Characterization of structural iron in smectites — an ab initio based XAS study

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Abstract

Fe-bearing clay minerals are abundant in argillaceous rocks as redox-active structural iron may control the sorption mechanism of redox sensitive elements on the surface of clay minerals. The extent and efficiency of the redox reactions depend on the oxidation state (\(\text{Fe}^{2+}/\text{Fe}^{3+}\) ratio) and structural distribution of the substituting cations in the TOT-layer of clay minerals. Even smectites with similar structure originating from different locations might have distinct arrangement of isomorphic substitutions (e.g. individual iron or Fe–Fe pairs). In this study, the proportion of different iron distribution in Milos–, Wyoming– and Texas–montmorillonite was determined by combining X-ray absorption spectroscopy (XAS) with ab initio calculations. The relaxed atomic structures of the smectite models with different arrangement of individual Fe atoms and Fe–Fe/Fe–Mg clusters served as the basis for the calculations of the XAS spectra. The combination of simulation results and measured Fe K-edge XAS spectra of Wyoming–, Milos– and Texas–montmorillonites suggested that iron is present as \(\text{Fe}^{3+}\) in the octahedral sheet. \(\text{Fe}^{3+}\) in Texas–montmorillonite has a tendency to form clusters, while no definitive statement about clustering or avoidance of Fe–Fe and Fe–Mg pairs can be made for Milos– and Wyoming–montmorillonite.
Iron bearing clay minerals are one of the main redox controlling phases in soils\textsuperscript{1}. They are important sorbents for organic and metallic contaminants as heterogeneous redox reactions on clay minerals control the mobility and bioavailability of redox-sensitive elements\textsuperscript{2–5}. Understanding the mechanisms of individual redox reactions and the iron redox cycle is important in the interpretation of geochemical modelling\textsuperscript{1,6}. However, redox processes are inherently complex phenomena and their detailed mechanism remained purely understood\textsuperscript{5,6}. The behavior of the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} redox pairs has been studied in iron oxides (e.g. hematite\textsuperscript{7,8}, goethite\textsuperscript{9,10}) and Fe-rich clay mineral (e.g. nontronite\textsuperscript{4,11–14}), however, the redox processes in low Fe-bearing clay minerals (e.g. montmorillonite\textsuperscript{3,15}) is much less understood\textsuperscript{5}. A recent experimental study indicated that structural iron in Wyoming–montmorillonite is more accessible for an interfacial electron transfer than Texas–montmorillonite leading to the conclusion that low Fe-bearing clay minerals even with similar composition might have distinct arrangement of isomorphic substitutions\textsuperscript{16}. The structure of Fe-bearing smectites can be described as layers of pseudo-hexagonally ordered sheets of alumina octahedral (O) sandwiched between two opposing siloxane tetrahedral (T) sheets (so called TOT-layer)\textsuperscript{17,18}. Most of the Fe-bearing clay minerals belong to 2:1 type of dioctahedral smectites in which only two thirds of the possible octahedral positions are occupied\textsuperscript{17}. One third of the octahedral sites are trans-symmetric and two thirds of the octahedral sites are cis-symmetric with respect to the orientation of the hydroxyl (OH\textsuperscript{–}) groups\textsuperscript{17,19}. It has been demonstrated that iron distribution in the octahedral and in the tetrahedral sheet strongly depends on the total Fe content\textsuperscript{5,20–22}. Iron mainly substitutes for Al in the octahedral sheet where it can occupy both the cis- and the trans-sites\textsuperscript{5,15,20,23,24}. It may have ordered distribution avoiding Fe–Fe or Fe–Mg pairing or it may form Fe–Fe and Fe–Mg edge sharing pairs of octahedra\textsuperscript{15,19,20}. Clustering usually occurs in iron rich smectites (e.g. nontronite\textsuperscript{2,11,25–27}), but it can also be observed in iron poor clay minerals\textsuperscript{5,15}. The structure of the dioctahedral Fe-rich end-member, nontronite is well-studied and the relative distribution in the octahedral sheet of many cations (e.g. Fe\textsuperscript{3+}, Mg\textsuperscript{2+}) is quantified\textsuperscript{5,12,13,28,29}. Much less is known about iron-poor smectites despite their importance in iron redox cycle of geochemical systems. The redox-active structural iron in clay minerals with low Fe content may control the sorption mechanism and the oxidation state of redox sensitive elements on the clay mineral surface\textsuperscript{5,15}. The uptake of ferrous iron on clays as well as the competitive sorption between Fe\textsuperscript{2+} and other
divalent cations present in the system greatly depend on the concentration, the redox state and the occupational site of structural iron\(^3,5,6,13,15,16,28,30,31\). The extent and efficiency of redox reactions depends on the specific structural environment and oxidation state of cations in the TOT-layer of clay minerals (e.g. Fe\(^{2+}/\text{Fe}^{3+}\), Mg\(^{2+}\))\(^5\). Due to electrostatic repulsion, Fe\(^{3+}\) forming Fe\(^{3+}–\text{Fe}^{2+}\) or Fe\(^{3+}–\text{Mg}^{2+}\) clusters are less efficient electron acceptor in the redox reaction\(^32\). In the best case, the phenomenon can be explained by the different structural characteristics of the montmorillonites.

