-x}\text{Al}_x)(\text{Al}_{2-y}\text{Mg}_y^2\text{M}^{2+}_{x+y})\text{O}_{10}(\text{OH})_2\text{E}^+_{x+y} \cdot n\text{H}_2\text{O}\], where E\(^+\) represents the interlayer cations, y and x the octahedral and tetrahedral substitutions (y > x for montmorillonite), respectively (Güven, 1988). The negative layer charge resulting from isomorphic substitutions is balanced by the sorption of exchangeable cations in interlayer sites (Sposito, 1984). The uptake kinetics of cation exchange is fast and exchangeable interlayer cations can be replaced by solute ions by varying the concentration of the aqueous ions (McBride et al., 1975; McBride, 1979; McBride, 1982; Sposito, 1984; Tang and Sparks, 1993; Chisholm-Brause et al., 1994; Verburg et al., 1995; Papelis and Hayes, 1996; Muller et al., 1997). In addition to cation exchange there is a pH-dependent uptake of metals on montmorillonite (Sposito, 1984). In this sorption process sorbate ions bond to the smectite surface by sharing one or several ligands (generally oxygens) with sorbent cations. With increasing pH or sorbate cation concentration, metal precipitation can occur. When the precipitate contains chemical species derived from both the aqueous solution and dissolution of the sorbent mineral, it is referred to as a coprecipitate (Stumm and Morgan, 1981).

Most studies on the uptake of contaminants in montmorillonite systems have been performed at the macroscopic level. Batch studies provide an efficient tool to determine distribution coefficients of metal ions and, under certain circumstances, they also allow differentiation between cation exchange and surface complexation processes occurring at the solid-water interface (Sposito, 1984). For example, the uptake of Ni on montmorillonite has been extensively investigated in our laboratory over a wide range of reaction conditions (pH,
ionic strength, initial metal concentration, and reaction time; Baeyens and Bradbury, 1997). Based on these data and the macroscopic surface properties of the clay (cation-exchange-capacity, surface charge) a ‘mechanistic’ surface complexation model was developed to predict the fate in the geosphere of radionuclides and other environmentally relevant metal ions (Bradbury and Baeyens, 1997). However, the ability of a particular surface complexation model to fit macroscopic data does not certify that this model is valid at the microscopic level. For example, macroscopic data does not allow unambiguous distinction between surface complexation and nucleation processes. A way to gain mechanistic information about metal interactions on solid surfaces is to combine batch studies with spectroscopic investigations. Using extended X-ray absorption fine structure (EXAFS), it has been demonstrated that Ni-, Co- and Zn-containing precipitates can form when clay minerals and Al- and Si-(hydr)oxides are treated with Ni, Co and Zn, and this even when the initial metal concentration in solution is undersaturated relative to the pure (oxyhydr)oxide forms of the metal (Towle et al., 1997; Scheidegger et al., 1998; Manceau et al., 1999b; Thompson et al., 1999a; Thompson et al., 1999b; Schlegel et al., 2001). Scheidegger et al. (1998) observed by EXAFS the formation of a layered double hydroxide (LDH) phase when pyrophyllite (a 2:1 clay which lacks isomorphic substitution) was treated with Ni. A Ni-Al LDH phase formed after a contact time between pyrophyllite and Ni of only a few minutes, suggesting that nucleation can occur rapidly in metal clay sorption systems. LDH formation has been reported for Co(II) and Zn(II) sorption on kaolinite and Al-(hydr)oxides (Towle et al., 1997; Thompson et al., 1999a; Thompson et al., 1999b). Similarly, the uptake of Co on quartz was shown to result in the neoformation of a trioctahedral clay-like structure (Manceau et al., 1999b).

Application of powder EXAFS to the uptake mechanism of metal ions on clay minerals has severe limitation. In most cases, the reciprocal space explored by EXAFS is relatively limited (at best $\Delta k = 14 \text{ Å}^{-1}$), which prevents the discrimination of atomic shells separated by less than 0.10 - 0.15 Å (Teo, 1986). This is typically the case in phyllosilicates. In montmorillonite, for example, X-ray absorbing atoms of the octahedral sheet are surrounded by neighboring atoms from the octahedral and tetrahedral sheets at $R \sim 3.00 - 3.10 \text{ Å}$ and $R \sim 3.13 - 3.28 \text{ Å}$, respectively (Fig. 1). This local structure results in a strong overlap of scattering contributions from the octahedral and tetrahedral cations, making any definitive structural interpretation of powder EXAFS data for phyllosilicates difficult (Manceau, 1990). Manceau and co-workers showed that this limitation can be overcome by polarized-EXAFS (P-EXAFS) spectroscopy.
X-ray synchrotron radiation is more than 95% linearly polarized in the central part of the horizontal plane, and the degree of polarization is further enhanced by Lorentz polarization effect in the monochromatic process (Hazemann et al., 1992). Consequently, for noncubic compounds it is possible to obtain angularly-resolved structural information by orienting an anisotropic sample in the electric field vector (\(\varepsilon\)) of the X-ray beam (Fig. 2). Early P-EXAFS measurements on minerals were performed on single crystals (Manceau et al., 1988), but Manceau et al. (1998, 1999a) demonstrated recently that this technique can be extended to fine-grained layered minerals, such as smectites. Its application requires strongly textured samples with a high degree of preferred orientation. In the case of smectites, preparing self-supporting films, in which individual platelets have their \(ab\) basal planes preferentially aligned parallel to the film surface, is relatively easy. The higher the texture strength, the greater is the anisotropy of EXAFS spectra. In P-EXAFS experiments with smectite films, the contribution of cations from the tetrahedral sheets (Al, Si) is minimized by orienting the layer \(ab\) plane parallel to \(\varepsilon\) and, conversely, the contribution of cations from the octahedral sheet (Al and Mg in montmorillonite) is extinguished in the perpendicular orientation of \(\varepsilon\). In P-EXAFS the apparent coordination number (\(CN_{\text{app}}^{\text{exafs}}\)) is (Schlegel et al., 1999):
\[
\frac{CN_{\text{exafs}}^{i,\alpha}}{CN_{\text{cryst}}^{j}} = 1 - \frac{\left(3\cos^2 \beta_j - 1\right)\left(3\cos^2 \alpha - 2\right)}{2}
\]  

(1)

with

\(\alpha\) = the angle between \(\varepsilon\) and the layer plane,

\(\beta\) = the angle between the film normal and the vector \((R_{ij})\) connecting the X-ray absorbing atom \(i\) to the backscattering atom \(j\),

\(CN_{\text{cryst}}^{j}\) = the crystallographic number of atoms in the \(j\) shell.

Equation (1) can be simplified for two "magic angles": \(CN_{\text{exafs}}^{i,\alpha} = CN_{\text{cryst}}^{j}\) for \(\alpha = 35.3^\circ\), regardless of the value of \(\beta\), and for \(\beta = 54.7^\circ\), regardless of the value of \(\alpha\).

![Figure 2](https://example.com/fig2.png)

Fig. 2: Orientation of the montmorillonite film with respect to the incoming X-ray beam: (left) electric field vector \(\varepsilon\) parallel to the layer plane; (right) \(\varepsilon\) perpendicular to the layer plane. After Schlegel et al. (1999a).
Schlegel et al. (2001) conducted P-EXAFS measurement with highly-oriented self-supporting hectorite films to investigate the impact of dissolved Si on the uptake of Zn at pH 7.3 and high Zn concentration ([Zn] = 520 μM) and ionic strength (0.3 M NaNO₃ solid/liquid ratio = 0.65 g/L). At low Si concentration (30 - 60 μM), small siliceous Zn polymers formed in structural continuity of the octahedral sheets of hectorite layers. At high Si concentration (530 μM), aqueous zinc and silicic acid formed a Zn phyllosilicate epitaxially grown on the edges of hectorite layers.

In this study, the uptake mechanism of Ni on montmorillonite at pH 8 and high Ni concentrations ([Ni] = 660 μM, solid/liquid ratio = 5.3 g/L) was investigated by EXAFS spectroscopy. The local structure around Ni atoms on montmorillonite was determined by P-EXAFS on dry films, and the possible evolution of the coordination environment of Ni with reaction time (1 - 206 days) was investigated by powder EXAFS on wet pastes.

2.2 Materials and Methods

2.2.1 Montmorillonite purification and characterization

The montmorillonite STx-1 used in this study was purchased from the Source Clay Minerals Repository of the Clay Minerals Society. XRD of the “as received” montmorillonite revealed the presence of minor quantities of calcite, quartz and kaolinite amounting to less than ~1 wt %. This natural clay contains ~0.9 % Fe₂O₃. It was thoroughly washed three times with 1 M NaClO₄ to convert the clay into the homo-ionic Na form. The < 0.5 μm size fraction was selected by successive washing with de-ionized water, combined with centrifugation (Baeyens and Bradbury, 1997). Soluble hydroxy-aluminium compounds were removed by acidic treatment (pH 3.5, for 1h) of the clay suspension. The pH was subsequently readjusted to 7.0. Possible traces of amorphous iron were dissolved by dithionate-citrate-bicarbonate treatment (Mehra and Jackson, 1960). With inductively coupled plasma optical emission spectroscopy (ICP-OES) and total digestion of the sample, the amount of extractable iron was determined to be approximately 30% of the total iron content. Sub-batches of clay suspensions were prepared at 0.2 M Ca(NO₃)₂ and 0.3 M NaClO₄ concentrations by dialysis (Baeyens and Bradbury, 1997). The final conditioned montmorillonite suspensions were stored at 4 °C in the dark to minimize microbial growth.

The cation exchange capacity (CEC) of the conditioned montmorillonite was determined to be 1010 meq kg⁻¹ by using the isotopic dilution method with Ca⁴⁵ (Baeyens and Bradbury, 1995a). The external surface area of the conditioned STx-1 Ca-montmorillonite was measured
by the N$_2$-BET technique to be 89 m$^2$g$^{-1}$. This value is in agreement with that determined by Van Olphen and Fripiat (84 m$^2$g$^{-1}$, Van Olphen and Fripiat, 1979).

2.2.2 Sample preparation for powder- and polarized-EXAFS

Powder EXAFS samples were prepared by adding 60 ml of a buffered Ni solution (pH 8.0, 1100 |μM, 0.2 M Ca(NO$_3$)$_2$) to 40 ml of a conditioned and purified Ca-montmorillonite suspension (pH 8.0, 0.2 M Ca(NO$_3$)$_2$; Baeyens and Bradbury, 1997) resulting in a solid to liquid ratio of 5.3 g/L and an initial Ni concentration of 660 |μM. It has been shown previously that the use of the buffer (4 mM Tris(hydroxymethyl)aminomethane adjusted with HNO$_3$ to pH 8) to maintain constant pH does not influence Ni uptake on montmorillonite (Baeyens and Bradbury, 1995b). The high ionic strength Ca electrolyte background was used to block cation exchange sites.

Ni uptake experiments were conducted in a glove box under N$_2$ atmosphere (CO$_2$ and O$_2$ < 5 ppm). Suspensions were centrifuged after a reaction time of 1, 14, 90 and 206 days. The wet pastes were filled into Plexiglas holders, then sealed and stored for 3 days in a refrigerator to keep them moist for powder EXAFS measurements. Ni, Al and Si concentrations in the supernatant solutions were measured by ICP-OES.

The initial Ni concentration (660 |μM) and the reaction pH (8.0) were chosen to achieve high Ni loadings on the montmorillonite while ensuring that the bulk solutions were undersaturated with respect to crystalline Ni(OH)$_2$(s). The theoretical solubility limit of Ni(OH)$_2$ in solution predicted from thermodynamic calculations were not particularly conclusive since log K$_{sp}$ (Ni(OH)$_2$) values reported in the literature varied over a wide range (~10.99 to -18.06) (Mattigod et al., 1997). Therefore, the stability of the Ni solution (pH 8, 1100 |μM [Ni], 0.2 M Ca(NO$_3$)$_2$) used for this study was checked over a time period of up to one year and it was observed that the Ni concentration in solution did not change. This finding is supported by Mattigod et al.’s study (1997), which showed that the solubility of Ni in Ni(OH)$_2$(s) at pH 8 (0.01 M NaClO$_4$) was > 3200 |μM after a reaction time of 90 days. Thus, it can be assumed that Ni removal from solution in our sorption system is not due to Ni(OH)$_2$(s) precipitation, as confirmed below by EXAFS results.

Based on thermodynamic constants compiled by Baes and Mesmer (1976) under the reaction conditions employed in this study ([Ni]$_{initial}$ = 660 |μM, pH = 8) Ni(II) was predominately present as Ni$^{2+}$ (aq.) ([Ni] = 6.55 × 10$^{-4}$ M) and the concentrations of hydrolyzed species such as Ni(OH)$^+$, Ni(OH)$_2^0$, Ni(OH)$_3^-$, Ni(OH)$_2^{2-}$, Ni$_2$(OH)$_3^{3+}$ and Ni$_4$(OH)$_4^{4+}$ were altogether < 10$^{-5}$ M.
A P-EXAFS sample was prepared by adding 200 ml of a buffered Ni solution (pH 8.0, 4 mM Tris(hydroxymethyl)-aminomethane, 0.3 M NaClO₄) to 40 ml of a conditioned and purified Na-montmorillonite suspension (pH 8.0, 0.3 M NaClO₄). The resulting solid to liquid ratio was 2.14 g/L and the initial Ni concentration was 660 µM. After 14 days of reaction time, 40 ml of the suspension was slowly filtrated through 47 mm diameter filters (Millipore, 0.4 µm pore size) and a highly oriented self-supporting film was prepared. The filtration was performed in a closed vessel under a continuous flow of argon. Excess of solution in the wet film was removed by washing with a few milliliters of de-ionized water before drying. Again, the supernatant solution was analyzed for Ni, Si and Al by ICP-OES. The Ni weight concentration in the clay film was low enough (0.65 wt%) to eliminate self-absorption effects (Tröger et al., 1992; Castañer and Prieto, 1997). The dried clay film was cut into 8 slices and stacked on a sample holder in order to get a sufficient thickness for measurements in fluorescence detection mode.

2.2.3 Quantitative texture analysis

X-ray diffraction texture analysis measurements were performed in reflection mode using a Huber texture goniometer mounted on a classical X-ray source. A point-focus incident beam of 0.5 x 0.5 mm and Cu Kα radiation were used. One slice of the self-supporting film was mounted on a single-crystal silicon wafer in order to avoid any background interference in the measurements. Pole figures were measured using a position sensitive curved detector (INEL CPS 120) having a 2θmax = 120° (Ricote and Chateigner, 1999). This configuration allows a rapid measurement (i.e., without Bragg angle scanning) of the whole profile of a given diffraction peak at each tilt angle (p) between the film plane and the diffraction plane. Previous measurements on similarly prepared films indicated that smectite films have an axially-symmetric (fiber) texture, with the fiber axis aligned along the normal to the sample plane (Manceau et al., 1998). Consequently, the complete film texture can be obtained by measuring the inclination of {001} crystallographic planes off the sample surface. This was achieved by selecting the (004) reflection and scanning the tilt angle from p = 0 to p = 85°, in 5° steps, with an integration time of 2h for each tilt angle position. The densities of the orientation distribution were calculated from the ρ-scan integrated intensities using direct normalization and taking a density of zero for ρ > 80° (for details see Manceau et al., 2000b). Distribution densities are expressed as ‘multiple of a random distribution’ or ‘mrd’ (Bunge and Esling, 1982), a perfectly random sample exhibiting a value of 1 mrd.
2.2.4 EXAFS data collection and reduction

Ni K-edge XAFS spectra were recorded on the X-11A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. All spectra were recorded at room temperature using a Si(111) monochromator and a 13-element Ge solid-state detector (Canberra). Higher order harmonics were suppressed by detuning the monochromator by 20% from the maximum intensity. The monochromator angle was calibrated by assigning to 8333 eV the first inflection point of the K-absorption edge spectrum of Ni metal. Powder-EXAFS spectra were recorded at \( \alpha = 45^\circ \) and P-EXAFS spectra at \( \alpha = 10^\circ, 35^\circ, 55^\circ \), and \( 80^\circ \). Several scans were averaged to improve the signal to noise ratio.

Data reduction was carried out with the WinXAS 97 1.3 software package (Ressler, 1998). The energy was converted to photoelectron wave vector units (Å\(^{-1}\)) by assigning the origin \( E_0 \) to the first inflection point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming \( k^2 \)-weighted \( \chi(k) \) functions between 3.2 and 10 Å\(^{-1}\) using a Bessel window function with a smoothing parameter of 4. Amplitude and phase shift functions were calculated with FEFF 8.0 (Rehr et al., 1991) using the structures of \( \beta \)-Ni(OH)\(_2\) and Ni-Talc (Perdikatis and Burzlaff, 1981) as references. Fits were performed in R space in the 0.6 to 3.5 Å interval. The amplitude reduction factor (\( S_0^2 \)) was determined to be 0.85 from the experimental \( \beta \)-Ni(OH)\(_2\) EXAFS spectrum. The deviation between the fitted and the experimental spectra (%Res) is given by:

\[
\text{%Res} = \frac{\sum_{i=1}^{N} |y_{\text{exp}}(i) - y_{\text{theo}}(i)|}{\sum_{i=1}^{N} y_{\text{exp}}(i)} \cdot 100
\]

where \( N \) is the number of points in the fit window, and \( y_{\text{exp}} \) and \( y_{\text{theo}} \) are the experimental and theoretical RSF values. The precision on the powder and P-EXAFS distances (R) was previously estimated to be \( \pm 0.02 \) Å for \( R_{\text{Ni-1-O}} \), and \( \pm 0.03 \) Å for \( R_{\text{Ni-Ni}} \) and \( R_{\text{Ni-St}} \), and \( \pm 0.5 \) for the coordination numbers (CN) (Scheidegger et al., 1998; Schlegel et al., 2002). The experimental uncertainty on \( \alpha \) in the P-EXAFS measurements is \( \pm 1^\circ \).
2.3 Results

2.3.1 Ni uptake kinetics

Fig. 3 shows the total amount and proportion of Ni uptake on montmorillonite over a time period of 1 to 206 days (pH = 8, [Ni]_{initial} = 660 μM, ionic strength = 0.2 M Ca(NO₃)₂, solid/liquid = 5.3 g/L). Sixteen percent of initial Ni was removed from solution after one day. The Ni uptake rate then gradually decreased with increasing reaction time, and the proportion of Ni uptaken amounted to 37% after 14 days, 77% after 90 days and 88% after 206 days. The total amount of Ni taken up by montmorillonite varied from 20 μmol/g after 1 day to 110 μmol/g after 206 days.

The insert in the figure shows the logarithm of the distribution ratio (RD) as a function of reaction time. RD is defined as:

\[ RD = \frac{C_{init} - C_t}{C_t} \cdot \frac{V}{m} \]

where:
- \( C_{init} \) = initial aqueous Ni concentration
- \( C_t \) = aqueous Ni concentration measured at time \( t \) days
- \( V \) = volume of liquid phase (L)
- \( m \) = mass of solid phase (kg)

The log \( RD \) values varied between 3.0 and 4.6. The variations of Si and Al concentrations in solution during the experiment were also monitored. The Si concentration ([Si]_aq) increased with increasing reaction time: 177 μM (1 day), 354 μM (14 days), 448 μM (90 days) and 580 μM (206 days). This evolution was linear between 14 days and 206 days (\( r^2 = 0.99 \)), corresponding to a constant Si release rate of \( 3.5 \times 10^{-14} \) mol m\(^{-2}\) s\(^{-1}\) (pH = 8.0; time range 14 - 206 days). This measured rate agrees with published values for the dissolution of montmorillonite: \( 3.2 \times 10^{-14} \) mol m\(^{-2}\) s\(^{-1}\) at pH = 7.5 (Scheidegger et al., 1997); \( 5.4 \times 10^{-14} \) mol m\(^{-2}\) s\(^{-1}\) at pH = 5 (Furrer et al., 1993), and \( 1 \times 10^{-15} \) mol m\(^{-2}\) s\(^{-1}\) at pH = 6 (Heydemann, 1966). The Al concentration was too low (< 0.22 μM) to produce reliable ICP-OES measurements.
Fig. 3: Ni uptake kinetics on montmorillonite. The amount of sorbed Ni (μmol/g), the relative Ni uptake (%), and the logarithm of the distribution ratio $R_D$ (insert) are plotted as a function of reaction time (days) ($pH = 8$, ionic strength = 0.2 M Ca(NO$_3$)$_2$, $[Ni]_{init} = 660$ μM, solid/liquid = 5.3 g/L).

### 2.3.2 Powder EXAFS

#### 2.3.2.1 EXAFS spectra

$k^3$-weighted EXAFS spectra for montmorillonite treated with Ni at pH 8 for 1, 14, 90 and 206 days are shown in Fig. 4a (Ni loading: 20 - 110 μmol/g). All spectra have a clear beat pattern at $k = 5$ Å$^{-1}$ and a multifrequency wave shape. These features indicate the presence of more than one ordered neighboring shell around Ni atoms, and therefore that outer-sphere complexation is not the predominant sorption mode. The node at about $k = 5$ Å$^{-1}$ gradually increases in intensity with increasing reaction time, and the spectral feature between 7 - 9 Å$^{-1}$ seemingly evolves with time, though this evolution is partly obscured by the spectral noise at low Ni loading. These two spectral modifications indicate a change of Ni coordination chemistry over time.
Fig. 4: a) $k^3$-weighted Ni K-edge EXAFS spectra of montmorillonite reacted with Ni for different reaction times (1, 14, 90, 206 days, [Ni] = 20 - 110 μmol/g, pH 8). The arrow indicates the appearance of a distinct feature at ~5.3 Å$^{-1}$ with increasing reaction time. b) $k^3$-weighted Ni K-edge EXAFS spectra of takovite (LDH compound).
2.3.2.2 Radial Structure Functions (RSFs) and simulations

The RSFs corresponding to EXAFS spectra presented Fig. 4a are shown in Fig. 5. The amplitude and position of first RSFs peaks (Ni-O contribution) are invariant with reaction time. The second RSFs peaks, however, increase in amplitude with time, but their positions remain constant. The R + ΔR position of ~2.75 Å (dotted line in Fig. 5) was observed in α-Ni(OH)₂, Ni-bearing clays and Ni-Al LDHs, and is characteristic of Ni-Ni interaction (Manceau and Calas, 1986; Manseau, 1990; Pandya et al., 1990; O'Day et al., 1994; Scheidegger et al., 1996a; Scheidegger et al., 1997; Mansour and Melendres, 1998; Scheidegger et al., 1998; Scheinost et al., 1999). This result indicates that Ni polymerized and that this phenomenon was induced by the clay since the Ni solution was undersaturated with respect to Ni(OH)₂(s).

Three nucleation products resulting from metal uptake on clay minerals have been suggested in the literature so far: (i) Ni-Al LDH (Scheidegger et al., 1998; Thompson et al., 1999a), (ii) oc-Ni(OH)₂ (Scheinost et al., 1999) and (iii) Zn-phyllosilicate (Schlegel et al., 2001). The possible nature of this precipitate is examined below.

(i) Ni-Al LDH (fit with O, Ni and Al). The assumption of a Ni-Al contribution in the numerical simulation yielded interatomic distances (R_{NI-Al} = 3.32 Å) incompatible with synthetic and natural Ni-Al LDH phases (3.03 - 3.07 Å; Scheidegger et al., 1998; Thompson et al., 1999a). Scheinost and Sparks (2000) showed that the χ(k²) spectrum for Ni-Al LDHs has a characteristic beat pattern between 8.0 and 8.5 Å⁻¹ which can be used as a fingerprint to unequivocally identify this species. This beat pattern is illustrated in Fig. 4b for takovite (Ni₆Al₂(OH)₁₆CO₃·H₂O; Scheidegger et al., 1997), and comparison of this spectrum with Ni treated montmorillonite supports the conclusion that no Ni-Al LDH phase formed in our montmorillonite samples.

(ii) oc-Ni(OH)₂ (fit with O and Ni). Structural parameters obtained from this two-shell fit are listed in Table 1. The EXAFS coordination number of the first shell (CN_{Ni,O}) is 5.3 ± 0.5. The bond distance (2.05 Å) is typical of six-fold coordinated Ni (Pandya et al., 1990). According to this structural model, Ni would be surrounded by 2.6 (t = 1d) to 5.8 (t = 206 d) neighboring Ni atoms at 3.07 - 3.08 Å. The increase of CN_{Ni,Ni} with reaction time suggests the nucleation and growth of a Ni phase. CN_{Ni,Ni} and R_{Ni-Ni} values of ~5.5 and ~3.08 Å, respectively, were reported previously for α-Ni(OH)₂ (Pandya et al., 1990; Scheinost and Sparks, 2000) and, therefore, the precipitation of this phase cannot be excluded on the basis of powder EXAFS spectroscopy. The formation of β-Ni(OH)₂, the most stable form of Ni(OH)₂, can be dismissed because in this polymorph R_{Ni-Ni} equals 3.12 - 3.13 Å (Pandya et al., 1990).
Fig. 5: Ni K-edge RSFs of montmorillonite treated with Ni for different reaction times (1, 14, 90, 206 days, 20 - 110 μmol/g, pH 8). The dashed line indicates the position of the Ni-Ni contribution in α-Ni(OH)₂ Ni-LDH and Ni-phyllosilicate.

Table 1: Structural information derived from the EXAFS analysis using a two-shell fit approach.

<table>
<thead>
<tr>
<th>Reaction time [days]</th>
<th>CN_{Ni-O}</th>
<th>R_{Ni-O} [Å]</th>
<th>σ²_{Ni-O} [Å²]</th>
<th>CN_{Ni-Ni}</th>
<th>R_{Ni-Ni} [Å]</th>
<th>σ²_{Ni-Ni} [Å²]</th>
<th>ΔE₀ [eV]</th>
<th>%Res</th>
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<td>0.006f</td>
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<td>0.008f</td>
<td>0.4</td>
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<td>2.06</td>
<td>0.006f</td>
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<td>0.008f</td>
<td>1.9</td>
<td>9.6</td>
</tr>
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<td>0.006f</td>
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<td>0.008f</td>
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</tr>
<tr>
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<td>0.006f</td>
<td>5.8</td>
<td>3.08</td>
<td>0.008f</td>
<td>2.5</td>
<td>7.7</td>
</tr>
</tbody>
</table>

CN, R, σ², ΔE₀ are the coordination numbers, interatomic distances, Debye-Waller factors and inner potential corrections. f: σ values were determined by P-EXAFS and fixed in the analysis of powder EXAFS spectra. The deviation between least-squares fitted and experimental spectra is given by the residual in percent, %Res.
Ni phyllosilicate (fit with O, Ni and Si). Results corresponding to this structural model are given in Table 2. The parameters for the first shell are logically identical to those of the previous model (CN\textsubscript{Ni-O} \sim 5.1 - 5.3 at R\textsubscript{Ni-O} \sim 2.04 - 2.05 Å). The CN\textsubscript{Ni-Ni} values increased from 1.6 to 4.3 with reaction time as compared to 2.6 to 5.8 in the previous model. The number of Si neighbors (CN\textsubscript{Ni-Si}) was as high as \sim 3.0 after only one day of uptake, and then stabilized to \sim 3.7 from 14 to 206 days. The Ni-Ni and Ni-Si distances (R\textsubscript{Ni-Ni} = 3.07 - 3.09 Å and R\textsubscript{Ni-Si} = 3.25 - 3.27 Å) well match those in Ni phyllosilicates (R\textsubscript{Ni-Ni} = 3.05 - 3.08, R\textsubscript{Ni-Si} = 3.26 - 3.27; Manceau and Calas, 1986; Charlet and Manceau, 1994).