X-ray absorption spectroscopy (XAS) is a widely applied tool to identify the preferred oxidation state and occupational site of iron in clay minerals\(^1,5,13,33\). For the quantitative interpretation, reference spectra of minerals are needed, in which the element of interest has well-characterized oxidation state. However, it is difficult to have material with pure Fe\(^{2+}\) or Fe\(^{3+}\) oxidation state because iron preferentially participates in redox-reactions leading to materials with mixed oxides\(^12,16,21\). Furthermore, iron can unequally be distributed between \(\text{cis}\) and \(\text{trans}\)-octahedral sites, which can barely or not at all be distinguished only by the experimental result of the spectroscopic method\(^5,13,34\). Hence, it is becoming an increasingly widespread practice to calculate the extended X-ray absorption fine structure (EXAFS) based on atomistic scale \(\text{ab initio}\) simulations. The theoretical simulations of X-ray absorption near edge structure (XANES) spectra for complex systems are still rare. Recent advances of the theory and computational algorithms in the density functional theory with the local spin-density approximation (DFT-LSDA) based model made it possible to obtain accurate Fe K-edge XANES spectrum of a Fe-bearing structure\(^35,36\).

In this work, we characterize the preferred oxidation state and distribution of iron in Milos–, Wyoming– and Texas–montmorillonite by modelling the measured XAS spectra of these clay minerals as a linear combination of theoretical spectra, which were obtained from \(\text{ab initio}\) geometry optimization calculation of Fe-bearing smectites. The effect of Fe–Fe and Fe–Mg clustering in the octahedral sheet on the XAS spectra was studied using several different dioctahedral smectite models with structural iron incorporation in the octahedral sheet.
2. Materials and methods

2.1. Modelling setup

In our study, we considered idealized defect free TOT layer of a 2:1 dioctahedral clay with the general formula of $4\cdot[(\text{Mg}_x\text{Fe}^{2+}_y\text{Fe}^{3+}_z\text{Al}_{8-x-y-z})(\text{Fe}^{3+}_n\text{Si}_{16-n})\text{O}_{40}(\text{OH})_8]^{(x+y+n)-}$. It is often used as the simplest structural prototype for dioctahedral clays, where only two thirds of the cation sites in the octahedral sheet are occupied opening a possibility for two distinct structural models.$^{17}$ In the cis-vacant model (cv-model), all trans-octahedra are occupied and half of the cis-octahedra are vacant, while in the trans-vacant case (tv-model), all trans-octahedra are vacant and all of the cis-octahedra are occupied (Figure 1)$^{37}$. Natural clay minerals can be found in both, cis- and trans-vacant forms.$^{19,20,23}$.

In both models, the structural optimizations were performed on a single clay particle without water in the interlayer. The dimensions of the orthorhombic supercell were $18.2\text{Å} \times 20.8\text{Å} \times 15.0\text{Å}$. Similar to previous works, the cell parameter in the “c” direction was fixed to $15\text{Å}$ to minimize the interaction between the periodic images.$^{36-38}$.

The incorporation of iron in the structure was considered as a substitution for aluminum in the octahedral sheet or for silicon in the tetrahedral sheet (Figure 1). Tetrahedral iron is evidently always in the trivalent state, since Fe$^{2+}$ has a too large ionic radius for this site.$^5$ In the octahedral sheet, both ferrous and ferric iron can occur. In the tv-model, iron is only present as cis-octahedral positions whereas, in the tv-model Fe can be present in both (cis- or trans-) octahedral positions (Figure 1). The effects of Fe–Fe clustering in the octahedral sheet was studied by replacing two Al octahedra by a Fe–Fe pair at different occupational sites (Figure 1d-g). The presence of Mg–Mg pairs as first and second neighbors produces geometrical distortions in the octahedral sheet due to the higher radius of Mg$^{2+}$, furthermore, the localized concentration of negative charge in the octahedral sheet would locally destabilize the structure.$^{39,40}$ Similarly, the presence of Fe$^{2+}$–Mg$^{2+}$ pairs can be ruled out because of the electrostatic repulsion argument. Thus, Fe–Mg clusters were modelled to Fe$^{3+}$–Mg$^{2+}$ pairs only (Figure 1h-l). In total, 26 different model structures were evaluated (Figure 1, Table 1).
**Figure 1.** Schematic views of smectite models with different distribution of structural iron. Panel a-l indicate only the octahedral sheet for the sake of clarity. The structures with single iron atom per supercell corresponding to a random distribution are shown in panel a-c, configurations of Fe-Fe clusters are shown in panel d-g, while Mg-Fe clusters are shown in panel h-l. The distribution of tetrahedral iron is shown in panel m,n. cv-models correspond to panel a-b, d-f, h-k and m, while tv-models are shown in panel c, g, l and n. Silica tetrahedra are shown with orange color, while Fe, Mg and Al polyhedral (both octahedra and tetrahedra) are shown with pink, blue and green colors, respectively. cis-octahedra are represented with lighter, while trans-octahedra are marked with darker colors. The different occupational sites can be distinguished by the different relative position of the hydroxyl groups (OH\(^-\)) shown with red spheres.
**Table 1.** Iron incorporation model, associated short name and panels of Figure 1 in which the corresponding model structure are. Illustrated relative energy differences are calculated for structures with the same stoichiometry and total charge.

<table>
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<tr>
<th>Tetrahedral/ octahedral Fe Vacancy type</th>
<th>Oxidation state(s), occupational site(s) of iron(s)(^a)</th>
<th>Short name of the model</th>
<th>Panel in Figure 1</th>
<th>Cation(^a)–Cation(^a) bond length(^b) [Å]</th>
<th>Energy difference(^b) [kcal/mol]</th>
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<td>-2.5 ± 5.0</td>
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<td>cvOctFe3c</td>
<td>a)</td>
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<td></td>
<td>Fe(^{2+}) \text{trans}</td>
<td>cvOetFe3t</td>
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<td>0.3 ± 5.0</td>
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<td>f)</td>
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<td>tvTetFe3</td>
<td>n)</td>
<td>—</td>
<td>-7.3 ± 5.0</td>
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</table>

\(^a\)Cation corresponds to Fe\(^{2+}\), Fe\(^{3+}\) or Mg\(^{2+}\) depending on the structure

\(^b\)More detailed information can be found in Table S1 in the Supporting Information

### 2.2. Ab initio calculations

The spin polarized electronic structures calculations were performed based on the density functional theory (DFT) using the Gaussian Plane Wave (GPW) method as it is implemented in the QUICKSTEP module of the CP2K code\(^{41,42}\). The scalar-relativistic norm-conserving pseudopotentials of Goedecker, Teter and Hutter (GTH)\(^{33,44}\) were applied to avoid the explicit consideration of the core electrons. For iron, the core electrons were described as [Ne] and
were taken as valence electrons. The wave functions of valence electrons were described by a linear combination of contracted Gaussian-type orbitals using MOLOPT basis sets optimized for the corresponding GTH pseudopotentials. An auxiliary basis set of plane waves up to 400Ry cutoff energy was employed to expand the electronic density. The exchange and correlation energy was calculated using the exchange-correlation functional of Perdew, Burke and Ernzerhof (PBE). Simulations with single iron in the (tetrahedral or octahedral) sheet were performed with a multiplicity \((2S+1)\text{Fe}^{2+} = 5\) for systems with a single ferrous iron and \((2S+1)\text{Fe}^{3+} = 6\) for systems with a single ferric iron, respectively. For models representing iron clustering with the same oxidation state, the multiplicity was set to \((2S+1)\text{Fe}^{2+} - \text{Fe}^{2+} = (2S+1)\text{Fe}^{3+} - \text{Fe}^{3+} = 1\). For \(\text{Fe}^{2+} - \text{Fe}^{3+}\) clusters, the multiplicity was set to \((2S+1)\text{Fe}^{2+} - \text{Fe}^{3+} = 2\).

Conventional DFT is known to underestimate the Coulomb repulsion between the localized 3d-electrons of Fe. In order to improve the description of these delocalized states within the DFT formalism, the so-called DFT+U method was applied. In this semi empirical approach, an additional potential characterized by the so-called Hubbard-parameter \((U_{\text{eff}})\) is applied to the selected 3d-states of Fe. The value of \(U_{\text{eff}}\) depends on the implementation and has to be calibrated. The calibration for Fe-bearing montmorillonites was performed in our previous paper, thus we used a fixed Hubbard-parameter with \(U_{\text{eff}} = 1.9\text{eV} \) value.

### 2.3. Calculations of EXAFS spectra

The EXAFS spectra were calculated based on molecular configurations derived from \textit{ab initio} structure optimizations. Real space multiple scattering theory was applied as it is implemented in the FEFF 8.40 software. For each atomic configuration, the scattering potential of the atoms were calculated self-consistently. The amplitude reduction factor \((S_0^2)\) was set to 1.0. Multi-scattering paths up to eight legs with path lengths up to 7.0Å were taken into account. The radius of the cluster for self-consistent full multiple scattering calculations was set to 5.0Å. A Debye-Waller factor of 0.006Å\(^2\) was used to take into account the thermal and structural disorder for the static configurations. Other parameters were kept to the default values. All calculated and measured spectra were normalized to the value of the first oscillation. The calculated EXAFS spectra served as the basis for the interpretation of the experimental data. The linear combination fit of the calculated to the experimental EXAFS spectra was performed according to Eq.1.
\[ Q = \left( k^3 \sum_i \left( a_i^2 \chi_i(k) \right) - \chi^{\text{exp}}(k) \right)^2 + \sum_i a_i^2 \rightarrow \text{min} \]  

where \( \chi_i(k) \) are the calculated and \( \chi^{\text{exp}}(k) \) is the experimental EXAFS spectra, \( a_i^2 \) are the optimized fitting parameters. The fitting was limited to the interval of \( k \left( \text{Å}^{-1} \right) \in [3.0, 9.0]^{36,37} \).