With the exception of CN\textsubscript{Ni-Si} values, structural parameters for the nearest (Ni-O) and next-nearest (Ni-(Ni,Si)) coordination shells were not modified by the addition of the Si shell in the spectral fit. CN\textsubscript{Ni-Ni} was higher when no Si backscattering shell was included in the fit because Ni-Ni and Ni-Si contributions at distances characteristic for Ni-hydroxides (R\textsubscript{Ni-Ni} \sim 3.1 Å) and Ni-phyllosilicates (R\textsubscript{Ni-Ni} \sim 3.1 Å, R\textsubscript{Ni-Si} \sim 3.2 - 3.3 Å) interfere (Manceau and Calas, 1986; Manceau, 1990). This phenomenon is illustrated in Fig. 6, which compares the FEFF 8 simulated contribution of two Ni atoms at 3.08 Å and two Si atoms at 3.26 Å. Over an extended k-range (4 - 11 Å\textsuperscript{-1}) the two EXAFS contributions are almost in phase and, therefore, the positive interference of the oscillations causes the coordination number of Ni to decrease when experimental data are fitted with Ni and Si shells instead of Ni only.

To further emphasize the problem arising from the overlap of the Ni and Si contributions, Fig. 7 shows the experimental and simulated Fourier transforms (FTs) for the montmorillonite sample reacted with Ni for 90 days. In spectrum a), Ni-O and Ni-Ni, and in spectrum b), Ni-O, Ni-Ni and Ni-Si, atomic pairs were included in the numerical simulation. Omission of the Si shell results in a small misfit of the imaginary part (%Res increased by 70 - 400%). It will be shown below that the two overlapping Ni-Ni and Ni-Si contributions could be successfully separated by P-EXAFS, thereby allowing us to choose between hypothesis two and three (i.e., \textalpha-Ni(OH\textsubscript{2} vs. Ni phyllosilicate).

Table 2: Structural information derived from the EXAFS analysis using a three-shell fit approach.

<table>
<thead>
<tr>
<th>reaction</th>
<th>Ni-O</th>
<th>Ni-Ni</th>
<th>Ni-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>CN\textsubscript{Ni-O}</td>
<td>R\textsubscript{Ni-O} [Å]</td>
<td>\sigma\textsuperscript{2} [Å\textsuperscript{2}]</td>
</tr>
<tr>
<td>[days]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.2</td>
<td>2.04</td>
<td>0.006f</td>
</tr>
<tr>
<td>14</td>
<td>5.3</td>
<td>2.05</td>
<td>0.006f</td>
</tr>
<tr>
<td>90</td>
<td>5.1</td>
<td>2.04</td>
<td>0.006f</td>
</tr>
<tr>
<td>206</td>
<td>5.3</td>
<td>2.05</td>
<td>0.006f</td>
</tr>
</tbody>
</table>

f: fixed to the value obtained by P-EXAFS.
Fig. 6: Simulation of $k^3$-weighted EXAFS contributions for two Ni-Ni pairs at 3.08 Å (solid line) and two Ni-Si pairs at 3.26 Å (dashed line). Spectra were calculated using FEFF 8 (Rehr et al., 1991). The $S_0$ and $\sigma^2$ values chosen for the simulation correspond to those determined from experimental spectra ($S_0=0.85$ and $\sigma^2=0.008 \text{ Å}^2$).

Fig. 7: Experimental and theoretical Fourier transforms (modulus and imaginary parts) of Ni K-edge EXAFS spectra for montmorillonite equilibrated with aqueous Ni (111 μmol/g) at pH 8 for 90 days. The simulations were performed by assuming either Ni-O and Ni-Ni (a), or Ni-O, Ni-Ni and Ni-Si (b) pairs. Solid line: experimental data, dotted line: least-squares fit.
2.3.3 Texture analysis

The distribution density of $c^*$ axes perpendicularly to the film plane, obtained from the variation of the diffracted intensity of the (004) reflection with the inclination $\rho$ angle, is shown in Fig. 8b. This plot corresponds to a radial cut of the (004) normalized pole figure presented in Fig. 8a. At $\rho = 0$ we observe a strong maximum with a density value of approximately 13 mrd, which indicates that most of montmorillonite platelets have their $(a,b)$ planes aligned parallel to the film plane. This texture strength is appreciably lower than that obtained when films are elaborated on a single crystal substrate as for HgI$_2$ thin films on (001)-KCl (up to 248 mrd) (Chateigner and Erler, 1997). The epitaxial-like control of the crystallites orientation is absent in the preparation of self-supporting clay films, and the orientation of the clay platelets is partly determined by their aggregation state, shape, and interaction with the solution during the deposition. However, the texture strength of the montmorillonite sample is similar to that measured for biotite (considered to have high texture levels) in highly deformed rocks (6 mrd) (Chateigner et al., 1999). The experimental $\rho$-scan curve was best-fitted with a Lorentzian distribution (solid line in Fig. 8b) having a full-width at half maximum (FWHM) of 32.8°. Manceau and Schlegel (2001) showed that no significant attenuation of the angular dependence of P-EXAFS spectra occurs when the dispersion spread of crystallites is less than 40 - 50° FWHM for parallel measurements ($\alpha = 0^\circ$, Fig. 2) and 30 - 40° FWHM for normal measurements ($\alpha = 90^\circ$, Fig. 2). Since the montmorillonite film has a FWHM dispersion of $\sim 33^\circ$, P-EXAFS spectra can be analyzed as a first approximation as a single-crystal.
Fig. 8: a) (004) normalized pole figure projected on the sample plane for the self-supporting montmorillonite film (linear scale, equal area projection). b) Integrated radial distribution densities of the c^- axes of montmorillonite crystals with respect to the normal of the film plane (\(\rho = 0^\circ\)).
2.3.4 P-EXAFS

In order to check that the drying of the film did not modify the overall coordination chemistry of Ni, the P-EXAFS spectrum of the film sample recorded at the magic angle was compared first to the powder EXAFS spectrum of a wet paste. The film and the paste samples contained a similar amount of Ni: 111 μmol/g for the former and 96 μmol/g Ni for the latter. Fig. 9 shows that these two spectra are almost identical, meaning that structural results obtained on the film could be safely compared to those obtained on wet pastes.

![Graph showing k^3-weighted Ni K-edge EXAFS spectra](image)

Fig. 9: Comparison of k^3-weighted Ni K-edge EXAFS spectra for a self-supporting film at α = 35° (111 μmol/g Ni, dotted line) and for a wet paste (96 μmol/g Ni, solid line).

Fig. 10 shows the angular dependence of the k^3χ(k) spectrum for the Ni treated montmorillonite film. With increasing α angle, the intensity of the shoulder at 5.3 Å⁻¹ increases and the wave frequency at 5.3 Å⁻¹ and 7.5 Å⁻¹ shifts. The changes in spectral shape and frequency indicate that the coordination chemistry of Ni is anisotropic and, specifically, that its coordination environment is oriented with respect to clay layers. The spectra clearly contain several isosbestic points, for which χ(k) is independent of k, over the whole k range. Isosbestic points are very sensitive to normalization errors during the reduction of raw X-ray absorption spectra. The fact that all the individual χ(k,α) spectra precisely cross at the same value in these
points provides a stringent proof of the reliability of P-EXAFS spectra even at high k values where the noise is the highest.

Fig. 10: $k^3$-weighted Ni K-edge P-EXAFS spectra of a Ni treated montmorillonite film at $\alpha$ angles of 10°, 35°, 55° and 80° (111 μmol/g, pH 8). The arrows points the two most important anisotropic spectral features.

Fig. 11 shows the experimental and simulated FTs of the Ni treated montmorillonite film. The amplitude of the first (Ni-O contribution) and second (Ni-Ni and Ni-Si contribution) RSF peaks decreases with increasing $\alpha$ angle, and the position of the second peak slightly shifts from $R + \Delta R = 2.75$ Å (a typical peak position for a Ni-Ni pair in sheet silicates, Manceau and Calas, 1986) at $\alpha = 10^\circ$ to $R + \Delta R = 2.8$ Å at $\alpha = 80^\circ$. Interestingly, this shift is associated with a displacement in opposite direction of the imaginary part in such an amount that at $\alpha = 80^\circ$ the maximum of the peak modulus and the minimum of the imaginary part are at the same $R + \Delta R$ position. This noteworthy angular evolution indicates that Ni has a different parallel and perpendicular local structure. Structural parameters derived from the data analysis of P-EXAFS spectra are reported in Table 3. Attempts to fit the second FT peak at $\alpha = 80^\circ$ with Ni-Ni and Ni-Si pairs failed, and a good fit was obtained with a single Si shell ($CN_{Ni-Si}^{\text{exaf}} = 6.0 \pm 0.5$, $R_{Ni-Si} = 3.26$ Å, $\sigma^2_{Ni-Si} = 0.008$ Å$^2$). This short range order in the perpendicular orientation is
characteristic of phyllosilicate-like structures (Manceau et al., 1998). To reduce the degree of freedom of the numerical simulations for $\alpha < 80^\circ$, some EXAFS parameters were constrained: $R_{\text{Ni-Si}}$ and $\sigma^2_{\text{Ni-Si}}$ were fixed to their values at $\alpha = 80^\circ$, and then held fixed at $\alpha \neq 80^\circ$. $R_{\text{Ni-Ni}}$, $\sigma^2_{\text{Ni-O}}$, $\sigma^2_{\text{Ni-Ni}}$, and the inner potential correction parameter, $\Delta E_0$, were determined at $\alpha = 35^\circ$, and then held fixed at $\alpha \neq 35^\circ$. At $\alpha = 10^\circ$ this fitting procedure resulted in $CN_{\text{exafs}}^{\text{Ni-Ni}} = 3.9 \pm 0.5$ at 3.08 Å and $CN_{\text{exafs}}^{\text{Ni-Si}} = 3.2 \pm 0.5$ at 3.26 Å (Table 3). With increasing angle, $CN_{\text{exafs}}^{\text{Ni-Ni}}$ decreased (e.g. $CN_{\text{exafs}}^{\text{Ni-Ni}} = 1.4 \pm 0.5$ at $\alpha = 55^\circ$) whereas $CN_{\text{exafs}}^{\text{Ni-Si}}$ increased (e.g. $CN_{\text{exafs}}^{\text{Ni-Si}} = 6.0 \pm 0.5$ at $\alpha = 80^\circ$). In contrast to the Ni-Si pair, which was detected at all angles, the Ni-Ni pair was completely extinguished in the perpendicular orientation.

Table 3: Structural information derived from the P-EXAFS analysis.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$CN_{\text{exafs}}^{\text{Ni-O}}$</th>
<th>$R_{\text{Ni-O}}$ [Å]</th>
<th>$\sigma^2_{\text{Ni-O}}$ [Å$^2$]</th>
<th>$CN_{\text{exafs}}^{\text{Ni-Ni}}$</th>
<th>$R_{\text{Ni-Ni}}$ [Å]</th>
<th>$\sigma^2_{\text{Ni-Ni}}$ [Å$^2$]</th>
<th>$CN_{\text{exafs}}^{\text{Ni-Si}}$</th>
<th>$R_{\text{Ni-Si}}$ [Å]</th>
<th>$\sigma^2_{\text{Ni-Si}}$ [Å$^2$]</th>
<th>$\Delta E_0$ [eV]</th>
<th>%Res</th>
</tr>
</thead>
<tbody>
<tr>
<td>10$^\circ$</td>
<td>5.7</td>
<td>2.04$^f$</td>
<td>0.006$^f$</td>
<td>3.9</td>
<td>3.08$^f$</td>
<td>0.008$^f$</td>
<td>3.2</td>
<td>3.26$^a$</td>
<td>0.008$^a$</td>
<td>1.4$^f$</td>
<td>2.0</td>
</tr>
<tr>
<td>35$^\circ$</td>
<td>5.4</td>
<td>2.04</td>
<td>0.006</td>
<td>2.6</td>
<td>3.08</td>
<td>0.008</td>
<td>4.2</td>
<td>3.26$^a$</td>
<td>0.008$^a$</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>55$^\circ$</td>
<td>5.0</td>
<td>2.04$^f$</td>
<td>0.006$^f$</td>
<td>1.4</td>
<td>3.08$^f$</td>
<td>0.008$^f$</td>
<td>5.2</td>
<td>3.26$^a$</td>
<td>0.008$^a$</td>
<td>1.4$^f$</td>
<td>3.3</td>
</tr>
<tr>
<td>80$^\circ$</td>
<td>4.6</td>
<td>2.04</td>
<td>0.006</td>
<td>6.0</td>
<td>3.26</td>
<td>0.008</td>
<td>1.4$^f$</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$CN_{\text{exafs}}$, $R$, $\sigma^2$, $\Delta E_0$ are the apparent coordination numbers, interatomic distances, Debye-Waller factors and inner potential corrections. $a$: fixed to the value determined at $\alpha = 80^\circ$; $f$: fixed to the value determined at $\alpha = 35^\circ$. 
Fig. 11: Polarization dependence of the Fourier transforms (modulus and imaginary parts) obtained from the EXAFS spectra presented in Fig. 10. The dash-dotted line indicates the position of the Ni-Ni contribution in α-Ni(OH)$_2$, Ni-LDH and Ni-phylllosilicate. Solid line: experimental data, dotted line: least-squares fit.
The $R_{\text{Ni-O}}$, $R_{\text{Ni-Ni}}$, and $R_{\text{Ni-Si}}$ values are characteristic of edge-sharing linkages between Ni octahedra and of corner-sharing linkages between Ni octahedra and Si tetrahedra (Manceau and Calas, 1986; Manceau, 1990), and thus suggest the formation of a phyllosilicate-like Ni phase. This interpretation is strengthened by the angular variations of $CN_{\text{Ni-Ni}}^{\text{exafs}}$ and $CN_{\text{Ni-Si}}^{\text{exafs}}$. The gradual decrease of $CN_{\text{Ni-Ni}}^{\text{exafs}}$ and increase of $CN_{\text{Ni-Si}}^{\text{exafs}}$ with increasing $\alpha$ implies $\beta_{\text{Ni-Ni}} > 54.7^\circ$ and $\beta_{\text{Ni-Si}} < 54.7^\circ$ (see Eq. [1]), as in phyllosilicate structures (Table 3). The $\beta$ angle of the Ni-Ni and Ni-Si pairs was calculated from Eq. [1] assuming a perfectly textured sample. Eq. [1] can be written as

$$\frac{CN_{j,\alpha}^{\text{exafs}}}{CN_{j}^{\text{cryst}}} = \frac{3}{2} \left( 1 - 3 \cos^2 \beta_j \right) \cdot \cos^2 \alpha + 3 \cos^2 \beta_j \quad (2)$$

$$\frac{CN_{j,\alpha}^{\text{exafs}}}{CN_{j}^{\text{cryst}}} = a \cdot \cos^2 \alpha + b \quad (3)$$

where ‘a’ and ‘b’ are regression coefficients. ‘a’ can be calculated from the linear regression of $CN_{j,\alpha}^{\text{exafs}}/CN_{j}^{\text{cryst}}$ with respect to $\cos^2 \alpha$ and the experimental $\beta_i$ value is obtained from:

$$\beta_{j}^{\text{exp}} = \arccos \sqrt{\frac{3 - 2a}{9}} \quad (4)$$

$CN_{\text{Ni-Ni}}^{\text{exafs}}$ and $CN_{\text{Ni-Si}}^{\text{exafs}}$ as a function of $\cos^2 \alpha$ are plotted in Fig. 12. Good linear correlations were obtained with regression coefficients $r^2 > 0.99$. Application of formula (4) yielded $\beta_{\text{Ni-Ni}} = 84^\circ$, thus indicating that Ni-Ni pairs are oriented essentially parallel to the film plane, as in phyllosilicates (Güven, 1988). The same procedure for the Ni-Si pair yielded $\beta_{\text{Ni-Si}} = 46^\circ$ in keeping with the off plane orientation of this pair as suggested previously ($\beta < 54.7^\circ$). The precision on $\beta$ was estimated to $\pm 9^\circ$ for $\beta_{\text{Ni-Ni}}$ and $\pm 12^\circ$ for $\beta_{\text{Ni-Si}}$ at the 95 % confidence level from the dispersion of $CN_{j,\alpha}^{\text{exafs}}$. The two experimental $\beta$ angles match within uncertainty with crystallographic values for montmorillonite (90° for the Oct-Oct pair and 34 - 35° for the Oct-Tet pair; Tsipursky and Drits, 1984). However, an even better match was obtained by correcting these values from the imperfect orientation of montmorillonite particles in the film plane using graphs published by Manceau and Schlegel (2001): $\beta_{\text{Ni-Si}}^{\text{real}} = 43^\circ$ and $\beta_{\text{Ni-Ni}}^{\text{real}} = 90^\circ$. 

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**Equations**

1. $\frac{CN_{j,\alpha}^{\text{exafs}}}{CN_{j}^{\text{cryst}}} = \frac{3}{2} \left( 1 - 3 \cos^2 \beta_j \right) \cdot \cos^2 \alpha + 3 \cos^2 \beta_j$
2. $\frac{CN_{j,\alpha}^{\text{exafs}}}{CN_{j}^{\text{cryst}}} = a \cdot \cos^2 \alpha + b$
3. $\beta_{j}^{\text{exp}} = \arccos \sqrt{\frac{3 - 2a}{9}}$
Fig. 12: Angular dependence of $CN_{\text{Ni-Ni}}^{\text{exafs}}$ (a) and $CN_{\text{Ni-Si}}^{\text{exafs}}$ (b). Points: experimental data, solid line: linear regression. $CN_{\text{Ni-Ni}}^{\text{exafs}} = 3.89 \cdot \cos^2 \alpha$ and $CN_{\text{Ni-Si}}^{\text{exafs}} = -2.97 \cdot \cos^2 \alpha + 6.14$ (solid lines). The uncertainty on CN is estimated to ± 0.5.
2.4 Discussion

2.4.1 Ni uptake kinetics and nature of the Ni precipitate formed

The study on the kinetics of Ni uptake on montmorillonite indicates that ~20 % of Ni sorbed within 24 h (pH 8, [Ni]_{initial} = 660 \mu M, 0.3 M Ca(NO_3)_2). Afterwards the Ni uptake rate decreased considerably, and the reaction was not complete even after a reaction time of 206 days (12 % of the initial Ni concentration remained in solution) (Fig. 3). The observed kinetics is common for transition metal uptake on clay and oxide surfaces (Kinniburgh and Jackson, 1981; Brümmer et al., 1988; Scheidegger et al., 1996a; Scheidegger et al., 1998; Schlegel et al., 2002). Traditionally, adsorption (strictly a two-dimensional process) is considered to be the predominant sorption mode responsible for metal uptake on mineral surfaces within the first few minutes to hours, whereas surface precipitation and/or nucleation processes are considered to be much slower, occurring on time scales of hours to years (Sparks, 1989; Sparks, 1995; Scheidegger et al., 1996b). Insight on the process responsible for the slow Ni uptake on montmorillonite was provided in this study by combining powder and polarized EXAFS. The formation of Ni-Ni pairs was observed after a reaction time of only one day, but it may have taken place much earlier because the formation of a Ni-Al LDH phase was reported to occur in 15 minutes on pyrophyllite, therefore suggesting that adsorption and nucleation processes can occur simultaneously over time scales of minutes. The enhancement of second RSF peaks with increasing reaction time (1 - 206 days, Fig. 5) is interpreted by a growth of the Ni nuclei. A similar phenomenon was reported by Scheidegger et al. (1998) regarding the ageing of Ni-Al LDH in Ni-clay and Ni-aluminum(oxide) sorption systems over a time period of months. Scheckel and Sparks monitored the formation of Ni precipitates in a gibbsite/amorphous silica mixture and proposed the formation of an \( \alpha \)-Ni(OH)_2 phase, which evolved to a Ni phyllosilicate within 6 months (Scheckel and Sparks, 2000). Ford et al. (1999) reported that a phyllosilicate-like phase could also formed from the ageing of Ni-Al LDH. After one year of reaction time, these authors observed that the local structure of the Ni phase was intermediate between that of Ni-Al LDH and Ni-Al phyllosilicate and they suggested a grafting of Si-tetrahedra onto Ni-Al LDH layers. In previous works the combination of wet-chemistry kinetics with powder EXAFS allowed the temporal changes in the structural environment of sorbed metals to be followed, and yielded a molecular level description of chemical processes occurring at the water/mineral interface (e.g., formation of a Ni nucleation phase with time). However, as explained previously, application of powder EXAFS to these Si-containing systems is problematic because the overlap of scattering contributions from Ni, Al, and Si shells.
often hinders the unambiguous discrimination of \( \alpha \text{-Ni(OH)}_2 \), Ni phyllosilicate and Ni-LDH precipitates.

In the present study, the information obtained using powder EXAFS was complemented by P-EXAFS, applied here for the first time on montmorillonite. The angular dependence of EXAFS spectra obtained on this aluminous smectite is comparable to that reported on the ferric smectite, nontronite (Manceau et al., 2000a; Manceau et al., 2000b), and enabled us to isolate contributions from Ni and Si atoms by probing the in-plane and out-of-plane structure of the Ni-sorbed montmorillonite. This technique provided firm evidence to the presence of Ni and Si backscattering atoms in the vicinity of sorbed Ni atoms, and at interatomic distances \( R_{\text{Ni-Ni}} = 3.08 \, \text{Å}, R_{\text{Ni-Si}} = 3.26 \, \text{Å} \) characteristic of Ni-containing phyllosilicates \( (R_{\text{Ni-Ni}} = 3.05 - 3.08 \, \text{Å}, R_{\text{Ni-Si}} = 3.26 - 3.27 \, \text{Å}, \) Manceau and Calas, 1986; Charlet and Manceau, 1994). These structural results demonstrate that the uptake of Ni on montmorillonite, under the reaction conditions employed in our experiment \( (\text{pH} \, 8, [\text{Ni}]_{\text{initial}} = 660 \, \mu \text{M}, \text{high ionic strength}) \), resulted in the neoformation of a nickelophyllosilicate. A similar uptake mechanism was reported for Co on quartz (Manceau et al., 1999b) and Zn on hectorite (Schlegel et al., 2001).

### 2.4.2 Structural relationship between the neoformed Ni phyllosilicate and montmorillonite

In this section the three possible structural relationships between the neoformed Ni phyllosilicate and the montmorillonite sorbent are discussed: existence of two separate phases and epitaxy of the Ni phyllosilicate in the \( ab \) plane or in the \( c^* \) direction of montmorillonite layers

P-EXAFS results clearly indicated that Ni-Ni and Ni-Si pairs have the same orientations as Al-Al and Al-Si pairs in montmorillonite particles. Therefore, the neoformed phyllosilicate is crystallographically oriented with respect to montmorillonite layers, which allows us to exclude a random mixing of the two types of solids. The key question then is to know whether the neoformed phyllosilicate is structurally linked to the montmorillonite surface, in either the \( ab \) or \( c^* \) direction, or forms a separate phase. Unfortunately it is not possible to answer it yet because no Ni-Al pairs, which would have attested for a specific binding of the neoformed phyllosilicate to the montmorillonite surface, were detected. An epitaxial growth of Zn-hectorite layers on the edges of Mg-hectorite was unambiguously identified by P-EXAFS by sorbing Zn on hectorite \( (\text{pH} \, 7.3, [\text{Zn}]_{\text{initial}} = 520 \, \mu \text{M}, [\text{Si}]_{\text{aq}} = 530 \, \mu \text{M}, 0.3 \, \text{M NaNO}_3, \text{solid/liquid} = 0.65 \, \text{g/L}, \text{reaction time} \, 9 \, \text{h}; \) Schlegel et al., 2001). To identify a possible bonding of Ni to Al-OH and Si-OH
surface functional groups of montmorillonite, it would be necessary to prevent the growth of the
nucleated Ni phase, for example by lowering the initial metal concentration or the pH. Alternatively, the possible structural relationship between the Ni phyllosilicate and
montmorillonite could be imaged by transmission electron microscopy (TEM). This method
was used by Scheidegger et al. (1996b) to demonstrate that Ni-Al LDH precipitate formed with
pyrophyllite was physically attached to pyrophyllite edges.

2.4.3 Influence of aqueous Si concentration on the neoformation of
phyllosilicates

The formation of a Ni phyllosilicate upon Ni sorption on montmorillonite did not require
the addition of Si in solution, whereas dissolved silica had to be added to precipitate a Zn
phyllosilicate on hectorite (Schlegel et al., 2001). The possible reasons for these two distinct
uptake mechanisms are: a) the different sorbate - sorbent systems (i.e., Ni vs. Zn;
montmorillonite vs. hectorite); b) a difference in chemical conditions, such as pH, reaction time
and solid/liquid ratio; and c) the higher dissolution rate of montmorillonite which provided
enough dissolved Si for the formation of the Ni phyllosilicate.

In the study by Schlegel et al. (2001), [Si]_{aq} = 530 μM was added and the nucleation of the
Zn phyllosilicate in the continuity of hectorite layers occurred after a reaction time of 9h
(pH=7.3, [Zn]_{initial} = 520 μM, 0.3 M NaNO₃, solid/liquid 0.65 g/L). The epitaxial growth of the
neoformed hydrous silicate was followed up to 120 h. When less Si ([Si] = 30 - 60 μM) was
added to the Zn/hectorite system no Zn phyllosilicate formed even after a reaction time of 96h.
In the present study (pH 8, [Ni]_{initial} = 660 μM, 0.2 M Ca(NO₃)₂, solid/liquid = 5.3 g/L), the
[Si]_{aq} amounted to 177 μM after 24 h and constantly increased to 580 μM until 206 days.
Therefore, the montmorillonite provided enough dissolved silica to form a Ni phyllosilicate.
One possible reason for the higher [Si] in the Ni/montmorillonite sorption system lies in the
eight times difference in the solid/liquid ratio which amounted to 0.65 g/L for hectorite and 5.3
g/L for montmorillonite. The difference in Si release rate between the two smectites can not
explain the difference in surface reactivity because this rate is 10 times smaller in
montmorillonite (3.5 × 10^{-14} mol m^{-2} s^{-1}) than in hectorite (3.2 × 10^{-13} mol m^{-2} s^{-1}). The XRD
pattern of the conditioned montmorillonite indicated the presence of small amounts of quartz
(<1%). It is possible that the dissolution of small quartz grains contributed to increase [Si]_{aq}
thus facilitating the neoformation of the Ni phyllosilicate in our montmorillonite sorption
system.
2.5 Conclusion

The present study documents for the first time the formation of a metal phyllosilicate upon sorption on a dioctahedral smectite, a mechanism which had been previously reported for the trioctahedral smectite, hectorite (Schlegel et al., 2001). The heterogeneous formation of phyllosilicates has important geochemical implication because layer silicates are stable minerals in midly acidic to basic pH conditions and can irreversibly bound metals in waste and soil matrices, as recently demonstrated in Zn-smelter impacted soils (Manceau et al., 2000c). Batch desorption experiments carried out in our laboratory also showed that the release of the sorbed Ni is strongly hindered even up to a time period of 100 days.
2.6 References


CHAPTER 3
IDENTIFICATION OF NEOFORMED NI-PHYLLOSILICATES UPON NI UPTAKE ON MONTMORILLONITE: A TRANSMISSION ELECTRON MICROSCOPY (TEM) STUDY
Abstract

In this study transmissions electron microscopy (TEM) observations in combination with energy dispersive spectroscopy (EDS) were conducted to investigate whether the precipitates formed upon Ni uptake on montmorillonite can be observed and identified. The reaction conditions employed in this study (pH 8, [Ni]_{init} = 660 and 3300 µM, 0.2 M Ca(NO₃)₂) were similar to those used in a previous P-EXAFS study revealing the neoformation of a Ni phyllosilicate phase upon Ni uptake on montmorillonite. Unconditioned montmorillonite was used in this TEM/EDS study since smectites particles in the unconditioned clay material were more resident to the electron beam compared to such in conditioned montmorillonite. To verify that the commonly used conditioning procedure of the clay material does not modify the findings, complimentary EXAFS measurements were performed with unconditioned and conditioned Ni treated montmorillonite.

The TEM investigations of Ni treated montmorillonite revealed the presence of small and thin particles consisting of only 3 to 5 lattice fringes with a lattice spacing characteristic for smectites. There are several arguments indicating that these small particles are neoformed phyllosilicates. The small particles could only be observed in Ni treated samples and their Ni content as probed by EDS is high (up to 10% NiO). Furthermore, the particles are rich in Si (up to 80%), do not exhibit a 2:1 Si to Al ratio common for smectites and unlike montmorillonite do not contain Fe. Finally, the particles were significantly more resistant to the electron beam than smectites and EXAFS measurements confirmed the presence of neoformed Ni phyllosilicates.