The norm \( \sum_i a_i^2 \) was included in the objective function to reduce the noise of the fit. The quality of the fit is defined as Eq.1.36,37.

### 2.4. XAS experiments

Four samples of low Fe-bearing montmorillonite samples were studied: one Milos– (Mil–), one Wyoming-1– (SWy1–) and two Texas– (STx1\(_1\), STx1\(_2\)) montmorillonite. All the samples were prepared from the “as received” material without any physical or chemical treatment. Mil–, SWy1– and STx1\(_1\)–samples were prepared as a self-supporting film, in addition, from the Texas–montmorillonite, a sample was pressed into a pellet (STx1\(_2\)–sample). The Fe K-edge XAS spectra were collected at the Stanford Synchrotron Radiation Lightsource (SSRL, Menlo Park, CA) at beamline 11-2 using a Si(220) double crystal monochromator and a Canberra 100-pixel Ge solid-state monolith detector. The self-supporting clay films were measured with polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy at four different angles (\( \alpha = 10^\circ; 35^\circ; 55^\circ; 80^\circ \)), where \( \alpha \) is the angle between the electric field vector (\( \varepsilon \)) and the layer plane of the self-supporting film. In P-EXAFS, neighboring atoms along the polarization direction of the X-ray beam are preferentially probed, and atoms located in a plane perpendicular to this direction are attenuated. To test the potential texture effects arising from the layered structures of the smectites, which tend to form samples having a certain degree of texture, one STx1 sample was pressed as a pellet (STx1) and measured at \( \alpha = 45^\circ \). Several scans were averaged to improve the signal to noise ratio. Higher order harmonics were rejected by detuning the monochromator by 30%. The monochromator angle was calibrated at the Fe K-edge by assigning the energy of 7112eV to the first inflection point of the K-edge absorption spectrum of Fe metal foil.

All the P-EXAFS extraction from raw data (see details in Supporting Information 2) and all the XAS data reduction was performed with the Athena/Artemis interface of IFEFFIT Software following standard procedures. The transformation from \( \chi(E) \) to \( \chi(k) \) were obtained by the conversion of the abscissa using Eq.2.
\[ k = \sqrt{\frac{2m_e}{\hbar^2} (E - E_0)} \]  

where \( k \) is the wavelength, \( m_e \) is the electron rest mass, \( \hbar \) is the reduced Planck-constant and \( E_0 \) is the edge energy. \( E_0 \) can automatically be determined by finding the first large peak of the first derivative of the \( \mu(E) \) spectrum in Athena\textsuperscript{56}, however, its value was usually underestimated leading to a shift of the spectra in the \( k \)-space. Therefore, we applied an alternative approach for our models. The EXAFS spectra of the models were quantitatively compared to measured ones. To obtain the best linear combination fit for each measured sample, their \( \chi(E) \) spectrum was transformed to several \( \chi(k) \) spectra using different \( E_0 \) around the edge energy estimated by Athena. Afterwards, linear combination fits of each measured EXAFS spectrum based on calculated ones were performed. The EXAFS quality numbers (\( Q_{\text{EXAFS}} \)) from Eq.1 were calculated as the function of \( E_0 \) (Figure S2 in Supporting Information\textsuperscript{2}). We accepted those fits for each montmorillonite type, which had the lowest \( Q_{\text{EXAFS}} \) value.

### 3. Results and Discussion

#### 3.1. EXAFS spectra

The calculated Fe K-edge EXAFS spectra for \( cv \)- and \( tv \)-model with ferric iron in the tetrahedral sheet as well as Fe\textsuperscript{2+} and Fe\textsuperscript{3+} located in the \( \text{cis} \) - and \( \text{trans} \) - occupational sites in the octahedral sheet are clearly distinct (Figure 2a)\textsuperscript{36}. The first difference between the spectra with distinct iron ionic state is a slight shift in the first oscillation at \( k \sim 4.3/4.5 \text{Å}^{-1} \). A double-bounced oscillation at \( k \sim 6.1/6.6 \text{Å}^{-1} \) was present only for structures containing ferric iron\textsuperscript{36}. Differences could also be seen in the third oscillation (\( k \sim 7.7/8.4 \text{Å}^{-1} \)) where the shoulders are located at the opposite side (left for Fe\textsuperscript{2+} and right for Fe\textsuperscript{3+})\textsuperscript{36}. The calculated spectra for the tetrahedral and the octahedral ferric iron clearly differ, as there is a \( k \sim 0.5 \text{Å}^{-1} \) shift in the entire tetrahedral ferric iron spectrum (Figure 2a,b). Iron in the \( \text{cis} \)- or \( \text{trans} \)-coordination (light and dark lines on Figure 2a) turned out to have a minor effect on the obtained spectra. The result is consistent with energy differences (Table 1).