The TEM study further indicates the presence of a variety of additional minerals (e.g., cristoballite, halloysite) and a Si rich gel phase. A Ni signal could only be detected in the latter phase at high Ni loadings, suggesting that Ni uptake is mainly controlled by smectites, respectively the neoformation of phyllosilicates and only to a minor degree by Si rich gel phases. Although TEM observations suggest that conditioning of the clay material is a rather severe treatment, the EXAFS further demonstrates that the conditioning did not modify the predominant uptake mechanism under the employed reaction conditions.
3.1 Introduction

Using extended X-ray absorption fine structure (EXAFS) spectroscopy, it has been demonstrated that Ni-, Co- and Zn-containing precipitates can form when clay minerals and Al- and Si-(hydr)oxides are treated with Ni, Co and Zn, and this even when the initial metal concentration in solution is undersaturated relative to the pure (oxyhydr)oxide forms of the metal (Towle et al., 1997; Scheidegger et al., 1998; Manceau et al., 1999; Thompson et al., 1999a; Thompson et al., 1999b; Morton et al., 2001; Schlegel et al., 2001; Dähn et al., 2002). For example, Scheidegger et al. (1998) observed the formation of a Ni-Al layered double hydroxide (Ni-Al LDH) phase when pyrophyllite (a 2:1 clay which lacks isomorphic substitution) was treated with Ni. The Ni-Al LDH phase formed after a contact time between pyrophyllite and Ni of only a few minutes, suggesting that nucleation in metal clay sorption systems can occur rapidly. Using polarized-EXAFS (P-EXAFS) Dähn et al. (2002) and Schlegel et al. (2001) showed the presence of neoformed phyllosilicates when di- and trioctahedral clay minerals (montmorillonite, hectorite) where treated with Ni and Zn at elevated pH and metal concentrations. The neoformed phases were oriented with respect to the octahedral smectite sheets and in the case of Schlegel et al. (2001) a structural link to hectorite particles could be discerned.

Several EXAFS studies revealing the presence of precipitates formed upon metal uptake on clay minerals were complemented with transmissions electron microscopy (TEM) investigations. For example, TEM was used to confirm the formation of a Ni-Al-LDH phase upon the Ni uptake on pyrophyllite (Scheidegger et al., 1996b). The authors observed surface deposits on pyrophyllite particles treated with Ni at pH > 7 which were not present in the untreated sample and which occurred preferentially along the edges of the pyrophyllite particles. Similarly, Thompson et al. (1999b) used TEM to discern the presence of a Co-Al-LDH phase formed upon Co uptake on kaolinite at elevated pH (pH 7.8). Nanometer-sized crystalline particles decorating edges and basal surfaces of kaolinite were observed in the Co treated material. Since the particles showed lattice fringes, the possibility that the observed nanometer-sized crystalline particles were attributable to small kaolinite particles could be ruled out. Due to the damage by the 300 kV electron beam kaolinite particles did not produce lattice fringes and could be identified based on their size and hexagonal morphology.

In this study TEM observations in combination with EDS analysis were conducted to investigate whether Ni phyllosilicates formed upon Ni uptake on montmorillonite can be observed. The reaction conditions employed in this study (pH 8, [Ni]_{initial} = 660 and 3300 μM, 0.2 M Ca(NO₃)₂) were similar to those used in a previous P-EXAFS study revealing the neoformation of a Ni phyllosilicate phase when montmorillonite was treated with Ni (Dähn et
al., 2002). In contrast to the previous experiments by Dähn et al. this study was conducted with raw montmorillonite. Complimentary EXAFS measurements were performed with unconditioned and conditioned Ni treated montmorillonite to check that the responsible uptake mechanism (neoformation of a Ni phyllosilicate) remained unchanged by using the raw material.

3.2 Materials and Methods

3.2.1 Montmorillonite characterization

The montmorillonite STx-1 used in this study was purchased from the Source Clay Minerals Repository of the Clay Minerals Society. XRD of the “as received” montmorillonite revealed the presence of minor quantities of calcite, quartz and kaolinite amounting to less than ~1 wt %. This natural clay contains ~0.9 % Fe₂O₃. While for the TEM investigations the raw material was used, EXAFS measurements were performed with raw as well as conditioned clay material. In the conditioning process the raw montmorillonite was thoroughly washed three times with 1 M NaClO₄ to convert the clay into the homo-ionic Na form. The < 0.5 μm size fraction was selected by successive washing with de-ionized water, combined with centrifugation (Baeyens and Bradbury, 1997). Soluble hydroxy-aluminium compounds were removed by acidic treatment (pH 3.5, for 1h) of the clay suspension. The pH was subsequently readjusted to 7. Amorphous iron was dissolved by dithionate-citrate-bicarbonate treatment (Mehra and Jackson, 1960). With inductively coupled plasma optical emission spectroscopy (ICP-OES) and total digestion of the sample, the amount of extractable iron was determined to be approximately 30% of the total iron content. Conversion to Ca-montmorillonite was achieved by partially filling dialysis bags with ~75 ml of the stock Na-montmorillonite suspensions and, after sealing shaking four such bags end-over-end in a 1-litre container filled with a purified 0.2 M Ca(NO₃)₂ solution. The background electrolyte was changed about three times per day, and this procedure was continued until the electrical conductivity of the conditioned Ca-montmorillonite equilibrated solution was equal to that of the original 0.2 M Ca(NO₃)₂. The final conditioned montmorillonite suspension was stored at 4 °C in the dark to minimize microbial growth.

The cation exchange capacity (CEC) of the unconditioned STx-1 Ca-montmorillonite is 844 meq kg⁻¹ (Van Olphen and Fripiat, 1979). The CEC of the conditioned montmorillonite was determined to be 970 meq kg⁻¹ by using the isotopic dilution method with ⁴⁵Ca (Baeyens and Bradbury, 1995). The external surface area of the unconditioned and conditioned STx-1 Ca-montmorillonite was measured by the N₂-BET technique to be 82 m²g⁻¹, respectively 89 m²g⁻¹. These values are in agreement with that determined by Van Olphen and Fripiat (84 m²g⁻¹, Van Olphen and Fripiat, 1979).
The pyrophyllite material used in this study was purchased from Ward Natural Science. The purification and conditioning process is described elsewhere (Scheidegger et al., 1996a). The external surface area of conditioned pyrophyllite measured by the N$_2$-BET technique was 93 m$^2$g$^{-1}$.

3.2.2 Sample preparation

TEM and EXAFS samples were prepared to achieve montmorillonite samples with low and high Ni loading. Samples with low Ni loading were prepared by adding 0.64 g as received STx-1 to 20 ml 0.2 M Ca(NO$_3$)$_2$. The pH was adjusted to 8 and 60 ml of a Ni solution ([Ni] = 1100 µM; pH 8.0, 0.2 M Ca(NO$_3$)$_2$) was added resulting in a solid to liquid ratio of 6.4 g/L and an initial Ni concentration ([Ni]$_{initial}$) of 660 µM. A previous study (Dähn et al., 2002) demonstrated that the Ni solution was stable over a time period of up to one year and thus, Ni uptake in this study was not due to Ni(OH)$_2$(s) precipitation in solution during anytime in the experiment. The high ionic strength Ca electrolyte background was used to block cation exchange sites. The experiments were conducted in a glove box under N$_2$ atmosphere (CO$_2$ and O$_2$ < 5 ppm). The samples were centrifuged after a reaction time of 14 (sample A; Table 1) and 60 days (sample B; Table 1) and the wet pastes were filled into Plexiglas holders, sealed and stored in a refrigerator to keep them moist prior to TEM and EXAFS measurements. ICP-OES measurements showed that the proportion of Ni uptaken varied from 43 µmol/g to 90 µmol/g (Table 1).

An additional sample with low Ni loading (sample E; Table 1) was prepared for EXAFS measurements using conditioned and purified Ca-montmorillonite (< 0.5 µm size fraction). Except the solid to liquid ratio (5.2 g/L) the reaction conditions were identical to those described above (Table 1). A sample with high Ni loading (sample C; Table 1) was prepared by adding 0.64 g as received STx-1 to 95 ml 0.2 M Ca(NO$_3$)$_2$. The pH was adjusted to 8 and 5 ml of a Ni solution ([Ni] = 6.6 $10^{-2}$ M, pH 3.0, 0.2 M Ca(NO$_3$)$_2$) was added. After 60 days of reaction time the proportion of Ni uptaken amounted to 403 µmol/g (Table 1).

For comparison a Ni treated pyrophyllite sample (sample E; Table 1) was prepared by adding 60 ml of a Ni solution (pH 8.0, [Ni] = 1.1 $10^{-3}$ M, 0.3 M NaNO$_3$) to 30 ml of a conditioned and purified pyrophyllite (< 2 µm size fraction) suspension (pH 8.0, 0.3 M NaNO$_3$). The experiment resulted in a Ni loading of 130 µmol/g (Table 1).

In addition to Ni, the supernatant solutions of the Ni treated clay samples were also analyzed for Si and Al by ICP-OES (Table 1). The Al concentration in the samples was too low (<6 µM) to produce reliable ICP-OES measurements. The Si concentration in the Ni treated clay samples varied between 282 - 527 µM.
Table 1: Samples analysed by TEM and EXAFS for unconditioned and conditioned montmorillonite and pyrophyllite.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Clay material</th>
<th>Clay treatment</th>
<th>Method</th>
<th>Solid/liquid ratio</th>
<th>Ni uptake</th>
<th>[Ni]</th>
<th>Reaction time</th>
<th>[Si]</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>montmorillonite</td>
<td>unconditioned</td>
<td>TEM, EXAFS</td>
<td>6.4</td>
<td>42(^a)</td>
<td>43</td>
<td>14</td>
<td>406</td>
</tr>
<tr>
<td>B</td>
<td>montmorillonite</td>
<td>unconditioned</td>
<td>TEM, EXAFS</td>
<td>6.4</td>
<td>89(^a)</td>
<td>90</td>
<td>60</td>
<td>527</td>
</tr>
<tr>
<td>C</td>
<td>montmorillonite</td>
<td>unconditioned</td>
<td>TEM</td>
<td>6.4</td>
<td>80(^b)</td>
<td>403</td>
<td>60</td>
<td>488</td>
</tr>
<tr>
<td>D</td>
<td>pyrophyllite</td>
<td>conditioned</td>
<td>TEM</td>
<td>2.1</td>
<td>40(^a)</td>
<td>130</td>
<td>14</td>
<td>285</td>
</tr>
<tr>
<td>E</td>
<td>montmorillonite</td>
<td>conditioned</td>
<td>EXAFS</td>
<td>5.2</td>
<td>32(^a)</td>
<td>40</td>
<td>14</td>
<td>282</td>
</tr>
</tbody>
</table>

\(^a\): Initial Ni concentration = 660 \(\mu\)M.
\(^b\): Initial Ni concentration = 3300 \(\mu\)M.
3.2.3 TEM

The TEM measurements were performed at CEA-Cadarache in France using a JEOL 2000 FX transmission electron microscope (TEM) operating at 200 kV. Energy dispersive spectroscopy (EDS) was performed using a Si-Li detector (Oxford Instruments). EDS analysis was performed in convergent beam mode with a probe size of ~10 nm. The counting time for the EDS analysis was 60 s with a deadtime of 0 - 10 % and a number of counts of 500 to 2000 counts/sec. The EDS data were semi-quantitative analyzed using the program TEMQUANT from ISIS (Oxford Instruments).

The TEM samples were prepared by diluting a small amount of the centrifuged wet montmorillonite and pyrophyllite pastes in de-ionized water and by transferring a drop (10 µL) of the diluted suspension to a gold mesh grid with a holey carbon support film. The drop was then allowed to dry slowly.

3.2.4 EXAFS data collection and reduction

Ni K-edge XAFS spectra were recorded at beamline BM1B (Swiss-Norwegian beamlines, SNBL) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). All spectra were recorded in fluorescence mode at room temperature using a Si(111) monochromator and a Stern-Heald-type detector (Lytle detector, The EXAFS Co.). Higher order harmonics were suppressed by using an Au coated mirror. The monochromator angle was calibrated by assigning to 8333 eV the first inflection point of the K-absorption edge spectrum of Ni metal. Several EXAFS scans were averaged to improve the signal to noise ratio.

Data reduction was carried out with the WinXAS 97 2.1 software package (Ressler, 1998). The energy was converted to photoelectron wave vector units (Å⁻¹) by assigning the origin E₀ to the first inflection point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming k³-weighted χ(k) functions between 3.2 and 10 Å⁻¹ using a Bessel window function with a smoothing parameter of 4. Amplitude and phase shift functions were calculated with FEFF 8.0 (Rehr et al., 1991) using the structures of β-Ni(OH)₂ and Ni-Talc (Perdikatsis and Burzlaff, 1981) as references. Fits were performed in R space in the 0.6 to 3.5 Å interval. The amplitude reduction factor (S₀²) was determined to be 0.85 from the experimental β-Ni(OH)₂ EXAFS spectrum. The deviation between the fitted and the experimental spectra (%Res) is given by:

\[%Res = \frac{\sum_{i=1}^{N} |y_{exp}(i) - y_{theo}(i)|}{\sum_{i=1}^{N} y_{exp}(i)} \cdot 100\]
where \( N \) is the number of points in the fit window, and \( y_{\text{exp}} \) and \( y_{\text{theo}} \) are the experimental and theoretical RSF values. The precision on the distances (R) was previously estimated to be \( \pm 0.02 \text{ Å} \) for \( R_{\text{Ni-O}} \), and \( \pm 0.03 \text{ Å} \) for \( R_{\text{Ni-Ni}} \) and \( R_{\text{Ni-Si}} \), and \( \pm 0.5 \) for the coordination numbers (Dähn et al., 2002).

3.3 Results

3.3.1 TEM observations

3.3.1.1 Untreated montmorillonite

Prior to study Ni treated montmorillonite samples it is important to investigate the raw and untreated clay material. The TEM observations revealed that, as expected, the material consists mainly of smectite particles. However, further mineral phases were identified in the material. The variety of mineral phases present in the unconditioned montmorillonite material is demonstrated in Fig. 1 in a low magnification image. For visualization purposes only a few of the smectite particles (sm) observed in the image are labeled. The image also shows cauliflower-like features which are characteristic for cristoballite (cb). The long (~900 nm) column shaped particle at the right side of the picture is halloysite (ha). The halloysite particle has a fiber-like structure (diameter ~70 nm) and is hollow in the middle. EDS analysis reveals that the halloysite crystal consists of ~50% Al\(_2\)O\(_3\) and ~50% SiO\(_2\). This finding is consistent with the structural formula of halloysite \((\text{Al}_4\text{O}_8\text{Si}_4\text{O}_{10})_4\text{H}_2\text{O}\). On the lower tip of the halloysite particle there is a diffused and cloudy feature that is a gel phase and consists of ~90% SiO\(_2\) and ~10% Al\(_2\)O\(_3\).

A high resolution image of a smectite particle is presented in Fig. 2. At the lower edge of this particle lattice fringes are visible (circled area in Fig. 4). Lattice fringes are observed when the edges of smectite particles are curved upwards. It this is the case, the layers of smectite particles are parallel to the beam, allowing the observation of (001) lattice fringes. The lattice spacing of the illustrated particle (12 Å) is characteristic for the spacing between (001) silicate layers in smectites (\(d_{001} = 12\) Å, Meike, 1989; Allen, 1993). EDS analysis revealed that the core of the smectite consists of 9% Al\(_2\)O\(_3\), 24% SiO\(_2\) and 0.1% FeO and suggests the presence of a 2:1 smectite mineral. It must be noted that the smectites particles in the untreated material were generally very fragile and suffered from radiation damage after exposing the sample to the electron beam for < 1 minute (i.e. the lattice fringes increasingly smeared out and finally disappeared).

The high resolution image also shows the presence of a Si rich gel phase (see above) associated to the smectite particle (dotted circled area in Fig. 2). Throughout the TEM studies,
similar gel phases exhibiting some kind of an association to the smectite particles were systematically observed.

Fig. 1: Low magnification photo of different mineral phases in as received untreated montmorillonite. Only a few smectite particles (sm) are labeled. The cauliflower-like features are crystoballite (cb), dark spots are clusters of Si (Si), the long column shaped particle is halloysite (ha) and with a gel phase (gel) at the lower tip.
3.3.1.2 Ni treated montmorillonite

In the following we investigated whether TEM/EDS can reveal any changes when the unconditioned sorbent material was treated with Ni. The TEM investigations showed the presence of the same mineral phases as observed in the untreated sorbent material (Fig. 1). For example, Fig. 3 illustrates an assembly of smectite, crystoballite, and halloysite particles and a gel phase that are present in a sample with low Ni loading (sample B).
EDS analysis on a series of cristoballite and halloysite particles and Si gel phases revealed the absence of a Ni signal in samples with low Ni loading (sample A and B). We could, however, obtain a Ni signal in the samples when smectites particles were analysed. These findings are illustrated in Fig. 4 showing a big smectite particle, a Si gel phase and a cristoballite particle (sample A). While the gel phase and cristoballite contain no Ni, EDS analysis indicates that the center of the thick smectite crystal (circled area) contains 1% NiO.

We also observed several smectites particles containing a significantly higher Ni content. The observed particles were generally very small and consisted of only a few lattice fringes. As an example, Fig. 5 shows a high magnification image of particles (sm1, sm2, sm3) with only 3 - 5 lattice fringes (sample B). The spacing of the lattice fringes in the particles is 11 - 12 Å and characteristic for smectites (see section 3.3.1.1). Smectite particles with only a few lattice fringes have never been observed in untreated montmorillonite, suggesting that their appearance is due to the presence of Ni.
Fig. 4: Smectite (sm), crystoballite (cb) and a gel phase in Ni treated montmorillonite sample (43 μmol/g, 14 days reaction time). The circled area marks the area of the EDS analysis of the smectite.
Fig. 5: Neoformed phyllosilicate (sm1 - sm3) in a Ni treated montmorillonite sample (90 μmol/g, 60 days reaction time). The circled area marks the area of the EDS analysis of sm3.

EDS analysis of the very fine tip of sm3 (circled area in Fig. 5) shows that the tip of this smectite particle contains 10% NiO, 10% Al₂O₃, 75% SiO₂. Because the particle is small (~5 nm) compared to the probed area (beam size of the EDS ~10 nm) we can assume that the Ni content of this particle is in reality even higher. The fact that the small particle (sm3) contains a high amount of NiO and SiO₂ and a low amount of Al₂O₃ suggests the presence of a Ni-Si phase. EDS analysis of the tip further indicates that this smectite particle lacks Fe. For comparison, in the untreated clay material the Fe content in smectites as measured by EDS varied between 0.1 to 1%. A further characteristic of Ni rich small particles is their resistance towards the electron beam. While smectites particles in the untreated material were generally very fragile and suffered from radiation damage after exposing the sample to the electron beam for < 1 minute, the Ni rich particles could withstand the electron beam for a much longer time (> 5 min).

TEM/EDS investigations with samples with a high Ni loading (sample C) revealed that again no Ni signal could be observed probing cristoballite and halloysite particles. In the case of high Ni loaded samples, however, Ni was not only observed probing smectites, but also probing associated Si rich gel phases. As an example Fig. 6 shows a high magnification image of a gel phase (circled area) which is sandwiched by two smectites (sample C). Whereas the tip of the thick smectite particle contains 10% NiO, 20% Al₂O₃, 64% SiO₂ and 0.5% FeO, EDS revealed that the gel phase contains 5% NiO, 19% Al₂O₃, 70% SiO₂ and no Fe.
Finally, Fig. 7 shows an image of a halloysite particle present in the Ni treated sorbent material (43 μmol/g, reaction time: 14 days). EDS data analysis revealed that the halloysite particle contains no Ni (~50% SiO₂ and ~50% Al₂O₃). The diameter of the fiber is ~150 nm and the particles show holes with a diameter of 8 - 20 nm (visible as bright spots). It is important to note that we did not observe such holes in halloysite particle in the unconditioned sorbent material (Fig. 1). We suspect that the holes are caused by dissolution of halloysite during the Ni uptake experiment and thus halloysite particles represent a potential source of Al and Si in the system.
3.3.1.3 Pyrophyllite

The preceding chapters (3.3.1.1-3.3.1.2) suggest that Ni rich smectites formed upon Ni uptake on montmorillonite. Since it is known that Ni uptake on pyrophyllite at similar reaction conditions can result in the formation of a Ni-Al LDH phase (Scheidegger et al., 1996a, 1996b, 1997), we have conducted TEM observations with a Ni treated pyrophyllite sample.
TEM sample for comparison. Fig. 8 shows a high magnification image of a pyrophyllite crystal (py) of a Ni treated pyrophyllite sample (sample D). EDS analysis shows that the pyrophyllite particle contains 30% Al$_2$O$_3$, 70% SiO$_2$ and no Ni nor Fe. This finding is consistent with the structural formula for pyrophyllite (Al$_2$Si$_4$O$_{10}$(OH)$_2$). The arrows in the image indicate the presence of dark spots with a diameter of 3 - 6 nm in a Si gel phase also present in the material. It is important to note that such dark spots were never observed in Ni treated montmorillonite nor in the untreated pyrophyllite (Scheidegger et al., 1996b). Therefore, one can suspect that the dark spots are small Ni clusters.

Fig. 8: Pyrophyllite particle (py) and Ni clusters (dark spots) in a Ni treated pyrophyllite sample (130 μmol/g, 14 days reaction time).
3.3.2 EXAFS

A previous P-EXAFS study has unambiguously shown that the Ni uptake on montmorillonite under similar reaction conditions resulted in the neoformation of a Ni phyllosilicate (Dähn et al., 2002). While in the previous Ni uptake study conditioned montmorillonite (STx-1) was used as sorbent material, the TEM investigations were performed with the unconditioned form of the same material.

We performed EXAFS experiments with Ni treated unconditioned and conditioned montmorillonite to check that the responsible uptake mechanism (neoformation of a Ni phyllosilicate) remained unchanged by using the raw material. The raw material also contains particles > 0.5 μm and minor minerals such as calcite, cristoballite, halloysite and Si gel phases (see section 3.2.1 and 3.3.1.1). The \( k^3 \)-weighted EXAFS spectra for montmorillonite treated with Ni at pH 8 for 14 days of reaction time are shown in Fig. 9a as an example (sample B and E). The figure shows that changes in the spectra are minor. The multifrequency wave shape suggests the presence of at least two backscattering pairs. The corresponding experimental and simulated Fourier transforms (FTs) are illustrated in Fig. 9b. The amplitude and position of first RSFs peaks (Ni-O contribution) do not differ in the two samples. The peak position of the second RSFs for both samples is identical (\( R + \Delta R \approx 2.75 \) Å) and characteristic for Ni-Ni pairs (Mancau and Calas, 1986; Manceau, 1990; Pandya et al., 1990; Scheidegger et al., 1996a; Scheidegger et al., 1997; Mansour and Melendres, 1998; Scheidegger et al., 1998; Scheinost et al., 1999; Dähn et al., 2002). The amplitude of the second RSF peak, however, is slightly higher in the unconditioned sample compared to the conditioned sample.

Structural parameters obtained by data analysis are listed in Table 2. Data analysis indicates that the first shell consists of 5.6 ± 0.5 Ni-O pairs at a bond distance (2.05 Å) that is typical of six-fold coordinated Ni (Pandya et al., 1990). In both samples Ni-Ni and Ni-Si distances were observed (\( R_{\text{Ni-Ni}} = 3.09 \) Å and \( R_{\text{Ni-Si}} = 3.26 - 3.28 \) Å) that match well with those in Ni phyllosilicates (\( R_{\text{Ni-Ni}} = 3.05 - 3.09, R_{\text{Ni-Si}} = 3.26 - 3.27 \); Mancau and Calas, 1986; Charlet and Manceau, 1994; Dähn et al., 2002). This finding confirms the formation of a Ni phyllosilicate phase in both samples and that the use of the unconditioned clay did not modify the predominant uptake mechanism under the employed reaction conditions.
Fig. 9: a) $k^3$-weighted Ni K-edge EXAFS spectra of montmorillonite reacted with Ni for 14 days reaction time for the unconditioned (solid line, [Ni] = 43 µmol/g) and the conditioned (dashed line, [Ni] = 40 µmol/g) clay material at pH 8. b) Corresponding experimental and theoretical FTs (modulus and imaginary parts). For the unconditioned (upper spectrum) and the conditioned (lower spectrum) clay.
Table 2: Structural information derived from the EXAFS analysis using a three-shell fit approach for 14 days of reaction time ([Ni] = 43 μmol/g, unconditioned and [Ni] = 40 μmol/g, conditioned montmorillonite).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni-O CN_{Ni-O}</th>
<th>R_{Ni-O} [Å]</th>
<th>σ^2 [Å^2]</th>
<th>Ni-Ni CN_{Ni-Ni}</th>
<th>R_{Ni-Ni} [Å]</th>
<th>σ^2 [Å^2]</th>
<th>Ni-Si CN_{Ni-Si}</th>
<th>R_{Ni-Si} [Å]</th>
<th>σ^2 [Å^2]</th>
<th>ΔE₀ [eV]</th>
<th>%Res</th>
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<tr>
<td>unconditioned</td>
<td>5.6</td>
<td>2.05</td>
<td>0.006</td>
<td>4.0</td>
<td>3.09</td>
<td>0.007</td>
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<td>3.26</td>
<td>0.007</td>
<td>0.6</td>
<td>3.6</td>
</tr>
<tr>
<td>conditioned</td>
<td>5.7</td>
<td>2.05</td>
<td>0.006</td>
<td>3.1</td>
<td>3.09</td>
<td>0.006</td>
<td>3.5</td>
<td>3.28</td>
<td>0.006</td>
<td>0.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

CN, R, σ^2, ΔE₀ are the coordination numbers, interatomic distances, Debye-Waller factors and inner potential corrections. f: fixed to the value obtained for Ni-Ni.

3.4 Discussion

3.4.1 Identification of Ni phyllosilicates

A previous P-EXAFS study has unambiguously shown that the Ni uptake on montmorillonite at elevated pH and Ni concentrations resulted in the neoformation of a Ni phyllosilicate (Dähn et al., 2002). In this study TEM observations in combination with EDS analysis were conducted to investigate whether Ni phyllosilicates can be identified in the Ni treated clay material.

The TEM images of untreated and Ni treated montmorillonite material (sample A-C) revealed the presence of smectite particles with a shape and lattice fringes characteristic for smectites (d_{001} = 12 Å; Meike, 1989; Allen, 1993). This finding suggests that the crystallinity of the smectites particles did not significantly change during the Ni uptake experiments. In the treated clay material we additionally observed small and thin particles consisting of only 3 to 5 lattice fringes (lattice spacing ~11 - 12 Å). There are several arguments indicating that these small particles are neoformed phyllosilicates.

i) Similar small particles were not observed in untreated clay material.

ii) Although these particles are very small in size their Ni content (~10%; sample B, Fig. 5) is significantly higher than the Ni content of smectites particles (~4%, sample B).

iii) While EDS analysis confirms that the smectite particles are consistent with the structural formula (2:1 ratio of Si to Al), the small particles are Si rich (~75% SiO₂) and Al poor (~10% Al₂O₃). Furthermore, while the Fe content in the smectites particles varied between 0.1 to 1% (FeO), the small particles contain no Fe.

iv) The small particles are significantly more resistant to the electron beam than montmorillonite particles.
We therefore conclude that the small particles observed in the TEM observation are neoformed Ni phyllosilicates. The finding that neoformed Ni phyllosilicates are present in the Ni treated montmorillonite sample is confirmed by the accompanying EXAFS measurements in this study. The EXAFS data reveal structural parameters characteristic for Ni phyllosilicates and thus unambiguously demonstrate that Ni uptake under the employed reaction conditions results in the neoformation of Ni phyllosilicate (see section 3.3.2).

Schlegel et al. (2001) investigated the uptake of Zn on hectorite and showed that neoformed phyllosilicates are growing at the edges of smectite particles and in the continuity of the octahedral sheets. Using TEM we were not able to observe whether the neoformed Ni-phyllosilicates have a structural link to montmorillonite particles. We observed small Ni rich particles identified as neoformed phyllosilicates either in the proximity of smectite particles as well as disconnected from smectite particles. This finding is similar to the TEM findings by Thompson et al. (1999b). Investigating the Co uptake on kaolinite the authors identified the presence of Co-Al-LDH precipitates that were not preferentially orientated with respect to the kaolinite particles and some of the precipitates lacked direct contact to kaolinite particles.

3.4.2 Ni associated to other mineral phases

In all Ni treated montmorillonite samples (sample A-C; see section 3.3.1.2) a Ni signal could be detected probing smectite particles. In contrast to smectites EDS analysis revealed that none of the other minor mineral phases present in the sorbent material (e.g., halloysite, calcite and crystoballite) contains Ni. The only exception to this finding are Si rich gel phases. While no Ni signal could be detected probing Si gel phases in samples with a low Ni loading (sample A and B), EDS analysis revealed the presence of a Ni signal (up to 5% NiO, see section 3.3.1.2) probing Si gel phases in a highly Ni loaded sample (sample C). The TEM/EDS findings thus suggest that Ni uptake is mainly controlled by smectites, respectively the neoformation of phyllosilicates and only to a minor degree by Si rich gel phases.

For comparison we also conducted TEM investigations with a Ni treated pyrophyllite sample. Using EXAFS it has been previously shown that Ni uptake on pyrophyllite at elevated [Ni] and pH resulted in the formation of a Ni-Al-LDH phase (Scheidegger et al., 1996a, 1996b, 1997). Indeed this TEM study suggests that Ni uptake on pyrophyllite did not result in the formation of small Ni rich particles consisting of a few lattice fringes (Ni phyllosilicate) as in the case of montmorillonite. Instead the TEM study indicates the presence of small (diameter 3 - 6 nm) dark spots with a high electron density which can presumably be interpreted as neoformed Ni-Al-LDH clusters. This TEM study confirms previous EXAFS studies demonstrating that Ni uptake on montmorillonite and pyrophyllite at similar reaction conditions result in the formation of different Ni phases (Ni phyllosilicate vs. Ni-Al-LDH).
3.4.3 Influence of the clay conditioning procedure

In metal uptake experiments with montmorillonite it is common that the clay material undergoes a conditioning process in order to gain the clay fraction (< 2 µm), to convert the clay into the homo-ionic form and to remove impurities and soluble hydroxy-aluminium compounds by acidic treatment. An additional conditioning process often used is the removal of amorphous iron. In this process the clay material is heated up to 80° C and strong reactants are used (dithionate-citrate-bicarbonate treatment, Mehra and Jackson, 1960). We have conducted TEM observations with unconditioned and conditioned montmorillonite to investigate whether the various conditioning steps did modify the morphology of the clay material and observed that the crystallinity of the smectites particles significantly decreased with each conditioning step. The lattices fringes became increasingly smeared out and the smectites particles suffered from radiation damage even when exposing the sample to the electron beam for only seconds. For these reasons the TEM investigations were conducted with unconditioned clay material.

To investigate the influence of the conditioning process on the uptake process, accompanying EXAFS measurements were performed with unconditioned as well as conditioned clay material. The EXAFS spectra were very similar and in both cases the data analysis revealed the presence of a Ni phyllosilicate phase (see section 3.3.2, Table 2). This finding suggests that the conditioning process did not modify the responsible uptake mechanism under the employed reaction conditions (see section 3.3.2, Table 2).

3.4.4 Possible sources of Si in solution required for the neoformation of phyllosilicates

In a previous P-EXAFS study Schlegel et al. (2001) observed the neoformation of a Zn phyllosilicate phase upon treating hectorite with Zn. Whereas the reaction with Zn did require the addition of Si, no Si addition was required to form neophyllosilicates upon Ni uptake on montmorillonite (this study; Dähn et al., 2002). The Si concentrations in this study (282 - 527 µM; Table 1) were comparable to the previous P-EXAFS study (177 - 448 µM, Dähn et al., 2002) and apparently sufficient for the neoformation of a Ni phyllosilicate. Dähn et al. (2002) speculated that one possible reasons for the distinct uptake mechanisms of Zn on hectorite vs. Ni on montmorillonite is that the dissolution of SiO₂ particles in the sorbent material contributed to an increased [Si]ₐq, thus facilitating the neoformation of Ni phyllosilicate in our experiments (this study, Dähn et al., 2002). The TEM study reveals the presence of a Si rich gel phase (see section 3.3.1.1 and 3.3.1.2) and thus confirms the above hypothesis. Another Si source observed in this study are halloysite particles. The TEM images suggest that halloysite particles do suffer severe surface alteration during the uptake
experiments. We suspect that the observed holes (Fig. 7) were caused by partial dissolution of the halloysite particles. This hypothesis is supported by the following fact. Whereas halloysite particles were still observable when the material was solely treated with Ni at near neutral conditions for 14 - 60 days (see section 3.2.1), no halloysite particles could be observed when the material did undergo the ‘aggressive’ conditioning process (see section 3.2.1 and 3.3.1.2).

3.5 Concluding remarks

This study confirms previous P-EXAFS studies on the uptake of metal ions on clay minerals (Schlegel et al., 2001; Dähn et al., 2002) and demonstrates that neoformed phyllosilicates can be discerned using TEM. Although TEM observations suggest that conditioning of the clay material is a rather severe treatment, the main Ni uptake process (neoformation of phyllosilicates) did not alter due to the conditioning procedure commonly used in metal uptake on clay minerals. This finding may suggest, that findings obtained in metal uptake experiments with purified and conditioned clay minerals can be extrapolated to predict the fate of heavy metals in clay rich natural settings.
3.6 References


CHAPTER 4
STRUCTURAL EVIDENCE FOR THE SORPTION OF METAL ION ON THE EDGES OF MONTMORILLONITE LAYERS. A POLARIZED EXAFS STUDY
Abstract

The nature of surface complexes formed upon Ni uptake onto montmorillonite (a dioctahedral smectite) has been investigated over an extended time period by polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy. Self-supporting films of Ni-sorbed montmorillonite were prepared by contacting Ni and montmorillonite at pH 7.2, high ionic strength (0.3 M NaClO₄) and low Ni concentration ([Ni]_{initial} = 19.9 μM) for 14 and 360 days reaction time. The resulting Ni concentration on the clay varied from 4 - 7 μmol/g. Quantitative texture analysis indicates that the montmorillonite particles were well orientated with respect to the plane of the film. The full-width at half maximum (FWHM) of the orientation distribution of the c* axes of individual clay platelets about normal to the film plane was 44.3° (14 days) and 47.1° (360 days). These values were used to correct the coordination numbers determined by P-EXAFS for texture effects. Ni K-edge P-EXAFS spectra were recorded at angles between the incident beam and the film normal equal to 10°, 35°, 55°, and 80°. Spectral analysis led to the identification of three nearest cationic subshells containing 2.0 ± 0.5 Al at 3.0 Å in the in-plane direction and 2.0 ± 0.5 Si at 3.12 Å and 4.0 ± 0.5 Si at 3.26 Å in the out-of-plane direction. These distances are characteristic of edge-sharing linkages between Al and Ni octahedra and of corner-sharing linkages between Ni octahedra and Si tetrahedra, as in clay structures. The angular dependence of the Ni-Al and Ni-Si contributions indicates that Ni-Al pairs are oriented parallel to the film plane, whereas Ni-Si pairs are not. The study reveals the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets and thus, that heavy metals binding to edge sites is a possible sorption mechanism for dioctahedral smectites. Data analysis further suggests that the number of neighboring Al atoms remains constant and that the structural order of the observed surface complexes increases with increasing reaction time while. Thus, it appears that over an extended reaction time period of one year the responsible uptake mechanism of Ni onto montmorillonite remained unchanged, and especially the diffusion of Ni in the octahedral layer could not be observed.
4.1 Introduction

Sorption, diffusion, and precipitation reactions at the clay minerals-water interface can severely retard the release of metal ions into the geosphere. For this reason smectites are used as geochemical barriers in nuclear waste repositories and landfills for hazardous chemicals. To predict the mobility and long-term behavior of heavy metals and radionuclides in smectitic settings a mechanistic understanding of the chemical processes at the smectite-water interface is of fundamental importance.

Geochemical processes at the mineral-water interface such as sorption, precipitation and dissolution, markedly affect the, speciation and bioavailability of metals in the environment. It is therefore important to determine the mechanism and the mineral phase responsible for the fate of contaminants in soils and aquatic systems. Among the natural occurring mineral phases are smectites the one that can severely retard the release of metals into the geosphere by uptake processes or the formation of new phases.

The term smectite is used to describe a family of expansible 2:1 phyllosilicate minerals having permanent layer charge between 0.2 and 0.6 charges per half unit cell. Main mineral species from the smectite family encompass montmorillonite, beidellite, nontronite, saponite, and hectorite. Smectites are constructed of a single octahedral sheet sandwiched between two tetrahedral sheets, with the octahedral sheet sharing the apical oxygens of the tetrahedral sheets. Smectites are divided into two subgroups, dioctahedral when only two of three octahedral sites per half unit cell are occupied and trioctahedral when all three sites are populated (Güven, 1988). In trioctahedral and dioctahedral structures octahedral cations are surrounded by 6 respectively 3 octahedral cations. The octahedral sheet has two different sites denoted M1 and M2 which have a different hydroxyl configuration (Fig. 1). M1 is the trans octahedron with OH groups located at opposing corners whereas M2 is the cis octahedron with the OH groups located on the same edge. Only two of the three octahedral positions per half unit cell (2 M2 + M1) are occupied, which can be either the two M2 sites (denoted herein as trans-vacant, tv) or the M1 and one of the two symmetrically independent M2 sites (denoted herein as cis-vacant, cv). Montmorillonite has cv 2:1 layers whereas beidellites and nontronites possess tv 2:1 layers (Tsipursky and Drits, 1984). The tv layers have a C2/m-layer symmetry, whereas cv layers are reduced to a C2-symmetry. The tetrahedral sheets of smectite are composed of a six-fold hexagonal ring of silica tetrahedra. Trioctahedral structures have a flat basal plane, whereas dioctahedral structures have a corrugated basal plane due to the presence of octahedral vacant sites. The Al-Al and Al-Si distances for M1, M2 and cv sites in montmorillonite are listed in Table 1.
Fig. 1: Structure of montmorillonite after (Tsipursky and Drits, 1984). The large M2 positions are vacant in montmorillonite.

Table 1: Al-Al and Al-Si distances in montmorillonite (Tsipursky and Drits, 1984).

<table>
<thead>
<tr>
<th>Site</th>
<th>Al-Al</th>
<th>Al-Si1</th>
<th>Al-Si2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of neighbors</td>
<td>Number of neighbors</td>
<td>Distance [Å]</td>
</tr>
<tr>
<td>M1</td>
<td>3</td>
<td>4</td>
<td>3.16-3.18</td>
</tr>
<tr>
<td>M2</td>
<td>3</td>
<td>2</td>
<td>3.15</td>
</tr>
<tr>
<td>cv</td>
<td>6</td>
<td>2</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>3.23</td>
</tr>
</tbody>
</table>
Smectites possess a large specific area and a high structural charge (up to 1000 meq per kg), imparting them with important sorptive properties. Layer charge arises from substitutions in either the octahedral sheet (typically from the substitution of low charge species such as Mg$^{2+}$, Fe$^{2+}$, or Mn$^{2+}$ for Al$^{3+}$ in dioctahedral species) or the tetrahedral sheet (where Al$^{3+}$ or occasionally Fe$^{3+}$ substitutes for Si$^{4+}$), producing one negative charge for each such substitution. The negative layer charge resulting from isomorphic substitutions is balanced by the sorption of exchangeable cations in interlayer sites (Sposito, 1984). The uptake mechanism of metal ions onto smectites depends on ionic strength, pH and the type of ion adsorbing. At low pH and low ionic strength cation exchange is the dominant process at the interlayer space. In addition to cation exchange there is a pH-dependent uptake of metals on smectites (Sposito, 1984). In this sorption process sorbate ions bond to the smectite surface by sharing one or several ligands (generally oxygens) with sorbent cations. At low sorbate cation concentration specific sorption to surface hydroxyl site (Al-OH, Si-OH) can occur (Schlegel et al., 1999). Metal ions can then directly bond to surface oxygen or hydroxyl groups of the sorbent. With increasing pH or sorbate cation concentration, metal precipitation can occur. When the precipitate contains chemical species derived from both the aqueous solution and dissolution of the sorbent mineral, it is referred to as a coprecipitate (Stumm and Morgan, 1981).

Most uptake studies of metals in clay systems have been performed using a macroscopic approach (batch studies). The focus of many of these studies has been on the determination of distribution coefficients, the use of adsorption isotherms, empirical and semi-empirical equations (e.g., Freundlich, Langmuir), and surface complexation models (e.g., constant capacitance, triple layer) to describe the sorption reactions of heavy metals. For example, the uptake of Ni on montmorillonite, a back-fill material used in nuclear waste repositories, has been extensively investigated in our laboratory (Baeyens and Bradbury, 1997) and a ‘mechanistic’ surface complexation model was developed to predict the fate of radionuclides (Bradbury and Baeyens, 1997). However, surface complexation models employ an array of adjustable parameters to fit experimental data, and it has been shown that often sorption data will equally well fit a number of the models (e.g., Westall and Hohl, 1980). Another major disadvantage of most surface complexation models (and equilibrium-based models in general), is that processes such as precipitation and diffusion are not accounted for. One must realize that equilibrium-based models simply describe macroscopic data and do not definitively prove a reaction mechanism. For these reasons the uptake of heavy metal on clay minerals has been directly studied at the molecular level using extended X-ray absorption fine structure (EXAFS) (O'Day et al., 1994; Scheidegger et al., 1998; Thompson et al., 1999; Dähn et al., 2001; Morton et al., 2001; Schlegel et al., 2001; Dähn et al., 2002a). Uptake mechanisms yet identified on dioctahedral phyllosilicates are the formation of a layered
double hydroxide (LDH) phase and the neoformation of a phyllosilicate phase (Scheidegger et al., 1998; Dähn et al., 2002a).

In a powder EXAFS study Scheidegger et al. (1998) observed the formation of Ni-Al LDH phase upon uptake of Ni on pyrophyllite (a dioctahedral 2:1 phyllosilicates which lacks isomorphic substitution). Using a combination of powder and P-EXAFS Dähn et al. (2002a) observed the neoformation of a Ni-phyllosilicate phase upon Ni uptake on montmorillonite (STx-1). In the latter study P-EXAFS has been employed because the application of powder EXAFS to determine the uptake mechanism of metal ions on clay minerals is limited by the extension of the explored reciprocal space (at best \( \Delta k = 14 \text{ Å}^{-1} \)), which precludes the discrimination of atomic shells separated by less than 0.10 - 0.15 Å (Teo, 1986). This is typically the case in phyllosilicates. In montmorillonite, for example, X-ray absorbing atoms in the octahedral sheet are surrounded by neighboring cations at \( R \approx 3.00 \text{ Å} \) in the octahedral sheet and \( R \approx 3.12 - 3.28 \text{ Å} \) in tetrahedral sheets (Fig. 1). This local structure results in a strong overlap of scattering contributions from the octahedral and tetrahedral cations. Manceau and co-workers showed that this limitation can be overcome by polarized-EXAFS (P-EXAFS) spectroscopy (Manceau et al., 1988; Manceau, 1990; Manceau et al., 1998).

4.1.1 P-EXAFS background

In P-EXAFS, neighboring atoms along the polarization direction of the X-ray beam are preferentially probed, while atoms located in a plane perpendicular to this direction are attenuated (see Fig. 1). Applying P-EXAFS to montmorillonite self-supporting films has the advantage of minimizing the contributions from the out-of-plane Si atoms from the tetrahedral sheet when the X-ray polarization vector is in the \( ab \) plane of the montmorillonite self-supporting film. Conversely, when the polarization vector is aligned normal to the film plane the contribution from octahedral layer cation vanishes.
Beam direction

\[ \alpha = 0^\circ \]  

\[ \alpha = 90^\circ \]

Fig. 2: Orientation of the montmorillonite film with respect to the incoming X-ray beam: (left) electric field vector \( \varepsilon \) parallel to the layer plane; (right) \( \varepsilon \) perpendicular to the layer plane. After Manceau et al. (1988).

Originally P-EXAFS was applied to single crystal phyllosilicate crystals (Manceau et al., 1988; Manceau et al., 1990). Recently Manceau et al. (1998; 1999a) demonstrated that this technique can be extended to fine-grained layered clay minerals. Self-supporting clay films can be prepared by filtration and the angular dependence between the electric field vector \( \varepsilon \) and the surface of a self-supporting clay film can be recorded. The angular variations of P-EXAFS spectra depend strongly on how perfect \( ab \) crystallographic planes of individual montmorillonite platelets are aligned parallel to the film surface (see Fig. 3). Therefore, quantitative determination of the orientation distribution (OD) of individual crystallites in the film is necessary to accurately determine coordination numbers, and to localize scattering atoms relative to the polarization direction. The OD of a film is obtained by X-ray diffraction (see section 4.2.3). In P-EXAFS one detects an apparent coordination number (\( CN_{\text{exafs}}^{j,a} \)), which is the effective number of atoms seen at the \( \alpha \) angle and which is modified by the mosaic spread of clay particles of the film plane (Manceau and Schlegel, 2001):

\[
\frac{CN_{\text{exafs}}^{j,a}}{CN_{j}^{\text{cryst}}} = 1 - \frac{3 \cos^2 \beta_{j}^{\text{cryst}}}{2} \frac{I_{\text{ord}}}{(3 \cos^2 \alpha - 2)}
\]  

\eqref{1}
with 
\( \alpha = \) the angle between \( \varepsilon \) and the layer plane,
\( \beta_{j}^{\text{cryst}} = \) the angle between the film normal and the vector \((R_{x})\) connecting the X-ray absorbing atom \( i \) to the backscattering atom \( j \),
\( \text{CN}_{j}^{\text{cryst}} = \) the crystallographic number of atoms in the \( j \) shell.

\( I_{\text{ord}} = \) function that account for the particle disorder; its value is one for perfectly ordered films and zero for an isotropic sample (Dittmer and Dau, 1998; Manceau and Schlegel, 2001).

\( I_{\text{ord}} \) is defined as (with \( \Omega \) the half-width at half maximum (HWHM) of the mosaic spread of clay particles of the film plane, \( \Omega \) is obtained from the OD):

\[
I_{\text{ord}} = \frac{\pi/2}{2} \left[ \int_{0}^{\pi/2} (3 \cos^{2} \alpha - 1) \exp(-\alpha^{2} \ln(2) / \Omega^{2}) \sin \alpha \, d\alpha \right]
\]

Equation (1) can be written as a function of \( \cos^{2} \alpha \):

\[
\frac{\text{CN}_{j,\alpha}^{\text{exafs}}}{\text{CN}_{j}^{\text{cryst}}} = \frac{I_{\text{ord}}}{2} \left( 3 - 9 \cos^{2} \beta_{j}^{\text{cryst}} \right) \cdot \cos^{2} \alpha + 3I_{\text{ord}} \cos^{2} \beta_{j}^{\text{cryst}} + 1 - I_{\text{ord}}
\]

\[
\frac{\text{CN}_{j,\alpha}^{\text{exafs}}}{\text{CN}_{j}^{\text{cryst}}} = a \cdot \cos^{2} \alpha + b
\]

where ‘\( a \)’ and ‘\( b \)’ are regression coefficients. ‘\( a \)’ can be obtained from a linear regression of \( \text{CN}_{j,\alpha}^{\text{exafs}} / \text{CN}_{j}^{\text{cryst}} \) with respect to \( \cos^{2} \alpha \) and the \( \beta_{j}^{\text{cryst}} \) value is obtained from:

\[
\beta_{j}^{\text{cryst}} = \arccos \sqrt{\frac{3 - 2a / I_{\text{ord}}}{9}}
\]

Equation (1) can be simplified for two “magic angles”: \( \text{CN}_{j,\alpha}^{\text{exafs}} = \text{CN}_{j}^{\text{cryst}} \) for \( \alpha = 35.3^\circ \), regardless of the value of \( \beta \) and \( I_{\text{ord}} \), and for \( \beta = 54.7^\circ \), regardless of the value of \( \alpha \) and \( I_{\text{ord}} \).
4.1.2 Objectives

The objective of this study is to gain direct structural evidence for the adsorption of metal ion on the layer edges of a dioctahedral smectite. First evidence for such a process was reported by Schlegel et al. for trioctahedral smectites investigating the uptake of Co and Zn on hectorite (Schlegel et al., 1999; Schlegel et al., 2002). For dioctahedral smectites, however, spectroscopic studies have so far only demonstrated the presence of layered double hydroxide and neoformed Ni-phyllosilicate phases upon the uptake of divalent metal ions (Scheidegger et al., 1998; Dähn et al., 2002a).

In this study, the uptake mechanism of Ni on montmorillonite at pH 7.2 and low Ni concentrations was investigated by P-EXAFS on dry self-supporting films as a function of time. The local structure around Ni atoms on montmorillonite was determined, and the possible evolution of the coordination environment of Ni was recorded over a time period of up to one year.

4.2 Materials and Methods

4.2.1 Montmorillonite purification and characterization

The montmorillonite STx-1 used in this study was purchased from the Source Clay Minerals Repository of the Clay Minerals Society. XRD of the “as received” montmorillonite indicated the presence of minor quantities of calcite, quartz and kaolinite amounting to less than ~1 wt%. This natural clay contains ~0.9 wt% Fe₂O₃. It’s structural formula is Na₀.₀₅Ca₀.₁₂Mg₀.₀₅(Al₁₅Fe(III)₀.₁Mg₀.₄)(Si₄)O₁₀(OH)₂ * n H₂O.

In a purification and conditioning processes was the < 0.5 μm montmorillonite fraction used in this study obtained. Briefly, the clay suspension was centrifuged and soluble hydroxy-aluminium compounds and traces of amorphous iron were removed. Details are given elsewhere (Dähn et al., 2002a). The cation exchange capacity (CEC) of the conditioned montmorillonite measured by the Ca⁴⁵ isotopic dilution method (Baeyens and Bradbury, 1995a) is 1010 ± 10 meq kg⁻¹. The external surface area of the conditioned STx-1 Ca-montmorillonite was measured by the N₂-BET technique to be 89 m²g⁻¹. This value is in agreement with that determined by Van Olphen and Fripiat (84 m²g⁻¹, Van Olphen and Fripiat, 1979)).
4.2.2 Sample preparation for polarized-EXAFS

The P-EXAFS samples were prepared by adding 200 ml of a buffered Ni solution (pH 7.2, 0.3 M NaClO₄) to 40 ml of a conditioned and purified Na-montmorillonite suspension (pH 7.0, 23.8 μM, 0.3 M NaClO₄, Baeyens and Bradbury, 1997). The resulting solid to liquid ratio was 2.14 g/L and the initial Ni concentration was 19.9 μM. It has been shown previously that the use of the buffer (8.3 mM (3-(N-Morpholino) propanesulphonic acid) to maintain constant pH did not influence Ni uptake on montmorillonite (Baeyens and Bradbury, 1995b). Experiments were carried out with the high ionic strength Na background electrolyte in order to block cation exchange sites. The Ni uptake experiments were conducted in a glove box under N₂ atmosphere (CO₂ and O₂ < 5 ppm) and at room temperature.

After 14 and 360 days of reaction time, 40 ml of the suspensions were slowly filtrated through 47 mm diameter filters (Millipore, 0.4 μm pore size) and two highly oriented self-supporting films were prepared. The filtration was performed in a closed vessel under a continuous flow of argon. Excess of solution in the wet films were removed by washing with a few milliliters of de-ionized water before drying. The supernatant solution was analyzed for Ni, Si and Al by ICP-OES. The Ni weight concentration in the clay films was low enough (< 0.05 wt%) to neglect self-absorption effects (Tröger et al., 1992; Castañer and Prieto, 1997). The dried clay films were cut into 8 slices and stacked on two sample holders in order to get a sufficient thickness for fluorescence measurements. In a previous study we have verified that the drying of the film did not modify the overall coordination chemistry of Ni (Dähn et al., 2002a).

Since the goal of this study was to investigate the sorption of Ni on montmorillonite, we selected reaction conditions (initial Ni concentration (19.9 μM); pH = 7.2) which should prevent the formation of Ni-Ni nucleation products such as NiOH₂ or Ni phyllosilicates and nevertheless allow to obtain analyzable EXAFS data (see section 4.3.3). To the best of our knowledge, the solubility products of Ni-silicate phases are not known and the log K_{sp}^{Ni(OH)₂} values reported in the literature vary over a wide range (-10.52 to -18.06; Britton, 1925; Mattigod et al., 1997; Plyasunova et al., 1998). To estimate the degree of saturation with respect to the solubility of Ni(OH)₂, the saturation index (SI) was calculated. SI is defined as the ratio of the ion activity product, IAP, to the solubility constant K_{sp}. This yields SI = \((\text{Ni}^{2+})^2/(\text{H}^+) \cdot K_{sp}\), where (Ni)²⁺ and (H⁺) are the activities of Ni²⁺ and H⁺ in solution. The calculation indicated that [Ni]_{initial} was clearly below the solubility limit of Ni(OH)₂ (SI < 0.06, with log K_{sp}^{Ni(OH)₂} = -10.52, (Plyasunova et al., 1998); SI < 2 × 10⁻⁹, with
log $K_{sp}^{Ni(OH)_{2}} = -18.06$, (Britton, 1925)). Thus, one can assume that Ni removal from solution is not due to Ni(OH)$_2$ formation in solution at any time during the experiments.

Ni speciation using a thermodynamic database (Baes and Mesmer, 1976) showed that under the reaction conditions employed ([Ni]$_{initial} = 19.9$ μM, pH = 7.2) Ni(II) was almost completely present as Ni$^{2+}$ (aq). The concentrations of hydrolyzed species such as Ni(OH)$^0$, Ni(OH)$_2^0$, Ni(OH)$_3^2$, Ni$_2$(OH)$_3^3$ and Ni$_4$(OH)$_4^{4+}$ were altogether < 2 x 10$^{-8}$ M.

4.2.3 Quantitative texture analysis

X-ray diffraction texture analysis measurements were conducted with Ni treated self supporting montmorillonite films using a Huber texture goniometer in reflectance mode, with monochromatized Cu K$_\alpha$ radiation focused to 0.5 x 0.5 mm. The complete film texture can be obtained by measuring the inclination of (001) crystallographic planes off the sample surface (Manceau et al., 1998). Fig. 3a illustrates the principle of obtaining the film texture on a diffractometer. Three rotation movements Bragg angle ($\theta_{hkl}$), azimuthal ($\varphi$) and tilt angle ($\rho$) are available. For a fixed $\theta_{hkl}$ all platelets are brought into a diffracting position by rotating the sample around $\varphi$ and $\rho$. The diffracted intensity is proportional to the number of montmorillonite planes that satisfy these orientations and Bragg conditions. Fig. 3b illustrates how individual particles are brought into diffracting position (black planes are diffracting).

We have measured {004} pole figures of a single slice of the montmorillonite film by scanning $\rho$ between 0 and 85° and $\varphi$ between 0 and 360° with angle increments of 5° with an integration time of 2h for each tilt angle position. The densities of the orientation distribution were calculated from the diffracted intensities integrated over all $\varphi$ and $\rho$ using direct normalization and taking a density of zero for $\rho > 80°$ (for details see Manceau et al., 2000b). Distribution densities are expressed as ‘multiple of a random distribution’ or ‘mrd’ (Bunge and Esling, 1982) and are equal to 1 for a random oriented sample.
Fig. 3: a) X-ray diffraction geometry used for texture analysis and b) a side view of (a) showing how individual crystallographic planes within in the film are brought to diffraction position by a rotation of $\rho$. After Manceau et al. (1998).