Fourteen different EXAFS spectra representing structurally distinct Fe–Fe clusters for \( cv \)-models were calculated (Figure 2c-e). In general, the spectra of Fe\textsuperscript{2+}–Fe\textsuperscript{2+} clusters (Figure 2c) were similar to the spectrum of a single Fe\textsuperscript{2+} octahedron (individual Fe\textsuperscript{2+} or Fe\textsuperscript{2+} in the octahedral sheet with short name “cvOctFe2c” and “cvOctFe2t” in Figure 2a). Similarly, the spectra of Fe\textsuperscript{3+}–Fe\textsuperscript{3+} clusters (Figure 2e) showed similarity to the spectrum of a single Fe\textsuperscript{3+}...
octahedron (individual Fe\textsuperscript{3+} or Fe\textsuperscript{3+} in the octahedral sheet with short name “cvOctFe3c” and “cvOctFe3t” in Figure 2a). The main sign of the similarity was the matching of the first peak position (k \textasciitilde 4.3\textpm{}0.05\textAA\textsuperscript{-1} for Fe\textsuperscript{2+} and k \textasciitilde 4.5\textpm{}0.05\textAA\textsuperscript{-1} for Fe\textsuperscript{3+}, respectively).

**Figure 2.** Modelled reference EXAFS spectra of Fe-bearing 2:1 clay minerals. In panel a and b, EXAFS spectra of single iron incorporation in the octahedral\textsuperscript{26} and tetrahedral sheet are presented, respectively. Fe-Fe clusters are shown in panel c-e (Fe\textsuperscript{2+}-Fe\textsuperscript{2+} in panel c, Fe\textsuperscript{3+}-Fe\textsuperscript{3+} in panel d, Fe\textsuperscript{3+}-Fe\textsuperscript{3+} in panel e), while Mg\textsuperscript{2+}-Fe\textsuperscript{3+} clusters correspond to panel f. Blue color represents Fe\textsuperscript{2+}, while Fe\textsuperscript{3+} is marked with green color. Turquoise color in panel d represents mixed (Fe\textsuperscript{2+}-Fe\textsuperscript{3+}) oxidation state. Cis-occupational sites are marked with lighter colors, darker colors show trans-occupational sites, while mixed (cis-trans clusters) are represented with medium bright colors, respectively. cv-model correspond to solid lines, while tv-model represented by dashed lines. A more detailed explanation about the panels can be found in Table 1.

Other features of the EXAFS spectra of the corresponding ionic state (right shoulder at the second and the third oscillation for Fe\textsuperscript{2+}; double-bounced oscillation and left shoulder at the third oscillation for Fe\textsuperscript{3+}) showed very good agreement for Fe\textsubscript{cis}-Fe\textsubscript{cis} and Fe\textsubscript{trans}-Fe\textsubscript{trans} as well as Fe\textsubscript{cis}-Fe\textsubscript{cis} and Fe\textsubscript{trans}-Fe\textsubscript{trans} clustering models, respectively. Although, the shape and the k positions of the oscillations for the Fe\textsubscript{cis}-Fe\textsubscript{trans} clustering models remained similar, the second and the third oscillations altered. For the Fe\textsuperscript{2+}–Fe\textsuperscript{2+} clusters (Figure 2c), the second oscillation is lower and the right shoulder of it is more characteristic. In the case of Fe\textsuperscript{3+}–Fe\textsuperscript{3+} clusters (Figure 2e), the double-bounced oscillation is more flattened and the left shoulder of
The spectra of Fe\textsuperscript{2+}–Fe\textsuperscript{3+} (Figure 2d) did not correspond neither to individual Fe\textsuperscript{2+} (“cvOctFe2e” and “cvOctFe2t” in Figure 2a), nor to individual Fe\textsuperscript{3+} spectra (“cvOctFe3c” and “cvOctFe3t” in Figure 2a). The position of the first oscillation was at \( k \approx 4.4 \pm 0.05 \text{Å}^{-1} \), while for the second oscillation, it varied around \( k \approx 6.2 \pm 0.1 \text{Å}^{-1} \) and for the third, double-bounced oscillation the position was at \( k \approx 7.70/8.5 \text{Å}^{-1} \) (Figure 2d). At the second oscillation, a right shoulder was shown, for which intensity depended on the occupational sites of the cluster. The EXAFS spectra of the \( cv \)-model with \textit{cis-cis} and \textit{trans-trans} occupational site were similar, while differences in the intensity at the second and the third oscillation could be observed for Fe\textsubscript{\textit{trans}}\textsuperscript{2+}–Fe\textsubscript{\textit{cis}}\textsuperscript{3+} (Figure 2d). The differences can be explained by the Fe–O–Fe scattering path (Table 1), which occurs only for clusters with different Fe\textsubscript{\textit{cis}}\textsuperscript{2+}–Fe\textsubscript{\textit{trans}}\textsuperscript{3+} and Fe\textsubscript{\textit{trans}}\textsuperscript{2+}–Fe\textsubscript{\textit{cis}}\textsuperscript{3+} occupational sites (Figure 1e).