4.2.4 EXAFS data collection and reduction

Ni K-edge XAFS spectra were recorded on the ID26 beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France (Gauthier et al., 1999). All spectra were recorded at room temperature using a Si(220) monochromator and a fast, highly linear, and low-noise PIN diode detector with a 6 µm thick Co filter (Gauthier et al., 1996). Higher order harmonics were rejected with two mirrors (Si and fused silica, Signorato and Solé, 1999). The monochromator angle was calibrated by assigning to 8333 eV the first inflection point of the K-absorption edge spectrum of Ni metal. P-EXAFS spectra were recorded with the electric field vector $\mathbf{e}$ at $\alpha = 10^\circ, 35^\circ, 55^\circ$ and $80^\circ$ with respect to the film plane. Several scans were averaged to improve the signal to noise ratio.

Data reduction was carried out with the WinXAS 97 2.1 software package (Ressler, 1998). The energy was converted to photoelectron wave vector units ($\text{Å}^{-1}$) by assigning the origin $E_0$ to the first inflection point of the absorption edge. Radial structure functions (RSFs)
were obtained by Fourier transforming $k^3$-weighted $\chi(k)$ functions between 3.2 and 10 Å$^{-1}$ using a Bessel window function with a smoothing parameter of 4. Amplitude and phase shift functions were calculated with FEFF 8.0 (Rehr et al., 1991) using the structures of β-Ni(OH)$_2$ and Ni-Talc (Perdikatsis and Burzlaff, 1981) as references. Fits were performed in R space in the 0.6 to 3.5 Å interval. The amplitude reduction factor ($S_0^2$) was determined to be 0.85 from the experimental β-Ni(OH)$_2$ EXAFS spectrum. The deviation between the fitted and the experimental spectra (%Res) is given by:

$$%\text{Res} = \frac{100}{N} \sum_{i=1}^{N} \left| y_{exp}(i) - y_{theo}(i) \right|$$

where $N$ is the number of points in the fit window, and $y_{exp}$ and $y_{theo}$ are the experimental and theoretical RSF values. The precision on the P-EXAFS distances ($R$) was previously estimated to be ≤ ± 0.02 Å for $R_{\text{Ni-O}}$, and ≤ ± 0.03 Å for $R_{\text{Ni-Al}}$ and $R_{\text{Ni-Si}}$, and ± 0.5 for the coordination numbers (CN$^{\text{calc}}$) (Dähn et al., 2002a; Schlegel et al., 2002). The experimental uncertainty on $\alpha$ in the P-EXAFS measurements is ≤ ± 1°.
4.3 Results

4.3.1 Ni uptake experiments

ICP-OES measurements showed that the proportion of Ni uptaken amounted to 43% (4 μmol/g, [Ni]eq = 11.9 μM) after 14 days and to 83% (7 μmol/g, [Ni]eq = 3.3 μM) after 360 days of reaction time. The Si concentration in solution increased from 110 to 320 μM, corresponding to an average Si release rate of 4.4 × 10^{-14} mol m^{-2} s^{-1} (pH = 7.2; time range 14 - 360 days). The measured Si release rate agrees with dissolution rates of montmorillonite in presence (3.5 × 10^{-14} mol m^{-2} s^{-1} (pH = 8.0; time range 14 - 206 days, Dähn et al., 2002a; 3.2 × 10^{-14} mol m^{-2} s^{-1}, pH = 7.5, Scheidegger et al., 1997) and absence of Ni respectively (5.4 × 10^{-14} mol m^{-2} s^{-1}, pH = 5, Furrer et al., 1993; and 1 × 10^{-15} mol m^{-2} s^{-1}, pH = 6, Heydemann, 1966). The Al and Mg concentration in solution was too low (< 4 μM) to produce reliable ICP-OES measurements.

4.3.2 Texture analysis

Intensities of ρ-scans were obtained by averaging for each ρ value the normalized densities of (004) pole figures over all φ angles. The variations of the diffracted intensity of the (004) reflection are shown in Fig. 4a) and b) for 14 and 360 days of reaction time, respectively. The curve shape were calculated from the ρ-scan integrated intensities using direct normalization and taking a density of zero for ρ > 80° (for details see (Manceau et al., 2000).

At ρ = 0 we observe a strong maximum with a density value of approximately 10 mrd (14 days) and 8.4 mrd (360 days) which indicates that most of montmorillonite platelets have their (a,b) planes aligned parallel to the film plane. The experimental ρ-scan curves were best-fitted with Gaussian distributions (solid line in Fig. 4a) and b). The fit resulted in a full-width at half maximum (FWHM) of 44.3° for the sample which was in contact with Ni for 14 days, and a FWHM of 47.1° for 360 days. These texture values will be used later to correct the coordination numbers and the experimental determined β angles for the imperfect orientation using equation (1) and (5) (see section 4.3.3).
Fig. 4: Integrated radial distribution densities of the c* axes of montmorillonite crystals with respect to the normal of the film plane ($\rho = 0^\circ$) for a) 14 and b) 360 days.
4.3.3 P-EXAFS

Fig. 5a and Fig. 5b show $k^3 \chi(k)$ P-EXAFS spectra of Ni treated self-supporting montmorillonite films recorded at various angles for a reaction time of 14 days and 360 days, respectively. The figures exhibit a pronounced angular dependence, consistent with a successful film preparation (see section 4.3.2). The two spectra recorded at $\alpha = 80^\circ$ have a clear beat pattern at $k = 5.3$ Å$^{-1}$. With increasing $\alpha$ angle, the intensity of the shoulder at 5.3 Å$^{-1}$ increases and the wave frequency at 5.3 Å$^{-1}$ shifts slightly. The spectra contain several isosbestic points, for which $k^3 \chi(k)$ is independent of $k$, over the whole $k$ range. Isosbestic points are very sensitive to normalization errors during the reduction of raw X-ray absorption spectra. The fact that all the individual $k^3 \chi(k, \alpha)$ spectra precisely cross at the same value in these points provides a stringent proof of the reliability of P-EXAFS spectra even at high $k$ values where the noise is the highest.

The changes in spectral shape and frequency indicate that the coordination chemistry of Ni is anisotropic, i.e. that its coordination environment is oriented with respect to clay layers. Furthermore, the anisotropy in the spectra is increasing with increasing reaction time (Fig. 5a (14 days), Fig. 5b (360 days)), suggesting that the average coordination environment of Ni is modified.

Fig. 6a and Fig. 6b show that in the corresponding experimental RSFs for 14 and 360 days reaction time there is a RSF peak (Ni-O contribution) at 1.54 Å in both samples (labeled A). With increasing $\alpha$ angle the amplitude of peak A decreases while the peak position remains constant. Beyond the first shell there are two further RSF peaks (labeled B1 and B2). Fig. 6a and Fig. 6b show furthermore, that most of the anisotropy observed in the $k^3 \chi(k)$ spectra is transferred to the RSF peaks B1 and B2 in the real space. Peak B2 is present at all angles and for both reaction times, whereas peak B1 ($R + \Delta R = 2.35$ Å, $\alpha = 10^\circ$) is only resolved after a reaction time of 360 days. With increasing $\alpha$ the intensity of peak B2 is increasing and the position shifts from $R + \Delta R = 2.98$ Å ($\alpha = 10^\circ$) to $R + \Delta R = 2.84$ Å ($\alpha = 80^\circ$).
Fig. 5: $k^3$-weighted Ni K-edge P-EXAFS spectra of a Ni treated montmorillonite film at $\alpha$ angles of 10°, 35°, 55° and 80° (pH 7.2). The arrows points the most important anisotropic spectral feature. a) reaction time 14 days (4 µmol/g), b) 360 days (7 µmol/g).
Polarization dependence of the RSFs obtained from the EXAFS spectra presented in Fig. 5. a) reaction time 14 days (4 μmol/g), b) 360 days (7 μmol/g).
Peak B1 can either correspond to a side-lobe peak, originating from the limited reciprocal space integrated in the Fourier transform (i.e., a truncation effect), or it may have structural origin. The first hypothesis can be disregarded for the following reasons. First a parameterized Bessel function was used which minimizes the intensity of a side-lobe (see section 4.2.4). Second, for a given Fourier-integration range, the ratio of intensities of the main and side-lobe peaks is constant. Thus, when the intensity of peak A remains constant, the intensity of peak B1 should remain constant as well. Examination of Fig. 6a and Fig. 6b shows that the intensities of peak A remained unchanged for $\alpha = 10^\circ$ (solid line Fig. 6a and b), whereas the intensity of peak B1 increases with time (14 vs. 360 days). Finally the peak B2 is asymmetric on its left side, suggesting that a further backscattering contribution is present at a shorter distance. The fact that peak B1 is most pronounce at $\alpha = 10^\circ$ demonstrates the ability of P-EXAFS to scrutinize especially the local order beyond the first coordination shell, which is precisely the scale needed to determine surface complexes formed upon Ni uptake on montmorillonite.

Structural parameters derived from a multi-shell fit in R-space are reported in Table 2 (14 days) and Table 3 (360 days). As an example the corresponding fitted FTs for 360 days are shown in Fig. 7 together with the experimental data of the Ni treated montmorillonite film. The figure indicates that the fit match the experimental data both for the real and the imaginary part well. Furthermore, Fig. 7 shows that the imaginary part is strongly depending on the $\alpha$ angle. The angular evolution of the modulus and the imaginary part indicates that Ni has a different parallel and perpendicular local structure.

Data analysis indicated that the first coordination shell is described best by O atoms at a bond distance ($R_{\text{Ni-O}}$) of 2.05 Å which is typical of six-fold coordinated Ni (Pandya et al., 1990). It was not possible to fit any of the experimental data using a Ni-Ni pair and/or a combination of Ni-Ni and Ni-Si/Al pairs. This finding suggests that no Ni nucleation phase formed in our sorption system under the employed reaction conditions. Furthermore, any attempts to fit the second FT peak with a single Ni-Si pair failed and a good fit with two Ni-Si pairs (Ni-Si1/Ni-Si2) was obtained only at $\alpha = 80^\circ$. To reduce the number of fit parameters the following EXAFS parameters were constrained at $\alpha$ different from $80^\circ$: $R_{\text{Ni-Si1}}$, $\sigma^2_{\text{Ni-Si1}}$, $R_{\text{Ni-Si2}}$ and $\sigma^2_{\text{Ni-Si2}}$ were fixed to their values at $\alpha = 80^\circ$, $R_{\text{Ni-O}}$, $\sigma^2_{\text{Ni-O}}$ and the inner potential correction parameter, $\Delta E_0$, were determined at $\alpha = 35^\circ$, and then held fixed at $\alpha \neq 35^\circ$. 
Table 2: Structural information derived from P-EXAFS analysis for the 14 day sample.

<table>
<thead>
<tr>
<th>α</th>
<th>Ni-O shell</th>
<th></th>
<th>Ni-Al shell</th>
<th></th>
<th>Ni-Si1 shell</th>
<th></th>
<th>Ni-Si2 shell</th>
<th></th>
<th>ΔE₀</th>
<th>%Res</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN_Ni-O</td>
<td>R_Ni-O</td>
<td>σ²</td>
<td></td>
<td>CN_Ni-Al</td>
<td>R_Ni-Al</td>
<td>σ²</td>
<td></td>
<td>CN_Ni-Si1</td>
<td>R_Ni-Si1</td>
</tr>
<tr>
<td>10°</td>
<td>5.5</td>
<td>2.03</td>
<td>0.005b</td>
<td></td>
<td>2</td>
<td>3.00c</td>
<td>0.006c</td>
<td></td>
<td>1.3</td>
<td>3.10a</td>
</tr>
<tr>
<td>35°</td>
<td>5.3</td>
<td>2.03</td>
<td>0.005</td>
<td></td>
<td>1.6</td>
<td>3.00c</td>
<td>0.006c</td>
<td></td>
<td>1.9</td>
<td>3.10a</td>
</tr>
<tr>
<td>55°</td>
<td>5.0</td>
<td>2.03</td>
<td>0.005b</td>
<td></td>
<td>0.9</td>
<td>3.00c</td>
<td>0.006c</td>
<td></td>
<td>2.6</td>
<td>3.10a</td>
</tr>
<tr>
<td>80°</td>
<td>4.8</td>
<td>2.03</td>
<td>0.005b</td>
<td></td>
<td>0</td>
<td>3.00c</td>
<td>0.006c</td>
<td></td>
<td>3.0</td>
<td>3.10a</td>
</tr>
</tbody>
</table>

CN_{P-EXAFS}, R, σ², ΔE₀ are the apparent coordination numbers, interatomic distances, Debye-Waller factors and inner potential corrections. a: fixed to the value determined at α = 80°, b: fixed to the value determined at α = 35°, c: fixed to the value obtained from the P-EXAFS analysis for the 360 day sample (Table 3).

Table 3: Structural information derived from P-EXAFS analysis for the 360 day sample.

<table>
<thead>
<tr>
<th>α</th>
<th>Ni-O shell</th>
<th></th>
<th>Ni-Al shell</th>
<th></th>
<th>Ni-Si1 shell</th>
<th></th>
<th>Ni-Si2 shell</th>
<th></th>
<th>ΔE₀</th>
<th>%Res</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CN_Ni-O</td>
<td>R_Ni-O</td>
<td>σ²</td>
<td></td>
<td>CN_Ni-Al</td>
<td>R_Ni-Al</td>
<td>σ²</td>
<td></td>
<td>CN_Ni-Si1</td>
<td>R_Ni-Si1</td>
</tr>
<tr>
<td>10°</td>
<td>5.2</td>
<td>2.04</td>
<td>0.005b</td>
<td></td>
<td>2.8</td>
<td>3.00c</td>
<td>0.006c</td>
<td></td>
<td>0.7</td>
<td>3.12a</td>
</tr>
<tr>
<td>35°</td>
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<td>0.005</td>
<td></td>
<td>2</td>
<td>3.00d</td>
<td>0.006c</td>
<td></td>
<td>1.5</td>
<td>3.12a</td>
</tr>
<tr>
<td>55°</td>
<td>5</td>
<td>2.04</td>
<td>0.005b</td>
<td></td>
<td>1</td>
<td>3.00d</td>
<td>0.006c</td>
<td></td>
<td>2</td>
<td>3.12a</td>
</tr>
<tr>
<td>80°</td>
<td>4.9</td>
<td>2.04</td>
<td>0.005b</td>
<td></td>
<td>0</td>
<td>3.00d</td>
<td>0.006c</td>
<td></td>
<td>2.5</td>
<td>3.12</td>
</tr>
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</table>

a: fixed to the value determined at α = 80°, b: fixed to the value determined at α = 35°, c: fixed to the value obtained for the Si1 shell, d: fixed to the value determined at α = 10°.
Fig. 7: Polarization dependence of the Fourier transforms (modulus and imaginary parts) and the corresponding least-squares fit for the 360 days sample. Solid line: experimental data, dotted line: least-squares fit.
Following the constraints described above, the second FT peak at $\alpha = 80^\circ$ could be fitted well with one Ni-Al and two Ni-Si pairs for both samples (Table 2 (14 days) and Table 3 (360 days)). With increasing angle, $\text{CN}^{\text{exafs}}_{\text{Ni-Al}}$ at 3.00 Å decreased (e.g. from $\text{CN}^{\text{exafs}}_{\text{Ni-Al}}$ (360 days) = 2.8 $\pm$ 0.5 at $\alpha = 10^\circ$ to $\text{CN}^{\text{exafs}}_{\text{Ni-Al}}$ (360 days) = 0 $\pm$ 0.5 at $\alpha = 80^\circ$) whereas $\text{CN}^{\text{exafs}}_{\text{Ni-Si}}$ at 3.10 - 3.12 Å and $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ at 3.26 - 3.27 Å increased (e.g. from $\text{CN}^{\text{exafs}}_{\text{Ni-Si}}$ (360 days) = 0.7 $\pm$ 0.5 and $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ (360 days) = 3.4 $\pm$ 0.5 at $\alpha = 10^\circ$ to $\text{CN}^{\text{exafs}}_{\text{Ni-Si}}$ (360 days) = 2.5 $\pm$ 0.5 and $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ (360 days) = 5.5 $\pm$ 0.5 at $\alpha = 80^\circ$) in both samples. In contrast to the Ni-Si pairs, which were detected at all angles, the Ni-Al pair was completely extinguished in the perpendicular orientation in both samples.

The sum of $\text{CN}^{\text{exafs}}_{\text{Ni-Si}} + \text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ can be compared with the sum of nearest Si neighbors of cations (Al, Mg, Fe) in the octahedral sheet of montmorillonite. Using equation (1) and assuming crystallographic $\beta$ values of phyllosilicates ($\beta_{\text{cryst}}$ = 33 - 35°) and $\alpha = 80^\circ$ one expects this sum to be ~8. This crystallographic value corresponds well with the coordination number of SiI and Si2 observed at $\alpha = 80^\circ$ ($\text{CN}^{\text{exafs}}_{\text{Ni-Si1}}$, $\alpha = 80^\circ$ + $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$, $\alpha = 80^\circ$ = 8, 360 days). With decreasing $\alpha$ the correspondence between crystallographic and experimental values for the sum of Si neighbors decreases. For example, for $\alpha = 35^\circ$ the coordination number of Si1 and Si2 ($\text{CN}^{\text{exafs}}_{\text{Ni-Si1}}, \alpha = 35^\circ$ + $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}, \alpha = 35^\circ$ = 5.5, 360 days) is slightly higher than those expected in phyllosilicates ($\text{CN}^{\text{cryst}}_{\text{Ni-Si1}} + \text{CN}^{\text{cryst}}_{\text{Ni-Si2}} = 4$). We suspect that the reason for the increasing disagreement is that for angles $\alpha < 80^\circ$ an additional Ni-Al pair contributes to the overall spectrum. A FEFF simulation supports this hypothesis and indicates that Ni-Al pairs at 3.0 Å are destructively interfering with the two Ni-Si pairs (at 3.1-3.12 Å and 3.26-3.27 Å).

Based on the variation of CN as function of $\alpha$ it is possible to determine the angle $\beta$ between the film normal and the vector connecting the X-ray absorbing atom (Ni) to the backscattering atoms (Si and Al) (See section 4.1.1 and Fig. 2). $\text{CN}^{\text{exafs}}_{\text{Ni-Al}}$, $\text{CN}^{\text{exafs}}_{\text{Ni-Si1}}$ and $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ for the Al and Si shells for the 14 and 360 days samples are plotted in Fig. 8, respectively Fig. 9, as a function of $\cos^2 \alpha$. Good linear correlations were obtained with regression coefficients $r^2 > 0.99$. The gradual decrease of $\text{CN}^{\text{exafs}}_{\text{Ni-Al}}$ and increase of $\text{CN}^{\text{exafs}}_{\text{Ni-Si1}}$ and $\text{CN}^{\text{exafs}}_{\text{Ni-Si2}}$ with increasing $\alpha$ imply $\beta_{\text{Ni-Al}} > 54.7^\circ$, and $\beta_{\text{Ni-Si1}}$ and $\beta_{\text{Ni-Si2}} < 54.7^\circ$ (see
section 4.1.1, equation (1)). The β angles for Ni-Al, Ni-Si1 and Ni-Si2 pairs were then calculated using equation (5). Assuming a perfectly ordered film (I_{ord} = 1) this approach yields for example for 360 day: $\beta_{\text{Ni-Al}} = 84^\circ$, $\beta_{\text{Ni-Si1}} = 39^\circ$, and $\beta_{\text{Ni-Si2}} = 47^\circ$ (Table 4).

In reality, some of the montmorillonite platelets in our sorption system are oriented off the film plane (Fig. 4). The values of the mosaic spread of the self-supporting films determined with quantitative texture analysis allow to correct the experimental determined β angles for the imperfect orientation using equation (5). Equation (2) was solved numerically because the integral in the numerator has no analytical solution (Manceau and Schlegel, 2001). This resulted in $I_{ord} = 0.73$ (14 days, FWHM 44.3°) and 0.70 (360 days, FWHM 47.1°). The corrected β values ($\beta^{\text{corr}}$) are shown in Table 4. The results indicate that Ni-Al pairs are oriented essentially parallel to the film plane and Ni-Si pairs are inclined out of the plane. The experimental β angles match within uncertainty with crystallographic values in montmorillonite (33° (cis sites) and 35° (trans sites), Tsipursky and Drits, 1984).

Table 4: Reduced slope of linear regressions and inclination of cationic shell from the second FT peak.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atomic shell</th>
<th>$S^a$</th>
<th>$\beta^{\text{exp}} b$</th>
<th>$\Delta\beta^{\text{exp}} c$</th>
<th>$\beta^{\text{real}} d$</th>
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</thead>
<tbody>
<tr>
<td>14 days</td>
<td>Al</td>
<td>1.38</td>
<td>81</td>
<td>9</td>
<td>90°</td>
</tr>
<tr>
<td></td>
<td>Si1</td>
<td>-0.97</td>
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<td>6</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Si2</td>
<td>-0.69</td>
<td>46</td>
<td>6</td>
<td>42</td>
</tr>
<tr>
<td>360 days</td>
<td>Al</td>
<td>1.46</td>
<td>84</td>
<td>8</td>
<td>90°</td>
</tr>
<tr>
<td></td>
<td>Si1</td>
<td>-1.24</td>
<td>39</td>
<td>7</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Si2</td>
<td>-0.56</td>
<td>47</td>
<td>7</td>
<td>44</td>
</tr>
</tbody>
</table>

a: Slope of the regression line normalized by $CN_{\alpha=35}^{\text{exafs}}$.
b: Inclination angle of the backscattering shell uncorrected from the film texture.
c: The precision on β was estimated from the dispersion of $CN_{\alpha=35}^{\text{exafs}}$ at the 95% confidence level.
d: Inclination angle of the backscattering shell uncorrected from the film texture.
e: The correction for texture effects yielded unrealistic important angular dependences. These $\beta^{\text{real}}$ values were bounded to maximum (90°) realistic values.
Fig. 8: Angular dependence of $\text{CN}_{\text{Ni-Al}}^\text{exafs}$ (a), $\text{CN}_{\text{Ni-Si1}}^\text{exafs}$ (b) and $\text{CN}_{\text{Ni-Si2}}^\text{exafs}$ (c) for 14 days. Points: experimental data, solid line: linear regression. $\text{CN}_{\text{Ni-Al}}^\text{exafs} = 2.2\cdot \cos^2 \alpha$, $\text{CN}_{\text{Ni-Si1}}^\text{exafs} = -1.8\cdot \cos^2 \alpha + 3.1$, and $\text{CN}_{\text{Ni-Si2}}^\text{exafs} = -3.0\cdot \cos^2 \alpha + 6.4$ (solid lines). The uncertainty on CN is estimated to ± 0.5.
Fig. 9: Angular dependence of $CN_{Ni-Al}^{\text{exafs}}$ (a), $CN_{Ni-Si1}^{\text{exafs}}$ (b) and $CN_{Ni-Si2}^{\text{exafs}}$ (c) for 360 days. Points: experimental data, solid line: linear regression. $CN_{Ni-Al}^{\text{exafs}} = 2.92 \times \cos^2 \alpha$, $CN_{Ni-Si1}^{\text{exafs}} = -1.86 \times \cos^2 \alpha + 2.6$, and $CN_{Ni-Si2}^{\text{exafs}} = -2.25 \times \cos^2 \alpha + 5.55$ (solid lines). The uncertainty on CN is estimated to ± 0.5.
Because at $\alpha = 10^\circ$ three contributions (Ni-Al, Ni-Si1 and Ni-Si2) are overlapping at a distance between 3.0 - 3.27 Å it is desirable to get a further prove for the presence and the intensity of the Ni-Al pair in the continuity of the octahedral sheet. The Al contributions at $\alpha = 10^\circ$ can be calculated from the knowledge of $\beta_\text{Ni-Si1}^{\text{real}}$ and $\beta_\text{Ni-Si2}^{\text{real}}$, and $CN_{\text{Ni-Si1}}^{\text{exafs}}$ and $CN_{\text{Ni-Si2}}^{\text{exafs}}$ at $\alpha = 80^\circ$ using equation (1).

In a first approach we have used theoretical crystallographic values ($\beta_\text{Ni-Si1}^{\text{cryst}} = 33^\circ$ and $\beta_\text{Ni-Si2}^{\text{cryst}} = 35^\circ$) for the subtraction of the Si1 and Si2 contribution at $\alpha = 10^\circ$. The Si1 and Si2 contributions were attenuated by $-25\%$ of its amplitude at $\alpha = 80^\circ$. For both samples this approach yielded: $CN_{\text{Ni-Si1},\alpha=10^\circ}^{\text{exafs}} = 0.6 - 0.7$ and $CN_{\text{Ni-Si2},\alpha=10^\circ}^{\text{exafs}} = 1.5 - 1.7$. We noted that the subtraction of the Si contributions by this approach was not sufficient to completely remove the Si contributions from the spectra at $\alpha = 10^\circ$. Therefore, we have disregarded the approach using crystallographic $\beta$ values and used instead $\beta^{\text{real}}$ angles determined experimentally. Accordingly, the amplitude of the Ni-Si1 and Ni-Si2 shells at $\alpha = 10^\circ$ was attenuated by 33% and 43% of its value at $\alpha = 80^\circ$ for 14 days; respectively 23% and 50% for 360 days. These reduction factors were then used to calculate $CN_{\text{Ni-Si1},\alpha=10^\circ}^{\text{exafs}}$ and $CN_{\text{Ni-Si2},\alpha=10^\circ}^{\text{exafs}}$ ($CN_{\text{Ni-Si1},\alpha=10^\circ}^{\text{exafs}} = 1.0$ and $CN_{\text{Ni-Si2},\alpha=10^\circ}^{\text{exafs}} = 2.7$ for 14 days; $CN_{\text{Ni-Si1},\alpha=10^\circ}^{\text{exafs}} = 0.6$ and $CN_{\text{Ni-Si2},\alpha=10^\circ}^{\text{exafs}} = 2.8$ for 360 days) and to subtract the contribution of Si atoms in the parallel orientation from the original spectrum at $\alpha = 10^\circ$. The RSFs obtained by this subtraction procedure are shown in Fig. 10 together with the original spectrum. The figure shows that the features observed in the 2.2 to 3.5 Å R-range in the original spectrum are caused by an interference of the Ni-Al and Ni-Si pairs. Fig. 11 shows the experimental FT after the removal of the Si contribution together with the corresponding fit. The fit shows a good match for the Ni-Al pair (also in the imaginary part). The corresponding fit results are presented in Table 5. When $\sigma_{\text{Ni-Al}}^2$ was fixed to the value obtained for the 360 days sample ($\sigma_{\text{Ni-Al}}^2 = 0.005$) $CN_{\text{Ni-Al},\alpha=10^\circ}^{\text{exafs}}$ increased from 1.5 to 2.3 at $\alpha = 10^\circ$. When $\sigma_{\text{Ni-Al}}^2$ of the 14 day sample was allowed to vary, $\sigma_{\text{Ni-Al}}^2$ increased from 0.005 Å$^2$ to 0.01 Å$^2$ and $CN_{\text{Ni-Al},\alpha=10^\circ}^{\text{exafs}}$ (14 days) increased from 1.5 to 2.2. Thus the fit results can be interpreted by either $\sigma_{\text{Ni-Al}}^2$ is decreasing or $CN_{\text{Ni-Al},\alpha=10^\circ}^{\text{exafs}}$ is increasing with increasing reaction time. To determine $CN_{\text{Ni-Al}}^{\text{cryst}}$ for the following discussion we have applied equation (1) to the obtained $CN_{\text{Ni-Al},\alpha=10^\circ}^{\text{exafs}}$ (with $\beta = 90^\circ$, $I_{\text{std}} = 0.79$ (14 days) and 0.77 (360 days)). This result for 14 days
in: \( C_{\text{Ni-Al}}^{\text{cryst}} (14 \text{ days}) = 1.5 \left( \sigma_{\text{Ni-Al}}^2 = 0.01 \text{ Å}^2 \right) \), and \( C_{\text{Ni-Al}}^{\text{cryst}} = 1 \left( \sigma_{\text{Ni-Al}}^2 = 0.005 \text{ Å}^2 \right) \) and for 360 days: \( C_{\text{Ni-Al}}^{\text{cryst}} = 1.6 \left( \sigma_{\text{Ni-Al}}^2 = 0.005 \text{ Å}^2 \right) \). The obtained \( C_{\text{Ni-Al}}^{\text{cryst}} \) compare well with the values of the multi-shell fit with two Si shells (e.g. for 360 days \( C_{\text{Ni-Al}}^{\text{cryst}} = 1.6 \) vs. \( C_{\text{Ni-Al}}^{\text{exafs}} = 2 \); Table 3).

The above data analysis approach demonstrates how P-EXAFS allows to improve the discrimination between contributions of overlapping atomic shells and to increase the EXAFS sensitivity. Furthermore, it proofs the consistency, of the overall spectral fit strategy.
Fig. 10: RSF of the original 10° spectrum (solid line) and the 10° spectrum after subtraction (dashed line) of the contribution of Si1 (dotted line) and Si2 (dash dotted line). For a) 14 and b) 360 days.
Table 5: Structural information derived from P-EXAFS analysis for Al at 10°.

<table>
<thead>
<tr>
<th>days</th>
<th>$CN_{Ni-O}^{exafs}$</th>
<th>$R_{Ni-O}$ [Å]</th>
<th>$\sigma^2$ [Å²]</th>
<th>$CN_{Ni-Al}^{exafs}$</th>
<th>$R_{Ni-Al}$ [Å]</th>
<th>$\sigma^2$ [Å²]</th>
<th>$\Delta E_0$ [eV]</th>
<th>%Res</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>5.3</td>
<td>2.03</td>
<td>0.005</td>
<td>1.5</td>
<td>3.01</td>
<td>0.005</td>
<td>-0.8</td>
<td>4.9</td>
</tr>
<tr>
<td>360</td>
<td>5.1</td>
<td>2.03</td>
<td>0.005</td>
<td>2.3</td>
<td>2.99</td>
<td>0.005</td>
<td>-0.8</td>
<td>5.0</td>
</tr>
<tr>
<td>14</td>
<td>5.3</td>
<td>2.03</td>
<td>0.005</td>
<td>2.2</td>
<td>3.01</td>
<td>0.01</td>
<td>-0.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

f: fixed to the value determined for the 360 day sample.

Fig. 11: Fourier transforms (modulus and imaginary parts) and the corresponding least-squares fit for a) the 14 and b) 360 day samples after subtraction of the Si contribution as described in the text. Solid line: experimental data, dotted line: least-squares fit.
4.4 Discussion

4.4.1 Ni environment

In this study the Ni uptake on montmorillonite was investigated by P-EXAFS measurements with highly oriented self-supporting Ni treated montmorillonite films. The P-EXAFS data show a pronounced angular dependence which allows to isolate in-plane and out-of-plane contributions in the P-EXAFS spectra. In a previous P-EXAFS and powder EXAFS study on Ni uptake onto the same montmorillonite at pH 8 ([Ni]initial = 0.66 mM; 0.3 M NaClO₄), was the formation of a neoformed Ni-phyllosilicate phase observed (Dähn et al., 2002a). The study indicated that the neoformed Ni-phyllosilicate phase was present after a short reaction time (1 day), suggesting that Ni nucleation in clay systems can occur fast. While the study yielded the identification of a neoformed Ni phase, the binding of Ni to surface sites of montmorillonite could not be shown. The observation of the latter mechanism was prevented due to the strong backscattering contribution of Ni-Ni pairs compared to Ni-Al pairs at distances form 3.0 - 3.1 Å. Therefore, in this study Ni uptake on montmorillonite was investigated at lower pH (7.2) and lower Ni concentration ([Ni]initial = 19.9 µM; see section 4.2.2). In spite of Ni loadings as low as 4 µmol/g (250 ppm sorbed Ni) good quality P-EXAFS data could be obtained (Fig. 4). Data analysis confirms the absence of Ni-Ni pairs in all the P-EXAFS spectra, even when the clay material was treated with Ni for a prolonged reaction time (360 days). This finding allowed us to investigate the binding of Ni to montmorillonite.

The P-EXAFS study indicates the presence of one Ni-Al and two Ni-Si pairs. The angular variations of CN_{Ni-Al}^{exafs}, CN_{Ni-Si}^{exafs} and CN_{Ni-Si2}^{exafs} observed in structural data of the Ni treated montmorillonite films (Table 2 and Table 3) indicate that the Ni-Al and the two Ni-Si pairs have the same orientations as Al-Al and Al-Si pairs in montmorillonite particles. The obtained \( \beta_{\text{real}} \) angles (\( \beta_{\text{real}}^{\text{Ni-Al}} = 90^° \), \( \beta_{\text{real}}^{\text{Ni-Si}} = 32^° - 38^° \) and \( \beta_{\text{real}}^{\text{Ni-Si2}} = 42^° - 44^° \)) are similar to \( \beta \) angles in the montmorillonite structure (\( \beta_{\text{cryst}}^{\text{Al-Al}} = 90^° \), \( \beta_{\text{cryst}}^{\text{Al-Si}} \sim 34^° \) and \( \beta_{\text{cryst}}^{\text{Al-Si2}} \sim 35^° \)).

Table 2 and Table 3 suggest that Ni-Al and Ni-Si bond distances determined by data analysis (\( R_{\text{Ni-Al}} = 2.99 - 3.01 \) Å, \( R_{\text{Ni-Si}} = 3.10 - 3.12 \) Å and \( R_{\text{Ni-Si2}} = 3.26 - 3.27 \) Å) are close to Al-Al and Al-Si bond distances in montmorillonite (Table 1, Tsipursky and Drits, 1984). Furthermore, the EXAFS study revealed the presence of a \( R_{\text{Si-Si2}} \) of 3.26 Å that is characteristic for tetrahedral Ni-Si linkages in Ni bearing clays (Manceau and Calas, 1986; Charlet and Manceau, 1994; Dähn et al., 2002a).
These above findings strongly support that Ni is structurally linked to the montmorillonite structure and we propose that Ni either bonded to the clay material as a surface complex or incorporated in the montmorillonite structure. The two possibilities will be discussed in the following sections in more details.

4.4.2 Structural relationship between the Ni and montmorillonite

4.4.2.1 Diffusion of Ni into the montmorillonite structure

The diffusion of Ni into montmorillonite was investigated by Muller et al. (Muller et al., 1997) by saturating montmorillonite with Ni cations and heating the clay material up to 350° C (Hoffman and Klemen, 1950) prior to EXAFS and XRD measurements. Data analysis indicated ~2 Ni-Fe and ~4 Ni-Al/Mg pairs at ~3.02 Å and ~4 Ni-Si pairs at ~3.25 Å. The structural data were interpreted as spectroscopic evidence for the diffusion of Ni into the cv sites of montmorillonite. One might now speculate that although we worked at room temperature, a similar process occurred in our sorption system over the time scale of one year.

To evaluate whether the diffusion of Ni into montmorillonite is a possible uptake mode we have simulated the diffusion of Ni into a cv position (Ni1 in Fig. 12a). Diffusion into tv sites can be excluded based on the arguments given in section 4.1. Assuming Ni diffuses into cv sites one would expect CN_{Ni-Al}^{\text{exafs}} to increase with time. Table 5 suggests that this is not the case when the system disorder was allowed to vary. Furthermore, one can assume that a Ni atom diffused into cv sites. The x-ray absorber is then surrounded by 6 Al at ~3.0 Å and 4 Si2 at ~3.23 Å (Table 1). Data analysis suggest <2 Al atom at 3.0 Å and ~4 Si at 3.26-3.27 Å (Table 2, Table 3 and Table 5). While the Ni-Si2 structural parameters agree well, there is a strong discrepancy in CN_{Ni-Al,\alpha=35°}^{\text{exafs}} (Table 5 vs. <2). One might argue, that CN_{Ni-Al,\alpha=35°}^{\text{exafs}} is lowered due to destructive interferences with substituting atoms in the octahedral sheet (Mg, Fe). While Al and Mg have a similar backscattering amplitude and phase shift at the Ni K-edge, the Ni-Al pairs are indeed out of phase with Ni-Fe pairs. Because the Fe content in the used montmorillonite material is low (17% wt Al+Mg, <1% wt Fe; corresponding to an atomic ratio of 1 (Al+Mg) : 0.03 (Fe) (see section 4.2.1) it is unlikely the CN_{Ni-Al,\alpha=35°}^{\text{exafs}} is significantly modified due to Ni-Fe pairs.

Thus, based on the arguments discussed above, it appears unlikely that the diffusion of Ni into the montmorillonite structure is the predominant process in this study.
Fig. 12: Simulated possible positions of Ni incorporated in the octahedral sheet and sorbed to the $ab$ plane of montmorillonite for a) cv and b) tv sites.

### 4.4.2.2 Sorption to montmorillonite edge sites

EXAFS data analysis indicates $CN_{\text{Ni-Al}}^{\text{cryst}} \sim 2 \pm 0.5$, $CN_{\text{Ni-Si1}}^{\text{cryst}} \sim 2 \pm 0.5$ and $CN_{\text{Ni-Si2}}^{\text{cryst}} \sim 4 \pm 0.5$ (see Table 2 and Table 3). In the following we want to discuss to what extent Ni surface complexes located at the edges of montmorillonite can explain the presented EXAFS findings of
this study. Fig. 12a and Fig. 12b illustrate examples of possible Ni surface complexes at the edges of montmorillonite. For visualization purposes the surface complexes are shown separately for sorption onto cv and tv edge sites (Fig. 12a and b). The figure illustrates two possible surface complexes formed at cv edge sites (Fig. 12a, Ni2: bonded to 2 Al atoms at ~3.0 Å and 2 Si2 atoms at R_{Ni-Si2} ~3.23 Å; Ni3: bonded to 3 Al atoms and 4 Si2) and at tv edge sites (Fig. 12b, Ni4: bonded to 2 Al atoms at ~3.0 Å and 4 Si1 at R_{Ni-Si1} = 3.16 - 3.18 Å; Ni5: bonded to 3 Al atoms and 2 Si1).

While CN_{Ni-Al} \sim 2 confirms that sorption of Ni onto cv- and to tv-like edge sites is a plausible sorption mode in this study, it does not allow to speculate whether sorption onto cv- or tv-like edge sites is the dominant uptake mode. A similar conclusion can be made for the neighboring Si atoms. It is clear from the proposed surface complexes above that neither sorption to tv-like nor to cv-like edge sites alone can account for the coordination numbers (CN_{Ni-Si1} < 2 and CN_{Ni-Si2} \sim 4). Thus, we propose that Ni is sorbed onto montmorillonite as a mixture of surface complexes bond to cv- and tv-like edge sites.

Schlegel et al. (1999) observed the presence of inner-sphere surface complexes by investigating the uptake of Co on hectorite (a magnesian trioctahedral clay) at pH 6.5 (0.3 NaNO3, solid/liquid 1.95 gL⁻¹, [Co]_{initial} = 100 µM, Co sorbed 37 µmol/g). Data analysis revealed the presence of two nearest cationic subshells containing 1.6 ± 0.5 Mg at 3.03 Å and 2.2 ± 0.5 Si at 3.27 Å. The angular dependence indicated that Co-Mg pairs are oriented parallel to the film plane, whereas Co-Si are not. The results were interpreted by the formation of Co inner-sphere mononuclear surface complexes located at the edges of hectorite platelets in the continuity of the octahedral sheet. The findings of this study are comparable to these by Schlegel et al. (1999) and demonstrate that heavy metals binding to edge sites is not only a sorption mechanism for trioctahedral smectites but also for dioctahedral smectites. Please note that our study shows the presence of two Si distances, Schlegel et al. (1999) observed only one characteristic Ni-Si-pair. This fact is consistent with the structural differences between di- and trioctahedral clays (see section 4.1).

4.4.3 Effect of surface loading and reaction on Ni surface complexes on montmorillonite

The number of edge sites can be estimated based on morphological information. In a previous study we have calculated the relative surface area of montmorillonite (2% for edge surfaces ((100), (110) and (010)) and 98% for the (001 surface) (Dähn et al., 2002b). Because sorption to planar sites is blocked due to the high ionic strength of the solution (0.3 M NaClO₃) we take only lateral surfaces into account. Based on the density of oxygen atoms at the
montmorillonite lateral surfaces it is then possible to estimate the number of possible edge sites (Tsipursky and Drits, 1984). This approach yields for the lateral surfaces 0.5 sites/nm² (excluding the (001) surface). This number is in the same order with the number of protonable edge sites of montmorillonite deduced by potentiometric titration (1.4 sites/nm², (Baeyens and Bradbury, 1995a)). The estimated site density obtained from different methods typically differs by a factor of 2 to 3 or even more (Keren and Sparks, 1995). Finally, we assumed that Ni is bond to two Al atoms from the montmorillonite structure (Table 2, Table 3 and Table 5) resulting in 0.26 sites/nm² lateral sites. This calculation yields that the samples (4 and 7 µmol/g) never exceed a monolayer coverage. The surface coverage from 10 to 18 % also explains why no Ni-Ni-pairs have been detected. In conclusion it is justifiable to assume that although the Ni concentration increased over time it had no effect on the uptake mode and that the same complexes formed in both samples.

4.5 Concluding remarks

The present study shows that the amount of Ni sorbed on the montmorillonite slowly increased over the course of one year. Similar slow sorption phenomena have been reported in the literature (e.g. Brümmer et al., 1988; McBride, 1994). It was speculated that slow metal uptake processes are caused by the diffusion of metals in the clay structure or the formation of new phases with time. However, no spectroscopic evidence supporting these speculations has been presented and the underlying structural mechanism has not been definitely resolved. This study shows that the diffusion of Ni atoms into the montmorillonite structure and the formation of new phases can be ruled out in our sorption system and that the slow uptake phenomenon is not due to a change in the uptake mechanism. We found spectroscopic evidence for the formation of surface complexes on the edge site of montmorillonite. Data analysis revealed that these surface complexes become more ordered with time. We can speculate that this increase in structural order with time can explain preliminary desorption experiments in our laboratory. The experiments at trace element concentration indicate that the release of Ni sorbed onto montmorillonite becomes increasingly hindered with prolonged reaction time. Since attachment of metal ions specifically bond to clay mineral surfaces can severely reduce their bioavailability and mobility in soil and water environments are the findings presented in this study of significant environmental relevance.
4.6 References


CHAPTER 5
TH UPTAKE ON MONTMORILLONITE: A POWDER AND POLARIZED EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) STUDY
Abstract

The uptake process of Th(IV) onto montmorillonite was studied using powder and polarized-EXAFS (P-EXAFS) spectroscopy. Sorption samples were prepared in 0.1 M NaClO\textsubscript{4} solutions either undersaturated (pH 2 and 3, [Th\textsubscript{initial}]: 2.7\texttimes{}10\textsuperscript{-6} - 4\texttimes{}10\textsuperscript{-5} M) or supersaturated (pH 5, [Th\textsubscript{initial}]: 4.3\texttimes{}10\textsuperscript{-5} - 4\texttimes{}10\textsuperscript{-4} M) with respect to amorphous ThO\textsubscript{2}. Th loading varied between 1 - 157 μmol/g at pH 3, 14 - 166 μmol/g at pH 5 and equaled 41 μmol/g at pH 2. At pH 5 and high surface loading the EXAFS spectrum resembled that of amorphous Th(OH)\textsubscript{4} suggesting the precipitation of a Th hydrous hydroxide. At low and intermediate surface coverage two O coordination shells at ~2.24 Å and ~2.48 Å, and one Si shell at 3.81 - 3.88 Å, were systematically observed regardless pH. The formation of Th nucleation products and Th-Si solution complexes, and the sorption of Th on a silica precipitate were excluded from the EXAFS spectra analysis and solution chemistry. In these conditions, Th was shown to bond the montmorillonite surface by sharing double corners with Si tetrahedra. This structural interpretation is consistent with surface coverage calculations which showed that the edge sites were saturated in the two highest concentrated samples (34 and 157 μmol/g) at pH 3.
5.1 Introduction

Thorium is a naturally occurring, weakly radioactive element which is predominately (>99%) present as thorium-232 (half-life $1.41 \times 10^{10}$ years). It occurs in a single redox state (+IV) and is therefore a suitable analogue for other tetravalent actinides. In a wide array of industrial products and processes, thorium is used (Weast and Astle, 1983). For example, Th acts as a catalyst for the oxidation of ammonia to nitric acid, and is used in magnesium alloys and in tungsten filaments for light bulbs and electronic tubes. Thorium is also added during the manufacturing of refractive glass, allowing the production of smaller and more accurate camera lenses.

In natural systems, Th is an important trace element with accurately known source terms (Santschi and Honeymann, 1989). It is widely distributed in small amounts in the Earth’s crust, being about as abundant as lead or molybdenum and three times as abundant as uranium (Weast and Astle, 1983). Th is present in small amounts in rocks, soils, surface- and ground waters, plants, and animals. For example, soils commonly contain an average of about 6 ppm thorium (Weast and Astle, 1983). There are several natural Th minerals, the most common being rare earth-thorium-phosphate minerals (e.g., monazite) and thorium silicate minerals such as thorite and huttonite.

Large quantities of waste arising from mining and oil and gas extraction contain naturally occurring radioactive material such as uranium, thorium and potassium (Paschoa, 1998). Furthermore are fly ashes from lignite power stations contaminated with Th (Savanonda et al., 1985). Due to its radioactivity and wide-spread industrial application, Th has become an environmental contaminant. However the most critical environmental aspect concerning Th is its safe disposal in nuclear waste repositories. The flow of ground water through a repository can potentially result in the release of radionuclides such as Th from waste matrices into the environment. The release of radionuclides can be considerably retarded due to interactions with clay minerals. For example, dioctahedral aluminous clays are foreseen as a backfill material in the Swiss concept for a high level radioactive waste repository (NAGRA, 1994). Thus, a detailed understanding of the sorption mechanisms of Th with montmorillonite and the extension to other tetravalent actinides is of great importance for the safety assessment of nuclear waste repositories.

Montmorillonite is a clay mineral with substantial isomorphic substitution. Montmorillonite, possess a 2:1 layered structure consisting of one octahedral sheet and two tetrahedral sheets (Güven, 1988). Exchangeable cations between the 2:1 units balance the negative charges generated by isomorphic substitution within the montmorillonite structure (Sposito, 1984). The uptake kinetics of cation exchange is fast and the cations such as Na$^+$ and
Ca\(^{2+}\) form outer-sphere surface complexes, which are easily exchanged with solute ions by varying the cationic composition of the solution. In addition to cation exchange there is a pH-dependent uptake of metals on montmorillonite (Sposito, 1984). In this sorption process sorbate ions bond to the smectite surface by sharing one or several ligands (generally oxygens) with sorbent cations as isolated complexes. With increasing pH or sorbate cation concentration, metal precipitation can occur. If the precipitate consists of chemical species derived from both the aqueous solution and dissolution of the mineral, it is referred to as a coprecipitate (Stumm and Morgan, 1981).

In the past, metal uptake on montmorillonite has been studied mainly using wet chemistry methods. For example the uptake of Cu, U, Cd, Ni, Zn and Ca on montmorillonite was investigated in this way (Peigneur et al., 1975; Garcia-Miragaya and Page, 1976; Inskeep, 1983; Zachara et al., 1992; Zachara et al., 1993; McKinley et al., 1995; Baeyens and Bradbury, 1997). Based on batch sorption data and the macroscopic surface properties of montmorillonite a 'mechanistic' surface complexation model was developed in our laboratory for the uptake of Ni, Zn and Eu (Bradbury and Baeyens, 1997; 2002).

Recently, uptake experiments on montmorillonite have been complemented by spectroscopic investigations. For example, Chen and Hayes (1999) investigated Co uptake on montmorillonite using extended X-ray absorption fine structure (EXAFS) and suggested the formation of a Co precipitate at elevated pH (pH >7; high ionic strength) and outer-sphere complexation at lower pH. The uptake of Sr on montmorillonite resulted in the formation of outer-sphere complexes, even up to pH 10 (Chen and Hayes, 1999). Strawn and Sparks (1999) have used EXAFS to distinguish between inner- and outer sphere complexes of Pb(II) on montmorillonite. At pH >6.8 and high ionic strength the formation of inner-sphere Pb complexes was proposed, whereas outer-sphere complexes of Pb seem to prevail at lower pH and ionic strength. The uptake of U(VI) on montmorillonite was investigated by Sylwester et al. (2000) using EXAFS. The EXAFS data suggested that the uptake of the uranyl ion onto montmorillonite at low pH occurs via ion exchange, leaving the uranyl structure intact. At near-neutral pH and in the presence of a competing cation, inner-sphere complexation predominates.

Manceau et al. (1998, 1999) have demonstrated that it is possible to gain further information upon the uptake processes of metal ions onto clay minerals by applying P-EXAFS to layered clay minerals. In P-EXAFS the contributions of cations from the tetrahedral sheets (Si in montmorillonite) are minimized by orienting the \(ab\) plane parallel to the electric field vector \(\mathbf{e}\) of the incident X-ray beam. Conversely, the contribution of cations from the octahedral sheet (Al and Mg in montmorillonite) is extinguished in the perpendicular orientation of \(\mathbf{e}\). P-EXAFS has been successfully used to determine uptake processes of Co and Zn on hectorite, and Ni on montmorillonite (Schlegel et al., 1999a; Dähn et al., 2001; Schlegel et al., 2001; Dähn
et al., 2002; Schlegel et al., 2002). For example, Dähn et al. (2001, 2002) observed the neoformation of a Ni-phyllosilicate phase upon Ni uptake on montmorillonite (STx-1) at high ionic strength and at near-neutral pH (0.3 M NaClO$_4$, pH 8, 111 µmol/g Ni sorbed on montmorillonite) using P-EXAFS.

In this study we have investigated the uptake process of Th onto montmorillonite using powder EXAFS at initial Th concentrations ([Th$_{initial}$]) both under- (pH 2 and 3) and oversaturated (pH 5) with respect to amorphous ThO$_2$. In addition P-EXAFS measurements with Th treated self-supporting clay films prepared at pH 2 ad 3 were conducted to investigate whether the sorbed Th is orientated with respect to the octahedral sheets of montmorillonite.

5.2 Material and Methods

5.2.1 Montmorillonite purification and characterization

The STx-1 montmorillonite used in this study was purchased from the Source Clay Minerals Repository of the Clay Minerals Society. XRD analyses of the “as received” montmorillonite indicated the presence of minor quantities of calcite, quartz and kaolinite (less than 1 wt%). This natural clay contains only ~0.9 wt% Fe$_2$O$_3$. The material was converted to the homo-ionic Na form by thoroughly washing three times with 1 M NaClO$_4$. The <0.5 µm size fraction was separated by successive washing with de-ionised water, combined with centrifugation (Baeyens and Bradbury, 1997). Soluble hydroxy-aluminium compounds were removed by an acid treatment at pH 3.5 for 1h. The pH was subsequently readjusted to 7.

Amorphous iron was dissolved through a dithionate-citrate-bicarbonate treatment (Mehra and Jackson, 1960). The amount of extractable iron was determined to be approximately 30% of the total iron content by inductively coupled plasma optical emission spectroscopy (ICP-OES) and total digestion of the sample. Aliquots of clay suspensions were prepared in 0.1 M NaClO$_4$ concentrations using dialysis methods (Baeyens and Bradbury, 1997). The final conditioned montmorillonite suspension was stored at 4 °C in the dark to minimize microbial growth.

The cation exchange capacity (CEC) was determined to be 1010 meq kg$^{-1}$ by using the isotopic dilution method with $^{45}$Ca (Baeyens and Bradbury, 1995). The external surface area of the conditioned STx-1 Ca-montmorillonite was measured by the N$_2$-BET technique to be 89 m$^2$g$^{-1}$. This value is in reasonable agreement with that determined by Van Olphen et al. (84 m$^2$g$^{-1}$; Van Olphen and Fripiat, 1979).
5.2.2 Sample preparation for powder- and polarized-EXAFS (P-EXAFS)

EXAFS and P-EXAFS samples were prepared at reaction conditions under- (pH 2 and 3) and oversaturated (pH 5) with respect to amorphous ThO₂. Powder EXAFS samples were prepared from the suspensions at pH = 3 as follows: 50 ml of conditioned and purified montmorillonite suspension (pH = 7, 0.1 M NaClO₄) were added to a 0.1 M NaClO₄ solution. The pH was adjusted to 3 with 0.1 M HNO₃. Th was then added from a 10⁻³ M Th(NO₃)₄·5H₂O stock solution (pH 3.0, 0.1 M NaClO₄) and the pH was readjusted to 3 and kept constant during the experiment. This procedure resulted in a 250 ml suspension at a solid to liquid ratio of 2.4 g/L for all samples. The initial Th concentrations varied from 2.7·10⁻⁶ to 4·10⁻⁴ M.

The Th sorption experiments were conducted in a glove box under N₂ atmosphere (CO₂ and O₂ < 5 ppm). After a reaction time of 7 days the suspensions were centrifuged and the wet pastes were filled into Plexiglas holders, sealed and stored for up to 7 days in a refrigerator to keep them moist prior to the powder EXAFS measurements. The supernatant solutions were analyzed for Th, Al and Si by ICP-OES. The silica concentration after 7 days of reaction time in our sorption system amounted to 360 μM. The Si release rate in the Th/montmorillonite system was determined to be 5.8 · 10⁻¹⁴ mol m⁻² s⁻¹ (pH = 3). The rate agrees well with the range of 6 - 7.2 · 10⁻¹⁴ mol m⁻² s⁻¹ measured by Heydemann (1966) over a 9 month period for the dissolution of montmorillonite at pH = 3 and suggests that the addition of Th did not influence the Si dissolution rate. The Al concentration in solution ([Al]ₐq) varied from 26 μM to 47 μM, and did not show any time dependency. Again, the Al concentration agrees well with the Al concentration observed by Heydemann (1966) in a Th-free montmorillonite system ([Al]ₐq = 30 - 47 μM, pH = 3).

The initial Th concentrations (2.7·10⁻⁶ - 4·10⁻⁴ M) and the reaction pH of 3 were chosen so as to achieve a wide range of Th loadings in the Th/montmorillonite system (1-157 μmol/g; relative Th uptake > 80 % in all samples) while ensuring that the bulk solutions remained undersaturated with respect to amorphous ThO₂. The stability of the Th stock solution (1·10⁻³ M Th(NO₃)₄·5H₂O, pH 3.0) used for this study was investigated and it was observed that the Th concentration did not change over a time period of up to one year. This finding is supported by a study of Rai et al. (2000) which indicated that a Th concentration of ~10⁻² M is stable up to a reaction time of 21 days in a supersaturated system at pH 3 (0.1 M NaClO₄).

To estimate the degree of saturation with respect to the solubility of Th (hydr)oxides we calculated the saturation index (SI) with respect to amorphous and crystalline ThO₂ using log Kₛₚ = -12 and -1.8 respectively (Hummel et al., 2002). SI is defined as the ratio of the ion activity product, IAP, to the solubility constant Kₛₚ. For example, for ThO₂ this yields
SI = (Th$^{4+}$/\[(H^+)^4\] · K$_{sp}$), where (Th$^{4+}$) and (H$^+$) are the activities of Th$^{4+}$ and H$^+$ in solution. The calculation revealed that our solutions at pH 3 are greatly undersaturated with respect to amorphous ThO$_2$ (SI<0.0004), but supersaturated with respect to the crystalline form. However, the mentioned data of Rai et al. (2000) as well as our stability test clearly show that crystalline ThO$_2$ does not precipitate from such diluted solutions. The formation of crystalline ThO$_2$ first requires the precipitation of the amorphous form, followed by ageing for long times. Thus, one can assume that Th removal from solution is not due to Th(hydr)oxides formation in solution at any time during the experiments. To the best of our knowledge, the solubility products of Th-silicate phases (e.g. thorite, huttonite) are not known.

Th speciation calculations based on the thermodynamic data of Baes and Messmer (1976) revealed for a total Th concentration of 10$^{-4}$ M that the dominating species is the free aqua ion Th$^{4+}$ (89%). The remaining part consists of hydrolysis products such as ThOH$^{3+}$, Th(OH)$_2^{2+}$ and Th(OH)$_4^{+}$ ([Th] < 8·10$^{-5}$ M).