The four EXAFS spectra of the Fe\textsuperscript{3+}–Mg\textsuperscript{2+} clusters for \( cv \)-model were very similar to the single incorporated ferric iron one (Figure 2f). Only small differences in the high of the double-bounced oscillation at \( k \approx 6.30/6.65 \text{Å}^{-1} \) and of the third peak’s shoulder at \( k \approx 7.70 \text{Å}^{-1} \) could be observed for Fe\textsubscript{\textit{trans}}\textsuperscript{3+}–Mg\textsubscript{\textit{cis}}\textsuperscript{2+} and Fe\textsubscript{\textit{cis}}\textsuperscript{3+}–Mg\textsubscript{\textit{trans}}\textsuperscript{2+} but not for Fe\textsubscript{\textit{cis}}\textsuperscript{3+}–Mg\textsubscript{\textit{cis}}\textsuperscript{2+} and Fe\textsubscript{\textit{trans}}\textsuperscript{3+}–Mg\textsubscript{\textit{trans}}\textsuperscript{2+}. The differences (similarly to Fe–Fe clustering) can be explained by the Fe–O–Mg scattering path (Table S1 in Supporting Information 1), which occurs only for clusters with different (Fe\textsubscript{\textit{trans}}\textsuperscript{3+}–Mg\textsubscript{\textit{cis}}\textsuperscript{2+} and Fe\textsubscript{\textit{cis}}\textsuperscript{3+}–Mg\textsubscript{\textit{trans}}\textsuperscript{2+}) occupational sites (Figure 1i,j).

The corresponding EXAFS spectra of a single iron atom in the octahedral and tetrahedral position of the spectra of \( cv \)- and \( tv \)-models agreed well (Figure 2a,b). The second and the third oscillation of the spectra of Fe–Fe and Fe–Mg clusters in the \( tv \)-model have higher intensities than of the corresponding Fe\textsubscript{\textit{cis}}–Fe\textsubscript{\textit{cis}} and Fe\textsubscript{\textit{cis}}–Mg\textsubscript{\textit{cis}} clusters of the \( cv \)-models, respectively. The EXAFS spectra of Fe–Fe and Fe–Mg clusters in the \( tv \)-model show higher similarity to the \( cv \)-models representing Fe\textsubscript{\textit{cis}}–Fe\textsubscript{\textit{trans}}, Fe\textsubscript{\textit{trans}}–Fe\textsubscript{\textit{cis}} or Fe\textsubscript{\textit{trans}}–Mg\textsubscript{\textit{cis}}, Fe\textsubscript{\textit{cis}}–Mg\textsubscript{\textit{trans}} models as Fe–O–Fe and Fe–O–Mg scattering paths occur in the \( tv \)-models of these clusters. However, there are also differences between the \( cv \)- and \( tv \)-model. The shoulder of the second oscillation for Fe\textsuperscript{2+}–Fe\textsuperscript{2+} clusters appear at the left side of the oscillation, while the shape of the double-bound oscillation for Fe\textsuperscript{3+}–Fe\textsuperscript{3+} clusters is different. In addition, the shoulder at the second oscillation of the Fe\textsuperscript{2+}–Fe\textsuperscript{3+} cluster of the \( tv \)-model is lacking.
3.2. Distribution of iron in low Fe-content montmorillonites

The measured EXAFS spectra of the Milos– (Mil–), Wyoming– (SWy1–) and two Texas– (STx1– and STx2–) montmorillonites were found to be rather similar. However, several sample specific characteristic features can be seen at the second oscillation at \( k \approx 6.1/6.6 \, \text{Å}^{-1} \) and in the intensity of the left shoulder of the third oscillation (Figure 3). The differences imply distinct iron distribution in the bulk structure for Milos–, Wyoming– and Texas– montmorillonites, while no differences between the two Texas–samples prepared as self-supporting film and pellet (STx1– and STx2–) could be observed indicating that texture effects in STx2–sample can be excluded.

The linear combination fits to the measured spectra for Mil–, SWy1–, STx1– and STx2– montmorillonite using the theoretically calculated ones as basis were performed to obtain a quantitative estimation of the preferential oxidation state and occupational sites of iron as well as the preferred type of the clustering (single Fe tetrahedron and octahedron, Fe–Fe and Fe–Mg clusters). *Cis–cis* and *trans–trans* occupational sites in the *cv*-vacant smectite models (Figure 1d,f,h,k) were considered to be structurally equivalent to individual Fe in the octahedral sheet because the two metal (Fe–Fe or Fe–Mg) ion did not influence each other valence orbital (Table S1 in Supporting Information 1). Thus, for Fe–Fe and Fe–Mg clusters in the *cv*-model, only *cis–trans* and *trans–cis* clusters were explicitly considered (Figure 1e,i,j). In the *tv*-model, Fe–Fe and Fe–Mg substitutions were considered as near neighbor clusters.

The best EXAFS linear combination fits (Figure 3a,c,e,f) indicated that iron is present almost exclusively in the Fe\(^{3+}\) form in all montmorillonite type (“Fit1” in Table 2). This result agreed well with the assumption of earlier studies\(^{22,36}\). The differences among the samples appeared in the distribution of iron. The results of linear combination fit suggested that iron has ordered distribution in Wyoming–montmorillonite, while in Milos– and Texas–montmorillonites 6–18% of iron takes part in Fe–Fe clusters (“Fit1” in Table 2). Fe–Mg clusters could provide up to 9–12% contribution in Texas–montmorillonites. Octahedral iron is equally distributed between the occupational sites in Wyoming– and Texas–samples, *trans*-site preference occurred only in Milos–montmorillonite (“Fit1” in Table 2). The energy comparison of the *cis/trans*-models with similar isomorphic substitutions and iron oxidation states indicated that there is no site preference in bulk smectites (Table 1).
Figure 3. Experimental EXAFS spectra (dots) with the corresponding best linear combination fits (solid lines) based on the contributions shown in Table 2. In panel a, red color corresponds to Mil-montmorillonite, orange color represents SWy-montmorillonite in panel b, while pink and purple colors show STx$_1^-$ and STx$_2^-$montmorillonites in panel c and d, respectively.
### Table 2. Parameters (contributions [%] and quality [–]) of the EXAFS linear combination fit of distinct smectite models for Mil, SWy1, STx1⁻ and STx1₂⁻montmorillonite

<table>
<thead>
<tr>
<th>Smectite model name¹</th>
<th>Mil [%]</th>
<th>SWy1 [%]</th>
<th>STx1⁻ [%]</th>
<th>STx1₂⁻ [%]</th>
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<td>Fit2</td>
<td>Fit3</td>
<td>Fit4</td>
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<td>2.68 2.68 2.76 2.80</td>
<td>2.57 2.58 2.62 2.67</td>
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</table>

¹Short name of the smectite models are explained in Table 1
²Fit1” corresponds to “best fit”, while “Fit2”, “Fit3” and “Fit4” are constrained models without tetrahedral iron, Fe–Mg and Fe–Fe pairs, respectively
³The results were derived from the raw data written in the first “section” of the table
⁴Only trans-vacant (tv) and Fe cis–Fe trans, Fe cis–Fe cis, Fe trans–Mg cis and Fe cis–Mg trans from cis-vacant (cv) structures were considered as Fe–Fe and Fe–Mg clusters, respectively
⁵The spectra of this model was not included in the fit due to fatal error of FEFF run
No tetrahedral iron can be found in Milos– or in Wyoming–montmorillonite (“Fit1” in Table 2), furthermore, in STx1₁⁻ and STx1₂⁻montmorillonite samples, the very low amount ~1–2% of tetrahedral iron is below the estimated absolute uncertainty (±15%)³⁷ for the linear combination fit (“Fit1” in Table 2). The results suggested that tetrahedral iron is negligible. To estimate the importance of tetrahedral iron for the fit quality, another fit (“Fit2”) with only octahedral iron substitution models was performed for the measured EXAFS data sets. The results indicate that the exclusion of the tetrahedral iron has negligible effect on the fits of Milos– and Wyoming–montmorillonites as their “Fit2” EXAFS spectra (Figure 3a-d) and the corresponding fitting parameters (contribution and quality number) were identical (Table 2) to the previous best fits (“Fit1”). Similar conclusion could be made for Texas–montmorillonite samples as tetrahedral iron models barely influence the shape of the EXAFS spectra (little increment in the left shoulder of the second oscillation) while the quality numbers agree with the best fit results within the uncertainty. The contribution of Fe–Fe and Fe–Mg clustering models in “Fit2” is increased, while small reduction of the individual Fe in the octahedral sheet is observed. Sensitivity analysis for Fe–Fe and Fe–Mg clustering were determined performing “Fit3” and “Fit4” without Fe–Fe and Fe–Mg pairs, respectively. The quality number of the fits show that the exclusion of Fe–Fe or Fe–Mg pairs from the fitting data set of reference spectra reduces the quality of the fit. In such a constraint fit, the contribution of the excluded clusters are redistributed among the remaining components of the fit. The omission of Fe–Fe pairs has larger effect on Milos– and Texas–samples, while the omission of Fe–Mg pairs shows more significant impact for the Wyoming-sample.

Conventional (“shell-by-shell”) P-EXAFS fits were also performed on the Mil–, SWy1– and STx1₁⁻samples (Supporting Information 2). The results revealed that quite a few constrains obtained from ab initio calculations (e.g. coordination number of Al, Fe and first O shell, co-varying $CN_{Fe-O/Al/Fe/Si}(\alpha)$ and $\alpha$ through a polarization parameter are necessary to reduce the number of independent fitting parameters (Supporting Information 2)⁵⁷,⁵⁸. The conventional P-EXAFS fitting results (Table S1 in Supporting Information 2) agree well with the interatomic distances and coordination numbers of relax structures containing Fe³⁺ (Table S1 in Supporting Information 1). However, the differences present in the P-EXAFS spectra of the three montmorillonite cannot be explained by using the “shell-by-shell” fit approach alone. The XANES spectra of the different smectite models were also calculated and compared to the measured Milos–, Wyoming– and Texas–montmorillonites (Supporting Information 2). The results show that tetrahedral iron models have very different XANES spectra compared to the
four measured spectra (Figure S3, S4 in Supporting Information 2). The measurement results agree well with the calculated XANES spectra containing only octahedral ferric iron (Figure S3, S4 in Supporting Information 2). However, XANES spectra turned out to be very similar for all (Figure S3 in Supporting Information 2).