At pH 5 (powder EXAFS), pH 2 (powder and polarized EXAFS) and pH 3 (polarized EXAFS) the clay suspensions were prepared using the same experimental procedure as described above. In the experiments at pH = 5 the initial Th concentration varied between 4·10$^{-5}$ and 4·10$^{-4}$ M. In this case, the solutions were oversaturated with respect to amorphous ThO$_2$ (Hummel et al., 2002).

Two self-supporting films for polarized EXAFS were prepared from suspensions, one at pH 2 and initial Th concentration of 10$^{-4}$ M (SI(am. ThO$_2$) < 10$^{-5}$) and another at pH 3 and initial Th concentration of 4·10$^{-5}$ M(SI(am. ThO$_2$)<0.0004). To prevent any significant clay dissolution, a reaction time of 6 hours was chosen for the pH 2 experiment. In spite of the short reaction time the procedure resulted in the removal of 99% of the Th from solution. To prepare highly oriented self-supporting films for P-EXAFS measurements 40 ml of the clay suspensions were slowly filtrated using a 47 mm diameter filter (Millipore, 0.4 μm pore size). The filtration was performed in a closed vessel under a continuous flow of Ar. Excess of salt and aqueous Th in the wet films was removed by careful washing with a few milliliters of de-ionized water before drying. The dried clay films were cut into 8 slices and stacked on sample holders in order to get samples thick enough for fluorescence measurements. Again, the supernatant solutions were analyzed for Th, Si and Al by ICP-OES.

In addition to the sorption samples, two reference aqueous solutions were prepared at pH 2. The first solution contained 10 mM Th$_{aq}$ (0.1 M NaClO$_4$). The second reference solution contained 5 mM Th$_{aq}$ and 0.1 mM Si$_{aq}$ (0.1 M NaClO$_4$).
5.2.3 Quantitative texture analysis

X-ray diffraction texture analysis measurements were performed in reflection mode using a Huber texture goniometer mounted on a classical X-ray source. A point-focus incident beam of 0.5 x 0.5 mm\(^2\) and Cu \(K_\alpha\) radiation were used. One slice of each self-supporting film was mounted on a single-crystal silicon wafer. Pole figures were measured using a position sensitive curved detector (INEL CPS 120) having a \(2\theta_{\text{max}} = 120^\circ\) (Ricote and Chateigner, 1999). This configuration allows a rapid measurement (i.e., without Bragg angle scanning) of the whole diffraction pattern at each tilt angle (\(\rho\)) between the film and the diffraction planes. Since self-supporting films of fine-grained layer minerals have an axially-symmetric (fiber) texture (i.e., random in-plane distribution of crystallite \(a\) and \(b\) axes) the complete film texture can be obtained by measuring the inclination of (001) crystallographic planes off the sample surface (Manceau et al., 1998). This was achieved by selecting the (004) reflection and scanning the tilt angle from \(\rho=0\) to \(\rho=85^\circ\), in 5° steps, with an integration time of 2h for each tilt angle position. The densities of the orientation distribution were calculated from the \(\rho\)-scan integrated intensities using direct normalization and taking a density of zero for \(\rho>80^\circ\) (for details see Manceau et al., 1998). Distribution densities are expressed as ‘multiple of a random distribution’ or ‘mrd’ (Bunge and Esling, 1982), a perfectly random sample exhibiting constant densities of 1 mrd.

5.2.4 EXAFS data collection and reduction

\(L_{\\beta}\)-edge EXAFS spectra of Th were recorded at the Rossendorf Beamline (ROBL) (Matz et al., 1999) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France using a Si (111) double crystal monochromator. Higher order harmonics were suppressed by using Pt coated mirrors. The monochromator position was calibrated by assigning the first inflection point of the K-absorption edge of metallic Y foil to 17038 eV. Powder-EXAFS spectra were recorded at 45° and P-EXAFS spectra were recorded with the electric field vector \(\varepsilon\) at 10°, 35°, 55° and 80° with respect to the film plane. Several scans were averaged to improve the signal to noise ratio. All spectra were measured at room temperature in fluorescence mode using a 4-element Ge solid-state detector.

Data reduction was carried out by using the WinXAS 97 2.0 software package (Ressler, 1998). The energy was converted to photoelectron wave vector units (\(\text{Å}^{-1}\)) by assigning the origin \(E_0\) to the first inflection point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming \(k^2\)-weighted \(\chi(k)\) functions between 2.9 and 10 \(\text{Å}^{-1}\) using a Bessel window function with a smoothing parameter of 4. All fits were performed in R-space.
in the range from 0.7 to 4.0 Å. Amplitude and phase shift functions were calculated with FEFF 8.0 (Rehr et al., 1991) using the structure of thorite (α-ThSiO₄) (Taylor and Ewing, 1978) as a reference. The amplitude reduction factor (S₀²) was set to 1.0 in order to reduce the number of free fit parameters (Moll et al., 1999).

The deviation between the fitted and the experimental spectra is given by the relative percentage of residual (% Res):

\[
\% \text{Res} = \frac{\sum_{i=1}^{N} |y_{\text{exp}}(i) - y_{\text{theo}}(i)|}{\sum_{i=1}^{N} y_{\text{exp}}(i)} \cdot 100
\]

with N the number of points in the fit window, and \(y_{\text{exp}}\) and \(y_{\text{theo}}\) the experimental and theoretical RSF values, respectively. Errors on structural parameters were estimated from the analysis of a series of reference compounds (see Table 1). The precision was estimated to be about ±0.02 Å for interatomic distances (R) and about ±25% for coordination numbers (CN).
5.3 Results

5.3.1 Reference compounds

Table 1 shows a comparison of structural parameters of reference compounds obtained by X-ray diffraction (XRD) with bond distances and coordination numbers obtained by EXAFS data analysis. This comparison allows uncertainties to be estimated in the quantitative EXAFS analysis. The table also shows a comparison with previous Th EXAFS studies allowing the phase and amplitude functions used in this study to be tested. In most previous studies EXAFS data analysis was performed using experimental phase and amplitude functions. In this study, however, theoretical phase and amplitude functions were calculated with FEFF 8.0 using the structure of thorite (ThSiO₄) (Taylor and Ewing, 1978). The structure of thorite was chosen because it provides the appropriate scattering paths (Th-O, Th-Si and Th-Th) for our data analysis.

The EXAFS analysis of crystalline ThO₂ yielded an average CN_{Th-O} of 7.2 ± 1.4 O atoms with R_{Th-O} = 2.42 Å (σ² = 0.005 Å²) and CN_{Th-Th} = 12.7 ± 2.6 with R_{Th-Th} = 3.96 Å (σ² =0.005 Å²). These structural parameters compare well with the structural parameters for ThO₂ as determined by XRD (CN_{Th-O} = 8, R_{Th-O} = 2.42 Å and CN_{Th-Th} = 12, R_{Th-Th} = 3.96 Å) (Wyckoff, 1963). Two other structural models were tested; thorite (α-ThSiO₄) and huttonite (β-ThSiO₄). In thorite the Th atom is coordinated by four axial and four equatorial O atoms. For the axial bonds each Th atom shares oxygens with the edges of 2 silica tetrahedra, with long Th-O and short Th-Si distances (R_{Th-O} = 2.47 Å, R_{Th-Si} = 3.16 Å; edge-sharing). Equatorial bonds link a Th atom with O atoms at the corner of silica tetrahedra, with short Th-O and long Th-Si distances (R_{Th-O} = 2.36 Å, R_{Th-Si} = 3.90 Å; corner-sharing). In huttonite, which has a more irregular structure (isomorphous to monazite) with nine O atoms coordinated with each Th atom, there is, instead, a range of Th–O distances, the shortest being 2.40 Å and the longest 2.81 Å, but again the equatorial O atoms are on average closer to Th than the axial O atoms. The average distances measured by X-ray diffraction in this case are 2.46 and 2.57 Å (Taylor and Ewing, 1978). EXAFS data analysis of thorite resulted in average coordination numbers and bond distances of 8.5 ± 1.7 O atoms at 2.38 Å (σ²=0.005 Å²), of 3.9 ± 0.8 Si atoms at 3.92 Å (σ²=0.005 Å²) and of 5.3 ± 1.1 Th atoms at 3.9 Å (σ²=0.005 Å²). These structural parameters compare well with the results of a previous EXAFS study (7.7 O atoms at 2.41 Å (Δσ²=0.0Å²), 2.9 Si atoms at 3.89 Å (σ²=0.005 Å²) and of 5.7 Th atoms at 3.90 Å (Δσ²=0.002 Å²), in which experimental phase and amplitude functions were used (Osthols et al., 1997). Furthermore, the EXAFS structural parameters compare well with the XRD parameters for thorite, except that the
1st Si shell is not detected in EXAFS (four equatorial O at 2.36 Å, four axial O at 2.47 Å, two Si at 3.16 Å, four Si at 3.9 Å and four Th at 3.9 Å, Taylor and Ewing, 1978). The EXAFS data analysis of huttonite resulted in shorter bond distances (2.32 and 2.50 Å) compared to XRD parameter (2.46 and 2.57 Å), whereas they agree well with distances (2.35 and 2.55 Å) obtained in an EXAFS study by Farges (1991).

The EXAFS data analysis of a Th solution (10 mM Th in 0.01 M HNO₃, pH 3) resulted in ~10 neighboring O atoms at 2.45 Å (Table 1). This finding is in good agreement with a study by Moll et al. (1999), in which ~11 Th-O pairs at 2.44 Å were determined for the spectrum of an acidic Th solution.

Table 1: X-Ray diffraction data and EXAFS results for reference substances.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Method</th>
<th>R [Å]</th>
<th>CN</th>
<th>σ² [Å²]</th>
<th>Link</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂</td>
<td>Th-O</td>
<td>XRD</td>
<td>2.42</td>
<td>8</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Th-Th</td>
<td>XRD</td>
<td>3.96</td>
<td>12</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.42</td>
<td>7.2</td>
<td>0.005</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Th-Th</td>
<td>EXAFS</td>
<td>3.96</td>
<td>12.7</td>
<td>0.005</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Thorite (α-ThSiO₄)</td>
<td>Th-O</td>
<td>XRD</td>
<td>2.36</td>
<td>4</td>
<td>equat.</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>XRD</td>
<td>2.47</td>
<td>4</td>
<td>axial</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.41</td>
<td>7.7</td>
<td>0.0⁵</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
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<td>Th-O</td>
<td>EXAFS</td>
<td>2.38</td>
<td>8.5</td>
<td>0.005</td>
<td>This work</td>
<td></td>
</tr>
<tr>
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<td>Th-Si</td>
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</tr>
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<td>Th-Si</td>
<td>XRD</td>
<td>3.90</td>
<td>4</td>
<td>equat.</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Th-Si</td>
<td>EXAFS</td>
<td>3.89</td>
<td>2.9</td>
<td>0.005⁵</td>
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<td>3</td>
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<tr>
<td></td>
<td>Th-Si</td>
<td>EXAFS</td>
<td>3.92</td>
<td>3.9</td>
<td>0.005</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Th-Th</td>
<td>XRD</td>
<td>3.90</td>
<td>4</td>
<td>0.005⁵</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Th-Th</td>
<td>EXAFS</td>
<td>3.90</td>
<td>5.7</td>
<td>0.002⁵</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Th-Th</td>
<td>EXAFS</td>
<td>3.90</td>
<td>5.3</td>
<td>0.005</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>Huttonite (β-ThSiO₄)</td>
<td>Th-O</td>
<td>XRD</td>
<td>2.46</td>
<td>5</td>
<td>equat</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>XRD</td>
<td>2.57</td>
<td>4</td>
<td>axial</td>
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</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.35</td>
<td>5.4</td>
<td>0.008⁵</td>
<td>4</td>
<td>4</td>
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<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.55</td>
<td>3.8</td>
<td>0.007⁵</td>
<td>axial</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.32</td>
<td>5.3</td>
<td>0.002</td>
<td>equat</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.50</td>
<td>7.7</td>
<td>0.005</td>
<td>axial</td>
<td>This work</td>
</tr>
<tr>
<td>Th(aq) 30 mM</td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.43</td>
<td>11</td>
<td>0.007</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.44</td>
<td>11.2</td>
<td>0.007</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.45</td>
<td>10.4</td>
<td>0.005</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Th-O</td>
<td>EXAFS</td>
<td>2.45</td>
<td>10.8</td>
<td>0.005</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

a: The terminology axial and equatorial linkage is discussed in the text.
b: Using experimental phase and amplitude functions.
5.3.2 Powder EXAFS of Th-sorbed montmorillonite at pH 3

Fig. 1 shows the $k^3$-weighted EXAFS spectra of montmorillonite treated with Th at pH 3 for 7 days. The Th loadings varied over a wide range from 1 to 157 μmol/g. The figure shows that the $k^3\chi(k)$ spectrum of the sample with the highest Th concentration (157 μmol/g) can be roughly approximated by a single sinusoidal oscillation over the entire $k$-range. With decreasing Th loading (34 - 1 μmol/g) the intensity of $k^3\chi(k)$ decreases and the wave frequency between ~6 and ~10 Å$^{-1}$ increases. Furthermore, there is a clear asymmetry in the 4 - 8 Å$^{-1}$ range which is most pronounced in the lower concentrated samples (1 - 12 μmol/g). These features indicate that the coordination of Th is changing with decreasing Th concentration.

The corresponding experimental RSFs are shown in Fig. 2. The figure shows that there are two RSF peaks for the highest concentrated samples (34 - 157 μmol/g) located at $R + \Delta R = 1.95$ Å and $R + \Delta R = 3.2$ Å. With decreasing Th loading, the first peak (Th-O contribution) decreases in amplitude and splits. In the lowest concentrated samples (1 - 4 μmol/g) there are RSF peaks located at $R + \Delta R = 1.4$ Å (short Th-O pair), at $R + \Delta R = 2.18$ Å (long Th-O pair) and at $R + \Delta R = 3.3$ Å. The intensity of the latter RSF peak increases with decreasing loading (157 - 1 μmol/g) and the figure suggests that its position slightly shifts to higher distances.

![Fig. 1: $k^3$-weighted Th L$_{III}$-edge EXAFS spectra for Th sorbed on montmorillonite at pH 3 and various Th concentrations.](image-url)
(R + ΔR = 3.2 Å - 3.3 Å) as the Th loading decreases. Again, the RSFs indicate that the chemistry of Th changed with its concentration.

As mentioned in the experimental section (see section 5.2.4) fitting was performed using a multishell approach (i.e., 0.7 to 4.0 Å range) in real space. The 1st coordination shell was fitted with Th-O pairs and the 2nd coordination shell with Th-Si pairs. As discussed later, we did not succeed in introducing Th-Th pairs in the EXAFS analysis of Th treated montmorillonite samples.

Fig. 2: RSFs of k^3-weighted Th LIII-edge EXAFS spectra for Th sorbed on montmorillonite at pH 3 and various Th concentrations.
5.3.2.1 First RSF peak(s)

As a first approach we tried to fit the Th-O coordination environment in the Th treated montmorillonite samples with a single O shell. With this fit strategy we previously succeeded in describing the Th-O coordination shell of Th in a 10 mM acidic aqueous solution (~11 O at 2.45 Å; Table 1, see section 5.3.1). The fit approach with one oxygen shell yielded satisfactory results only for the sample with the highest Th loading (157 μmol/g, CN$_{Th-O2}$ = 8.1 at 2.44 Å, Table 2). To reduce the number of fit parameters, the Debye-Waller factor (DW) of the oxygen shell was fixed to the value previously determined for the aqueous Th solution (σ$^2$ = 0.005 Å$^2$). We also tried to fit the sample with the second highest Th loading (34 μmol/g) with one O shell. The approach yielded a low Th-O coordination number (CN$_{Th-O}$ = 5.8 at 2.46 Å) and a fit residual more than 50% larger than for the highest concentrated sample (Table 2). This finding is not surprising since Fig. 2 clearly indicates a splitting of the Th-O shell in two RSF peaks. The existence of two O shells is not uncommon in Th compounds and is found for example in thorite and huttonite (Table 1).

Consequently, in the next step the sorption samples loaded with 1 - 34 μmol/g Th were analyzed assuming two distinct Th-O pairs (Table 2). For crystal chemical reasons the total number of oxygen atoms in the first and second shell should not exceed 10 - 11 (Moll et al., 1999). Therefore was the DW of the first oxygen shell fixed to σ$^2$ = 0.002 Å$^2$ resulting in a total coordination number of ~10 for the two Th-O pairs. Table 2 shows that the first Th-O peak(s) of montmorillonite (1 - 34 μmol/g) treated with Th at pH = 3 consists of ~3 Th-O pairs at 2.23 - 2.24 Å and ~6 - ~8 Th-O pairs at 2.45 - 2.48 Å. The corresponding experimental and simulated Fourier transforms (FTs) of a Th/montmorillonite sample (Th loading: 4 μmol/g) are illustrated in Fig. 3.
Table 2: Structural information derived from the EXAFS analysis of the sorption samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Th-O₁</th>
<th>Th-O₂</th>
<th>Th-Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNₑ₆₆₇₂[Å] [Å²]</td>
<td>σ²[Å²] [Å²]</td>
<td>CNₑ₂rå₄₆₇₂[Å] [Å²]</td>
</tr>
<tr>
<td>157 μmol/g, pH 3</td>
<td>8.1</td>
<td>2.44</td>
<td>0.005</td>
</tr>
<tr>
<td>34 μmol/g, pH 3</td>
<td>5.8</td>
<td>2.46</td>
<td>0.005</td>
</tr>
<tr>
<td>34 μmol/g, pH 3</td>
<td>2.9</td>
<td>2.23</td>
<td>0.002</td>
</tr>
<tr>
<td>12 μmol/g, pH 3</td>
<td>3.0</td>
<td>2.24</td>
<td>0.002</td>
</tr>
<tr>
<td>4 μmol/g, pH 3</td>
<td>3.0</td>
<td>2.24</td>
<td>0.002</td>
</tr>
<tr>
<td>1 μmol/g, pH 3</td>
<td>3.1</td>
<td>2.24</td>
<td>0.002</td>
</tr>
<tr>
<td>41 μmol/g, pH 2</td>
<td>3.1</td>
<td>2.22</td>
<td>0.002</td>
</tr>
<tr>
<td>166 μmol/g, pH 5</td>
<td>3.4</td>
<td>2.28</td>
<td>0.002</td>
</tr>
<tr>
<td>40 μmol/g, pH 5</td>
<td>3.0</td>
<td>2.26</td>
<td>0.002</td>
</tr>
<tr>
<td>14 μmol/g, pH 5</td>
<td>3.1</td>
<td>2.25</td>
<td>0.002</td>
</tr>
</tbody>
</table>

f Value held fixed during the fitting procedure.
We have used in our data analysis Gaussian radial distribution functions (harmonic model) to fit the experimental data. Østhols et al. (1997) could also successfully fit their experimental data of the uptake of Th on amorphous silica using a harmonic approach. To check for the occurrence of non-Gaussian (anharmonic) distributions we used the cumulant expansion model (Crozier et al., 1988) with the sample which contains 4 μmol/g Th. Also the fit with the cumulant expansion model was like all other fits performed in R-space in the range from 0.7 to 4.0 Å. Since the second Th-O shell located at 2.45 - 2.48 Å is the dominant backscattering contribution in all spectra, the 3rd and 4th cumulant expansion was limited to this shell (Bunker, 1983). The structural parameter significantly changed using the cumulant expansion. The Th-O distances of both O shells decreased by ~0.07 Å. Furthermore, CN_{Th-O1} decreased from 3 to 1.5, whereas CN_{Th-O2} increased from 6 to 8. Only the Th-Si distances and the Si coordination number remained unaffected (for a detailed discussion see section 5.3.2.2). Since a short distance of 2.17 Å has never been reported in Th compounds before, we suspect that the improvement of the fit is a purely mathematical artifact due to the introduction of two additional variable fit parameters (9 vs. 7; number of independent parameter is 16 according to Nyquists theorem; Stern, 1993) and therefore we have disregarded this approach.

![Experimental and theoretical Fourier transforms](image)

**Fig. 3:** Experimental and theoretical Fourier transforms (modulus and imaginary parts) of k^3-weighted Th LIII-edge EXAFS spectra for Th sorbed on montmorillonite (pH 3, 4 μmol/g Th). The simulations were performed by assuming Th-O1, Th-O2 and Th-Si pairs. The solid line represents the experimental data and the dashed line the fit of the real and imaginary parts.
5.3.2.2 Second RSF peak

Fig. 2 shows that in all spectra there is a RSF peak at $R + \Delta R = 3.2 - 3.3$ Å. Data analysis indicated that the peak is fitted best by assuming 2.1 - 2.9 Si atoms at a distance of 3.81 - 3.87 Å (Table 2). We also evaluated the possibility of the presence of a second Si shell. A second Si shell has been observed at 3.16 Å in a XRD study of thorite for example (Taylor and Ewing, 1978). Indeed, the approach indicated that a small number (< 1) of Th-Si backscattering pairs located at 3.25-3.28 Å improved the fit residual by 20-40% compared to fits with two Th-O and one Th-Si shells. However, this alternative fit approach had only a minor influence on the structural parameters presented in Table 2 ($CN_{\text{Th-Si}}$ and $R_{\text{Th-Si}}$: ~2.7 at 3.82 - 3.84 Å vs. 2.7 - 2.9 at 3.81 - 3.83 Å). Any attempt to introduce Th-Th backscattering pairs in the fit failed. Further support for the absence of Th-Th pairs is given below.

5.3.3 Powder EXAFS of Th-sorbed montmorillonite at pH 2

In order to test the presence of a Th nucleation phase in the pH 3 samples, a Th montmorillonite sample was prepared under reaction condition (pH = 2, $[\text{Th}] = 41$ μmol/g, 0.1 M NaClO₄), strongly undersaturated with respect to amorphous ThO₂ (see section 5.2.2). Fig. 4 shows the $k^3$-weighted Fourier back-transformed spectra of second RSF peaks ($R + \Delta R = 2.9 - 3.7$ Å; see Fig. 2 and dotted line in Fig. 7b) of montmorillonite samples treated with Th at pH 3 (1 μmol/g) and pH 2 (41 μmol/g). No difference in phase is detectable in these two spectra and the difference in amplitude is very small suggesting that the second RSF peak in the two spectra has the same structural origin. Indeed, Table 2 confirms that the structural parameters obtained are similar in both samples (e.g., 2.7 - 2.8 Th-Si pairs at 3.81 Å). The similarity of the spectra furthermore proofs that no Th-Th pair is present in the pH 3 EXAFS samples.
Fig. 4: $k^3$-weighted EXAFS functions obtained by Fourier back-transforming the second RSF peaks for a Th sorption sample at pH 3 and pH 2.

5.3.4 Polarized EXAFS of Th-sorbed montmorillonite at pH 2 and 3

Fig. 5 shows the density of orientation of the $c^*$ axes for the clay particles perpendicularly to the film prepared at pH 2. At $\rho = 0$ the density value is as high as 9.4 mrd, thus attesting that the dispersion of the individual crystallite $c^*$ axes from perfect alignment is relatively low (Manceau et al., 1998). The orientation distribution function was well reproduced by a Gaussian distribution (solid line in Fig. 5) having a full-width at half maximum (FWHM) of 43°. The sample approaches the distribution characteristic of a powder (i.e., 1 mrd) at $\rho \sim 40^\circ$. The second film prepared at pH 3 (not shown) reached similar texture values as the film described above (9.8 mrd at $\rho = 0$ and a FWHM 43°).

In a previous P-EXAFS study (Dähn et al., 2002) texture values of a Ni treated self-supporting montmorillonite film (STx-1) were determined (13 mrd at $\rho = 0$ and a FWHM of 32.8°) which were sufficient to introduce pronounced anisotropy signatures in the P-EXAFS spectra. The angular dependence allowed identifying the presence of a neoformed Ni phyllosilicate phase in the sorption system. The texture values obtained in this study (~10 mrd at $\rho = 0$, FWHM 43°) are slightly different than in the Ni study. Nevertheless if the Th sorption
Fig. 5: Dispersion of c\textsuperscript{\textdegree} axes of montmorillonite particles off the film normal (\(\rho=0\text{\textdegree}\)) for 41 \(\mu\text{mol}/\text{g}\) Th sorbed on montmorillonite at pH 2.

complexes are oriented relative to the film plane, their P-EXAFS spectra should display an angular dependence.

P-EXAFS spectra were recorded at \(\alpha = 10\text{\textdegree}, 35\text{\textdegree}, 55\text{\textdegree}\) and \(80\text{\textdegree}\) (\(\alpha = \) the angle between the electric field vector and the plane of the self-supporting film). The \(k^2\)-weighted P-EXAFS spectra and the corresponding RSFs of the Th treated self-supporting clay film prepared at pH 2 are shown in Fig. 6a) and b). The figures illustrate that the P-EXAFS spectra of the clay film have no significant polarization dependence. The same result was obtained for a self-supporting Th treated montmorillonite film (3 \(\mu\text{mol}/\text{g}\); FWHM 43\textdegree, not shown) prepared at pH 3.
Fig. 6: $k^3$-weighted Th L$_{III}$-edge polarized EXAFS spectra (a) and corresponding RSFs (b) at experimental $\alpha$ angles of 10°, 35°, 55° and 80° for 41 $\mu$mol/g Th sorbed on montmorillonite at pH 2.
5.3.5 Th solutions

To investigate whether the Th-Si shell at 3.81 - 3.84 Å arises from Th adsorption on the clay or from a Th-Si solution complex, Th reference solutions with and without Si were prepared (pH 2; solution 1: [Th]$_{aq}$ = 10 mM; solution 2: [Th]$_{aq}$ = 5 mM, [Si$_{aq}$] = 0.1 mM; see section 5.2.2). The Si concentration in the solution 2 was similar to that measured in the montmorillonite suspensions (0.16 mM, pH = 2, reaction time: 6h). Fig. 7a shows the k$^3$-weighted EXAFS spectra of the Th reference solutions and a Th sorption sample (pH 2, 41 µmol/g). The k$^3$-weighted EXAFS spectrum of the Th sorption sample clearly differs from the spectra of the Th reference solutions, whereas the spectra of the reference solutions with and without Si are almost identical. This finding indicates that the sorption samples and the reference solution have a different structural origin. Further support for this finding is provided by the corresponding RSFs in Fig. 7b. The figure indicates that the first RSF peak is not split in the reference solutions. Furthermore, the RSF peak at $R + \Delta R = 3.3$ Å, present in all the sorption samples at pH 2 and 3 (Fig. 2 and Fig. 6b), and which has been showed previously to be characteristic for Th-Si pairs (Table 2), is absent in the RSF spectra of the Th solutions and indicates that the Th-Si pair is due to the presence of the sorbent material and not to an aqueous Si complex. Finally, data analysis indicated that the aqueous samples could be fitted by assuming only one Th-O backscattering pair (Table 1). Accordingly, the first peak consists of 10 - 11 O atoms at 2.45 Å, which is in good agreement with a previous study on the structural environment of Th in an acidic solution (Moll et al., 1999).
Fig. 7: $k^3$-weighted Th L$_{\text{III}}$-edge EXAFS spectra and RSFs for two Th aqueous solutions and a Th sorption sample at pH 2 (41 μmol/g).
5.3.6 Powder EXAFS of Th-sorbed montmorillonite at pH 5

To investigate whether Th nucleation occurs when the pH in the Th/montmorillonite system is raised, a set of sorption samples was prepared at pH 5 (Th loading: 14 - 166 μmol/g). As discussed in section 5.2.2, the solutions from which these samples were made were over-saturated with respect to amorphous ThO₂.

Fig. 8 shows k³-weighted EXAFS spectra of montmorillonite treated with Th at pH 5 (Fig. 8a) and the corresponding RSFs (Fig. 8b). For the two samples with lower Th loadings (14 and 40 μmol/g) the amplitude and peak position of the first and the second RSF peaks (R + ΔR = 1.92 Å and 3.28 - 3.34 Å) agree with those observed for higher Th loadings at pH 3 (Fig. 2). For the highest concentrated sample there is no second peak at R + ΔR = 3.3 Å and instead a new RSF peak appears at a higher distance (R + ΔR = 3.88 Å), suggesting a change in the average Th coordination environment.