4. Implication of the structural position of Fe in bulk montmorillonite

This study reveals structural differences in Fe-bearing Milos–, Wyoming– and Texas–montmorillonites. The very distinct EXAFS and XANES spectra of tetrahedral iron indicate that there is no significant amount of tetrahedral iron in low Fe-bearing smectites. Potential presence of tetrahedral iron suggested in earlier studies cannot be confirmed on the basis of studied data.

The proportion of Fe–Fe and Fe–Mg clustering in different montmorillonite samples needs separate discussion. Depending on the total number of Fe and Mg substitutions in the sample, there is a finite probability of clusters to form in case of random (e.g. no energetically preferred interaction) distribution of Mg and Fe sites. The positive or negative deviation of EXAFS fitting results from the expectation value for a random distribution of sites will indicate an energy driven preferential cluster formation or avoidance, respectively. The probability of randomly formed cluster was evaluated by Monte Carlo simulation for the given composition of in SWy1–, STx1– and Mil–montmorillonite (Supporting Information 1). Number of Fe–Mg and Fe–Fe clusters estimated for STx1–montmorillonite from the EXAFS fit is significantly larger than the expected value for a random distribution. This result is consistent with data reported by Vantelon et al. and the estimation of lattice energy for cluster formation (Table S2 in Supporting Information 1). For the Mil– and SWy1–montmorillonite, the number of clusters predicted by EXAFS is comparable with the random distribution. Taking into account the modelling uncertainties and intrinsically low amount of Fe and Mg substitutions, no definitive statement about possible slight clustering or avoidance of Fe–Fe and Fe–Mg pair can be made for Mil– and SWy1–montmorillonite based on the fitting results.

The differences in the iron distribution explain the varying Fe uptake behavior of these montmorillonites. Due to the electrostatic repulsion, ferric iron present in Fe$^{3+}$–Mg$^{2+}$ clusters is a less efficient electron acceptor in the redox reaction than in Fe$^{3+}$–Fe$^{3+}$ clusters or individual Fe$^{3+}$ in the octahedral sheet. Fe$^{3+}$–Mg$^{2+}$ clusters could be present in Texas–samples but not in Wyoming–montmorillonite. This would explain the higher redox capacity of SWy1–
montmorillonite derived from a wet chemistry and XAS spectroscopy measurement\textsuperscript{16}. There
might be certain electron small polaron hopping conduction pathways, which assist the
oxidative sorption of iron \(\text{Fe}^{2+}_{\text{aq}} \rightarrow \text{Fe}^{3+}_{\text{surf}}\). Therefore, in addition to the surface specifications
(e.g. surface site, protonation scheme, inner-/outer-sphere complex), the effect of cation
substitution in the bulk structure should also be studied.

Our investigations had to deal with the challenge of XAS measurements of low iron amount.
Although the linear combination fit of the calculated spectra showed very good agreement with
Milos–montmorillonite sample, the fit had lower quality for Wyoming– and Texas–
montmorillonites. Potential explanation could be the presence of \(\text{Al}^{3+}\) substitution in the
tetrahedral sheet, which were not considered in this study but have an impact on the bulk
structure.

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Supporting Information

Supporting Information 1: Details on theoretical studies
Supporting Information 2: Details on P-EXAFS data analysis and XANES calculations

References


Wehrli, B.; Bradbury, M. H. Fe(II) Sorption on a Synthetic Montmorillonite. A
6978–6986.
511 (36) Kéri, A.; Dähn, R.; Krack, M.; Churakov, S. V. Combined XAFS Spectroscopy and *Ab 
Initio* Study on the Characterization of Iron Incorporation by Montmorillonite. *Environ. 
514 (37) Churakov, S. V.; Daehn, R. Zinc Adsorption on Clays Inferred from Atomistic 
516 (38) Churakov, S. V. *Ab Initio* Study of Sorption on Pyrophyllite: Structure and Acidity of 
518 (39) Sainz-Díaz, C. I.; Palin, E. J.; Hernández-Laguna, A.; Dove, M. T. Octahedral Cation 
Ordering of Illite and Smectite. Theoretical Exchange Potential Determination and 
521 (40) Sainz-Díaz, C. I.; Timón, V.; Botella, V.; Artacho, E.; Hernández-Laguna, A. Quantum 
Mechanical Calculations of Dioctahedral 2:1 Phyllosilicates: Effect of Octahedral Cation 
525 (42) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. 
QUICKSTEP: Fast and Accurate Density Functional Calculations Using a Mixed 
530 (44) Krack, M. Pseudopotentials for H to Kr Optimized for Gradient-Corrected Exchange-
532 (45) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular 