The structural parameters of the pH 5 samples are listed in Table 2. Data analysis was conducted using the same fit constraints as for the pH 3 samples (see 5.3.2). In all pH 5 samples the first RSF peak was described best by a short and a long Th-O backscattering pair (3.0 - 3.4 O at 2.25 - 2.28 Å and 7.2 - 7.8 O at 2.45 - 2.47 Å). These values compare well with the Th-O structural parameter at pH 3.

For the pH 5 samples with lower Th loading (14 and 40 μmol/g) data analysis further suggests a reduced number of Th-Si pairs compared to the sorption samples prepared at pH 3 (1.4 - 1.7 at ~3.87 Å vs. 2.5 - 2.9 at ~3.83 Å; Table 2). The reduced CNₘ-Si could be caused by the fact that a fraction of the Th atoms at pH 5 is no longer directly bonded to the montmorillonite surface and forms an outer-sphere complex. The reduced CNₘ-Si can also be an indication for the presence of a small amount of Th-Th pairs. Th-Th and Th-Si pairs are interfering destructively at 3.90 Å, and thus result in a reduced amplitude of the EXAFS spectra. For the pH 5 sample with the highest Th loading (166 μmol/g), neither a model with one Th-Th and one Th-Si pair nor a model with two Th-Th pairs at different distances provided a reasonable fit to the experimental spectrum. Nevertheless, it is possible to propose an 'uptake' mode for Th in this sample. In Fig. 9 the EXAFS spectra of thorite (Farges, 1991) and amorphous Th(OH)₄ are compared to the 166 μmol/g Th sorption sample prepared at pH 5. The likeness of the sorption sample and the Th amorphous precipitate is striking, and suggests the formation of a similar precipitate at high Th concentration. However, it was not possible to fit Th(OH)₄ data with just one or two Th-Th pairs. The reason probably lies in the fact that the structure of the Th(OH)₄ compound is too disordered to be fitted with a two-Th shell harmonic model (Östhols et al., 1997).
Fig. 8: \( k^3 \)-weighted Th L\(_{III}\)-edge EXAFS spectra (a) and corresponding RSFs (b) for Th sorbed on montmorillonite at pH 5 and various Th concentrations.
5.4 Discussion

5.4.1 Nature of the uptaking phase

EXAFS data of montmorillonite treated with Th at pH 2, 3 and 5 indicated the presence of a Th-Si pair at 3.81 - 3.88 Å in all Th sorbed montmorillonites, except for the most concentrated sample at pH 5. Furthermore, data analysis suggests the presence of two oxygen subshells in the first coordination environment of thorium (Table 2).

The finding of the presence of two oxygen subshells in the first coordination environment of thorium agrees with previous EXAFS studies on the uptake of cations onto montmorillonite (Strawn and Sparks, 1999; Sylwester et al., 2000). Sylwester et al. (2000) observed that at pH > 6.4 (0.1 M NaClO₄) the equatorial U-O pair splits when uranyl is sorbed onto montmorillonite. At lower pH (< 0.01 M NaClO₄) however, no splitting was observed and the EXAFS structural parameters were similar to those of the aqueous uranyl ion. Similarly, Strawn and Sparks (1999) observed that Pb uptake on montmorillonite resulted in a splitting of the oxygen shell at pH > 6.7 and 0.1 M NaClO₄ ionic strength, whereas the Pb-O distances and O coordination numbers were characteristic of Pb^{2+}(aq) at lower pH and ionic strength.
In the following we want to discuss whether the EXAFS findings can be explained by the formation of Th solution complexes, the precipitation of Th phases or the sorption of Th onto the mineral substrate.

5.4.1.1 Complexation in solution

To evaluate whether the formation of Th solution complexes is an important process in our experimental system, EXAFS spectra of Si-free and Si-containing Th reference solutions were compared with the spectra of Th treated montmorillonite. While the spectra of the Si-free and Si-bearing solutions were identical, they showed no similarities with the spectra of Th treated montmorillonite, indicating that Th-Si solution complexes were not formed to any significant amount and are not relevant in this study (see section 5.3.5, Fig. 7).

This finding is further supported by EXAFS data analysis. While the Th/montmorillonite samples exhibit Th-O pairs at 2.24 Å and 2.48 Å and a Th-Si pair at 3.84 Å, Th reference solutions were fit best with a single Th-O pair at 2.45 Å (Table 1). Th-O distances between 2.44 and 2.48 Å observed in the references solutions as well as the Th/montmorillonite samples are characteristic of Th-H2O bonds (2.44 - 2.45 Å) (Table 1, and Moll et al., 1999).

5.4.1.2 Precipitation of a Th (hydr)oxide

This study indicated that, based on EXAFS data analysis, the presence of Th nucleation products can be excluded in montmorillonite samples which were treated with Th at lower pHs (pH 2 and 3; Fig. 4, Table 2, section 5.3.2 and 5.3.3).

In order to determine whether Th nucleation products were formed at higher pH values, uptake experiments were performed at pH 5 and initial Th concentrations exceeding the solubility limit of amorphous ThO2 (pH 5; see section 5.2.2 and 5.3.6). The spectrum of the most concentrated Th/montmorillonite samples (166 µmol/g) is similar to the spectrum of amorphous Th(OH)4 (Fig. 9), suggesting the formation of a Th-hydroxide-like precipitate in the sample. We were unable to fit the spectra with Th-Th pairs (see Table 2; section 5.3.6). Östhols et al. (1997) explained the absence of Th-Th pairs in amorphous Th(OH)4 by proposing a large degree of disorder and a spread in Th-Th distances preventing the detection of nearest Th neighbors.

In the lower concentrated samples prepared at pH 5 no similarity to the spectrum of amorphous Th(OH)4 could be observed although also these samples were oversaturated with respect to amorphous ThO2 (see section 5.2.2 and 5.3.6). We can only speculate that the likely absence of amorphous Th(OH)4 is caused by a fast uptake of Th on montmorillonite resulting in remaining [Th]aq = 4·10^{-6} M in solution which is undersaturated with respect to amorphous ThO2 (SI = 0.004).
5.4.1.3 Th sorption on silica and dissolution of montmorillonite

The structural parameters obtained in our study (Table 2) agree with the findings of a previous EXAFS study on the uptake of Th on highly reactive amorphous silica at pH=3 (Östhols et al., 1997; 1.7-2.7 O at 2.27-2.34 Å vs. 3.0-3.1 O at 2.24 Å (this study), 4.4-5.4 O at 2.53-2.56 Å vs. 5.8-6.4 O at 2.47-2.48 Å (this study), and 1.3-2.7 Si at 3.79-3.89 Å vs. 2.7-2.9 Si at 3.81-3.83 Å (this study)). Thus the sorption of Th on a silica phase is compatible with the EXAFS results and needs to be examined further.

XRD data indicated the presence of a small amount of quartz (<1%; see section 5.2.1) in the conditioned clay material used in this study. Thus, quartz represents a potential SiO₂ sorbent in our system. The BET surface area of quartz (1 m²/g; White, 1996) is however small compared to the BET surface area of montmorillonite (89 m²/g; this study) and the amorphous silica used by Östhols et al. (170 m²/g), making the sorption of Th on quartz an unlikely uptake process for Th in our experiments.

Another potential SiO₂ sorbent in our system is the presence of an amorphous silica phase that could have been formed by precipitation of Si from solution. The Si concentration in Th treated montmorillonite samples was monitored. The Si release rate (~10⁻¹⁴ mol m⁻² s⁻¹) agrees well with the Si release rate of montmorillonite reported in the literature (see section 5.2.2). The fact that the Si release rate was not modified due to the presence of Th indicates that the precipitation of Th-silicate is not likely. Since the solubility of amorphous Si is significantly higher (4100 µM; Rimstidt and Barnes, 1980) than in Th sorption experiments we doubt that SiO₂ precipitates under the reaction conditions used and therefore we conclude that sorption of Th onto an amorphous silica phase is not an important uptake process in this study. Besides Si, the concentration of Al in solution was monitored during the experiments. The low Al concentration (30 - 47 µM) indicated no change with time. The fact that [Al]ₐq remained constant while [Si]ₐq increased during the experiment might suggest the selective dissolution of tetrahedral SiO₄ layers (incongruent dissolution), while octahedral Al-layer would remain stable.

Based on the previous discussion we can exclude the formation of a Th-Si solution complex, a Th precipitate (in all but the most concentrated sample at pH 5) and the uptake of Th on a SiO₂ phase. Thus, the only remaining possibility to explain the EXAFS data is a structural link of Th to the montmorillonite surface.

5.4.2 Topological relationship between Th polyhedra and Si tetrahedra

The Th-Si bond length of 3.81 - 3.88 Å in all Th sorbed montmorillonites, except the most concentrated sample at pH 5, is similar to the Th-Si EXAFS distance in thorite (3.90 Å) in which the bridging of Th to Si tetrahedra via corner-sharing linkage results in the presence of a
short Th-O distance ($R_{\text{Th-O}} = 2.36$ Å, see section 5.3.1). Therefore, by comparison with the thorite structure, we propose that Th bonds to the montmorillonite surface by sharing corners with tetrahedral Si and the short Th-O distance ($2.23 - 2.24$ Å) is assigned to the Si-O-Th bond (Fig. 10). The similarity of $CN_{\text{Th-Si}}$ ($2.5 - 2.9$) and $CN_{\text{Th-01}}$ ($\sim3$) values (Table 2) suggests that SiO$_4$ tetrahedra are linked to Th through a single O atom and that Th forms multidentate corner-sharing surface complexes. The data suggest the formation of a tridentate corner-sharing complex, but this can be questioned for the following reasons. The uncertainty on the coordination number in this EXAFS study is at least 25% (see section 5.2.4). Thus, it is not possible to definitely differentiate between a double-, triple- or fourfold-corner-sharing surface complex. Furthermore, one should keep in mind that EXAFS measures an averaged signal and thus an average coordination number is obtained. For example, a coordination number of three for Th-Si pairs could be explained not only by three neighboring Si 'atoms', but also by a 1:1 mixture of two and four Si neighbors. As an example for possible coordination environments of Th in the Th/montmorillonite system, Fig. 10 illustrates how Th and Si could be connected via a double corner-sharing complex. In the figure, Th is coordinated to 6 O atoms from water molecules. Data analysis indicated 6 - 8 Th-O pairs at $2.44 - 2.48$ Å in the Th treated montmorillonite samples (Table 2) which attributed to Th-H$_2$O bonds (see section 5.4.1). Since the total number of coordinated O atoms in solid Th compounds and aqueous solutions ranges from eight to eleven, a $CN_{\text{Th-O2}}$ of 6 - 8 is not unreasonable, assuming that two O atoms are coordinated to silica tetrahedral via a double corner-sharing complex.
5.4.3 Structure of Th surface complexes

The question now to discuss is how Th is bond to the montmorillonite surface. The possibility that Th is incorporated into the montmorillonite structure can rejected because of the considerable size of the Th(IV) ion (1.02 Å) compared to the ionic radii of cations present in the montmorillonite structure (Si(IV) (0.40 Å), Al(III) (0.53 Å), Mg(II) (0.71 Å) and Fe(III) (0.63 Å); Shannon, 1976). A specific bond of Th atoms to the (001) surface of montmorillonite can be rejected since cation exchanged was prevented due to the high ionic strength (0.1 M NaClO₄). Since from the previous discussion the only remaining possibility is that Th is forming a surface complex at the montmorillonite surface, we have illustrated possible Th positions for the montmorillonite structure (Fig. 11) based on the EXAFS bond distances (Table 2). In the following we will discuss some possibilities for a structural link of the Th to the (100), (110) and (010) surfaces of montmorillonite.
Fig. 11 and Fig. 12 illustrate the montmorillonite structure with models of possible Th surface complexes. In Fig. 11 it was assumed that Th sorbed onto a montmorillonite structure which did undergo congruent dissolution, whereas in Fig. 12 Th sorbed onto a montmorillonite in which the Si tetrahedra were preferentially dissolved (incongruent dissolution; see section 5.4.1.3). In neither case we could find positions which are exactly matching 2 - 3 short Th-O pairs at 2.24 Å and 2 - 3 Th-Si pairs at 3.83 Å. Nevertheless, we could find possible positions where a Th atom can sorb onto montmorillonite with slightly different distances. Th surface complexes (Th1-Th6, Fig. 11 and Fig. 12) have 2-3 neighboring O atoms at 2.3-2.9 Å and

Fig. 11: Idealised particle of montmorillonite bounded by the most common cleavage surfaces, on which 3 possible Th surface complexes are shown. The nearest Th-O bonds (thick lines) are shown for all 3 complexes. Nearest Th-Si or Th-Al bonds (broken lines) are shown for complexes Th1 and Th3, but were omitted for Th2 for clarity. Structure of montmorillonite after Tsipursky and Drits (1984).
Fig. 12: Simulation of selective dissolution of SiO₄ tetrahedra. This figure is analogous to Fig. 11, but the octahedral sheet is now protruding perpendicular to the (100) and (010) planes due to Si dissolution. Again, 3 possible Th surface complexes are shown.

Th-Si/Al pairs at ~3.9 Å. For example, the complexes Th1 to Th3 shown in Fig. 11 possess 2 Si neighboring atoms at 3.8 - 3.9 Å. Th1 has additionally two Si and one Al neighbor at 3.6 Å. In case that montmorillonite is dissolved incongruently, the illustrated surface complexes (Th4 - Th6) possess 1-2 Al neighbors in 3.8 - 3.9 Å and 2 Al neighbors at 3.5 Å (Th4 and Th5; Fig. 12).

While EXAFS clearly indicated the presence of Th-Si and/or Th-Al pairs at ~3.9 Å, no backscattering pairs were detected at 3.5 - 3.6 Å. It is not uncommon in EXAFS data analysis that certain distances can not be observed. For example thorite can be fitted reasonably well without taking into account two Th-Si pairs at 3.16 Å, although the presence of this shell is proven by XRD (see section 5.3.1, Taylor and Ewing, 1978). The system disorder can cause
backscattering pairs to remain undetected. Thus, it is possible that surface complexes such as those illustrated in Fig. 11 and Fig. 12 can yield the structural results given in Table 2.

The hypothesis that the system disorder prevents the detection of backscattering pairs is supported by the fact that the spectra at pH 2 and pH 3 (Fig. 4 and Table 2) are almost identical, although the Th surface loading varies by a factor of 40 (for a detailed discussion on surface loading see below). This finding could be understood in the context, that there is a wide variety of Th surface complexes which are bound to the montmorillonite surface in different configurations and bond angles.

This hypothesis is supported by the P-EXAFS experiments which were performed on self-supporting clay films treated with Th at pH 2 and 3. The Th P-EXAFS spectra showed no anisotropy in the spectra although the self-supporting clay films were well orientated (Fig. 6; see section 5.3.4). Because in P-EXAFS measurements backscattering pairs in the in-plane direction are strongly attenuated when the X-ray polarization vector is parallel to film plane, seems the lack of a P-EXAFS dependency to indicate that Th is not sorbed to the montmorillonite in the continuity of the octahedral sheet in a single surface complex (see section 5.1). A mixture of surface complexes like e.g Th1, Th2, Th4 and Th5 which all have bonds to Si that form different angles would severely decrease the P-EXAFS angular dependence (Fig. 11 and Fig. 12). It is therefore possible that there is a series of similar complexes in which Th polyhedra bridge to the montmorillonite surface in such a manner that the average angle of the Th-O and Th-Si pairs with respect to the c* direction (β) is ~54.7°. At this particular β-angle polarized and powder EXAFS spectra are identical (Manceau et al., 1990) and would eliminate any angular dependence in P-EXAFS measurements.

5.4.4 Effect of surface loading

The results discussed so far suggest that Th is bonded as a surface complex to the montmorillonite surface. To address the question whether the available sorption sites on the montmorillonite surface are saturated, the degree of surface coverage (ratio of the amount sorbed to the amount required to form a monolayer on the particle surface) was estimated.

The number of edge sites can be estimated based on morphological information. Since we lack morphological information on montmorillonite, we used dimensions of hectorite particles (Schlegel et al., 1999b) to calculate the relative surface area. The relative surface area of montmorillonite edge surfaces (100), (110) and (010) is 2%, assuming that the morphology of montmorillonite and hectorite is similar, although it is not really the case since hectorite particles have an unusual lath-shape.

Based on the density of oxygen atoms at the montmorillonite lateral surfaces it is then possible to estimate the number of edge sites (Tsipursky and Drits, 1984). This yields
0.5 sites/nm² for the lateral surfaces. Because sorption to planar sites was blocked due to the high ionic strength of the solution (0.1 M NaClO₄) it is reasonable to assume that mainly edge sites are involved in the uptake process. The estimated number of edge sites (0.5 sites/nm²) is in the same range as the number of protonable edge sites of montmorillonite deduced by potentiometric titration (1.4 sites/nm², Baeyens and Bradbury, 1995). To finally estimate the degree of surface coverage in this study we assumed that Th shares on average 2.5 O atoms with Si tetrahedra from the crystal lattice (Table 2) resulting in 0.2 sites/nm² lateral sites. Thus, the edge sites are saturated (surface coverage >100 %) when the amount of Th is >32 µmol/g.

Interestingly, the EXAFS spectra and the structural parameters of the low concentrated sample prepared at pH 3 (1 - 12 µmol/g; surface coverage of 3 - 38 %) are different compared to those of the most concentrated sample (157 µmol/g; surface coverage of 600 %). The latter EXAFS spectrum gains certain similarity with the spectrum of an aqueous Th solution (Fig. 7) and CN_{Th-Si} appears to be slightly reduced (2.1 vs. 2.7-2.9) compared to samples with a lower surface loading. This finding might indicate that Th is additionally sorbed as an outer-sphere complex when the edge sites are saturated.

### 5.5 Concluding remarks

The present study investigated for the first time the uptake of Th onto montmorillonite. Two O coordination shells at ~2.24 Å and ~2.48 Å, and one Si shell at 3.81 - 3.88 Å, were systematically observed at low and intermediate surface coverage and under reaction conditions either undersaturated or supersatured with respect to amorphous ThO₂. The study showed that at low and intermediate surface coverage the formation of Th nucleation products and Th-Si solution complexes, and the sorption of Th on a silica precipitate can be excluded from the EXAFS spectra analysis and solution chemistry and that instead Th is bond to the edges of montmorillonite particles by sharing double corners with Si tetrahedra.
5.6 References


CONCLUSIONS

Kinetic and EXAFS investigations were used in this thesis to determine the uptake mechanisms of Ni and Th onto montmorillonite over a wide range of reaction conditions. Below the major findings and the consequential conclusions are summarized.

A P-EXAFS study on highly oriented self-supporting Ni treated montmorillonite films revealed that at low Ni concentrations and near neutral pH the Ni atoms were forming surface complexes at the edge sites of montmorillonite. The surface complexes were part of the octahedral sheet of montmorillonite. They became more ordered as the reaction time increased. This improved structural order with time could explain the preliminary desorption experiments in our laboratory. The experiments at trace element concentrations indicated that the release of Ni sorbed onto montmorillonite was slowing down with prolonged reaction time. These findings are of significant environmental relevance, because attachment of metal ions specifically bond to clay mineral surfaces can severely reduce their bioavailability and mobility in soil and water environments.

P-EXAFS experiments further revealed that the treatment of montmorillonite with Ni at elevated pH (pH = 8) and Ni concentrations results in the neoformation of Ni-phyllosilicates. The obtained orientation and angular dependence of the Ni and Si shells of the Ni-phyllosilicates revealed neoformed layers parallel to the montmorillonite layers. The presence of Ni-phyllosilicates in the Ni/montmorillonite uptake system could be confirmed with complementary TEM/EDS investigations. The TEM observations of Ni treated montmorillonite revealed the presence of small and thin particles consisting of only 3 to 5 lattice fringes with a lattice spacing characteristic for smectites. The small particles could only be observed in Ni treated samples. Their Ni content as probed by EDS was high, indicating that these small particles were neoformed phyllosilicates. The heterogeneous formation of phyllosilicates has important geochemical implications. Layer silicates are stable minerals in mildly acidic to basic pH conditions and can bind metals in waste and soil matrices. Furthermore, montmorillonite is abundant in the environment. The sequestration of sorbed trace metals in sparingly soluble phyllosilicate structures can therefore permanently reduce their migration in the geosphere.

Finally, L-edge EXAFS measurements of thorium were performed to investigate the uptake mechanisms of Th onto montmorillonite. This radionuclide was used as analog for tetravalent actinides. The EXAFS study revealed that the uptake of Th onto montmorillonite at low pH (pH < 3) results in the formation of surface complexes at the edges of montmorillonite
crystals. At higher pH and higher Th concentrations EXAFS spectra resembling that of amorphous Th(OH)$_4$ were observed, suggesting that a Th hydroxide-like phase precipitated upon treating montmorillonite with Th. Due to its radioactivity and wide-spread industrial application, Th has become an environmental contaminant. For example, fly ashes from lignite power stations are contaminated with Th and waste arising from mining and oil and gas extraction contains radioactive material such as uranium and thorium. However, the most critical environmental aspect concerning Th is its safe disposal in nuclear waste repositories. The release of radionuclides from a nuclear waste repository can be considerably retarded due to the formation of inner-sphere surface complexes at clay minerals. Thus, the finding that Th specifically bonds to the montmorillonite surface is an important step towards a molecular-level understanding of the long-term fate of radionuclides in waste repositories.

**OUTLOOK**

Open questions to be analyzed

The present study showed how wet chemistry experiments can be combined with EXAFS and TEM measurements to successfully determine the uptake process of metals on clay mineral surfaces. This thesis in particular contributes to the understanding of the uptake behavior of metals onto dioctahedral clay minerals. However, some questions raised by this study remained open.

For example, the study revealed that the diffusion of Ni atoms into the montmorillonite structure over a time period of up to 1 year did not occur. It is questionable whether this finding can be extrapolated to significantly longer time periods. Nuclear waste repositories need to remain safe over periods of 1000 to 1 million years and thus the regulatory authorities require predictions on the long-term fate of radionuclides. To extrapolate findings on the uptake of contaminants onto clay minerals to prolonged time scales it is necessary to enhance the reaction processes by elevating the reaction temperature. For example, by saturating montmorillonite with Ni cations and heating the clay material up to 350°C Muller et al. (1997) demonstrated the diffusion of Ni atoms into cis vacant octahedral sites of montmorillonite.

Another critical issue for assessing the long-term safety of waste repositories and for predicting the fate of contaminants in the geosphere is the release of heavy metals sorbed onto mineral surfaces. Desorption processes often control the mobility of metals in natural systems and thus impact environmental quality and human health. The present study as well as most studies in the literature focused on the determination of uptake processes at the water-mineral
interface. Recently, preliminary Ni desorption experiments at trace element concentrations were conducted in the Waste Management Laboratory at PSI. The studies showed that the observed Ni release rate decreased the longer montmorillonite had been in contact with Ni, possibly suggesting that metal ions can become stronger bound to the clay as incubation time increases. The increase in structural order with increasing reaction time observed in this study is another indication that the surface complexes can rearrange and become stronger bound to clay mineral surfaces as the contact time evolves. A detailed spectroscopic study and a molecular-level understanding on such processes are, however, still lacking.

In the past many sorption models have been developed based on batch and spectroscopic data on the uptake of a specific divalent metal ion onto mineral surfaces. Often the authors used such models to predict the uptake behavior of other divalent metal ions on the same mineral assembly. The findings of this study show similarities with the findings from a study on the uptake of Zn on hectorite (Schlegel et al., 2001; Schlegel et al., 2002). In both studies the authors observed the formation of surface complexes located at the edges of clay particles at low metal loadings and intermediate pH and the neoformation of phyllosilicates at high loadings and higher pH. In order to understand the later finding from a thermodynamic perspective the solubility products of phyllosilicates need to be determined. Presently, such information is lacking in thermodynamic databases.

The uptake of Th onto montmorillonite in this study was studied at low pH to prevent the formation of Th precipitates but to reach a sufficient Th loading for EXAFS measurements. It would be interesting to investigate the Th uptake onto montmorillonite at near neutral pH to verify that the findings of this study can be extrapolated to higher pH. In order to prevent the formation of precipitates it will be necessary either to work with a flow reactor or to spike the montmorillonite suspension several times with a Th stock solution which is undersaturated with respect to amorphous Th (hydr)oxides. In a next step complementary TEM/EDS investigations could be performed to confirm the presence of Th (hydr)oxides at higher Th and lower proton concentrations in the Th/montmorillonite uptake system. Like in the Ni/montmorillonite system it will be useful to investigate the desorption behavior of Th. Finally, the absence of a P-EXAFS dependence requires further investigations. It should be verified that Th surface complexes on other minerals like hectorite are lacking this P-EXAFS dependence too.

It must be emphasized that in this study a pure mineral phase (> 99% montmorillonite) was used. It will be important in the future to investigate how the results of this study can be applied to systems consisting of mixed mineral phases. For instance, the backfill material
bentonite foreseen in the Swiss concept for a high level radioactive waste repository is a mixture of several clay mineral phases. Bentonite (MX-80) as mined in Wyoming and South Dakota (USA), has a montmorillonite content of 75%. The most important additional components are quartz (15%), feldspar (5-8%), carbonates (1.4%), pyrite (0.3%) and organic carbon (0.4%) (Grauer, 1986). Studies of chemical species transfer in waste repositories classically rely on the assumption that the fate of radionuclides is primarily determined by sorption reactions on most predominant mineral phases. This assumption, however, can break down when highly reactive mineral phases are present in the sorption system. For instance, recent micro X-ray fluorescence (XRF) and micro XAS experiments demonstrated that the sorption of zinc in sandy contaminated soils is not controlled by the most abundant quartz grains, but by the minor iron and manganese oxide phases (Manceau et al., 2000). Another example of the importance of minor mineral phases that can be overlooked by bulk measurements is the fate of plutonium in the tuff of Yucca Mountain in Nevada (Duff et al., 1999). The tuff consists of more than 95% zeolite minerals, and less than 1% oxides, with only a small fraction of the latter being Mn oxides. However, by using a X-ray microprobe facility at the Advanced Photon Source (APS), Pu$^{5+}$ was found not only to be associated specifically with the Mn oxides, but also to have been oxidized to Pu$^{6+}$ by Mn$^{3+}$/Mn$^{4+}$. Neglecting the major role of minor minerals would result in significant errors in calculations of the transport and sequestration of contaminants in the geosphere.

**Methodological advances**

The use of high resolution analytical X-ray probes to investigate the uptake behavior of metals in clay systems will, however, be difficult because the absorption length of the X-rays is about 100 μm (at 8 keV in a SiO$_2$ matrix) and therefore larger than the particles. Furthermore, the size of clay particles varies from nanometer (e.g. smectite) to micrometer (e.g. kaolinite and dickite), and thus only the size of the latter minerals is in the same order as the X-ray beam (1 x 1 μm$^2$) presently available at 3rd generation synchrotron facilities. It can be assumed that in the near future in the hard X-ray regime a beam size in the nanometer range at new highly brilliant synchrotron sources will be obtained. The use of zone plates for example currently allows achieving a focus of ~ 0.05 x 0.05 μm$^2$ with the disadvantage of loosing flux. Improvements in brightness are expected by the future availability of the X-ray Free Electron Laser (XFEL). The XFEL delivers coherent X-ray pulses of about 100 fs length (compared to about 30 ps at state-of-the-art synchrotron radiation sources) in an energy range up to 12 keV and the peak brilliance per pulse exceeds present sources by eight or more order of magnitude (TESLA, 2001).
With simultaneous improvements in X-rays sources, X-ray optics, detector technology and sample positioning it should become feasible that XAS will become a tool for investigations of molecular-scale processes on the sub-micron level in the hard X-ray regime and to probe separately individual reactive phases (e.g. quartz, smectite, feldspar...) in natural mineral assembles.

References


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