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Evaluation of Redox-Active Iron Sites in Smectites Using Middle and Near Infrared Spectroscopy

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Abstract

Redox processes of structural Fe in clay minerals play an important role in biogeochemical cycles and for the dynamics of contaminant transformation in soils and aquifers. Reactions of Fe(II)/Fe(III) in clay minerals depend on a variety of mineralogical and environmental factors, which make the assessment of Fe redox reactivity challenging. Here, we use middle and near infrared (IR) spectroscopy to identify reactive structural Fe(II) arrangements in four smectites that differ in total Fe content, octahedral cationic composition, location of the negative excess charge, and configuration of octahedral hydroxyl groups. Additionally, we investigated the mineral properties responsible for the reversibility of structural alterations during Fe reduction and re-oxidation. For Wyoming montmorillonite (SWy-2), a smectite of low structural Fe content (2.8 wt%), we identified octahedral AlFe(II)–OH as the only reactive Fe(II) species, while high structural Fe content (>12 wt%) was prerequisite for the formation of multiple Fe(II)-entities (dioctahedral AlFe(II)–OH, MgFe(II)–OH, Fe(II)Fe(II)–OH, and trioctahedral Fe(II)Fe(II)Fe(II)–OH) in iron-rich smectites Ölberg montmorillonite, and ferruginous smectite (SWa-1), as well as in synthetic nontronite. Depending on the overall cationic composition and the location of excess charge, different reactive Fe(II) species formed during Fe reduction in iron-rich smectites, including tetrahedral Fe(II) groups in synthetic nontronite. Trioctahedral Fe(II) domains were found in tetrahedrally charged ferruginous smectite and synthetic nontronite in their reduced state while these Fe(II) entities were absent in Ölberg montmorillonite, which exhibits an octahedral layer charge. Fe(III) reduction in iron-rich smectites was accompanied by intense dehydroxylation and structural rearrangements, which were only partially reversible through re-oxidation. Re-oxidation of Wyoming montmorillonite, in contrast, restored the original mineral structure. Fe(II) oxidation experiments with nitroaromatic compounds as reactive probes were used to link our spectroscopic evidence to the apparent reactivity of structural Fe(II) in a generalized kinetic model, which takes into account the presence of Fe(II) entities of distinctly different reactivity as well as the dynamics of Fe(II) re-arrangements.

1 Introduction

The Fe(II)/Fe(III) redox couple plays an essential role as electron acceptor and donor in biogeochemical cycles and is of great relevance for remediating soil and water contaminants (Christensen et al., 2001; Ernstsens, 1996; Kenneke and Weber, 2003; Rugge et al., 1998) as well as maintaining the integrity of backfill materials in waste repositories (Anastacio et al., 2008). In contrast to the detailed understanding of electron transfer processes at the Fe oxide-water interface (Williams and Scherer, 2004; Larese-Casanova and Scherer, 2007; Yanina and Rosso, 2008), much less is known about the factors determining the redox activity of Fe in clay minerals. Structural Fe in smectites is accessible to microorganisms for (dissimilatory) Fe(III) reduction (Kostka et al., 2002) and the resulting Fe(II) bound within the mineral lattice is also a viable reductant of organic compounds and metals (Hofstetter et al., 2006, 2003; Lee and Batchelor, 2003; Ilton et al., 2004; Peretyazhko et al., 2008). Because the reduction of clay mineral bound Fe(III) is not subject to reductive dissolution to the same extent as Fe oxides (Kostka et al., 1999a; Weber et al., 2006), Fe in clay minerals has been proposed to act as renewable source of redox equivalents in soils and sediments (Ernstsens et al., 1998). However, redox reactions of Fe(II)/(III) in clay minerals depend on a variety of mineralogical and environmental factors that make an assessment of Fe redox reactivity very challenging.

Various spectroscopic studies have elaborated on the consequences of Fe reduction and re-oxidation for the structural environment of Fe within the octahedral sheet of iron-rich clay minerals and proposed reaction mechanisms (Drits and Manceau, 2000; Hunter and Bertsch, 1994; Hunter et al., 1999; Komadel et al., 1990, 2006; Lear and Stucki, 1987; Manceau et al., 2000b). On the basis of insights gained from infrared (IR), UV-visible, and X-ray absorption spectroscopy it was proposed that different Fe(II)/Fe(III) clusters form in the octahedral sheet upon changes of Fe redox state. Investigation of absorption bands for Fe(II)-Fe(III) intervalence electron transfer led to the conclusion that Fe(III) is reduced in a way that Fe ions must occupy adjacent octahedral sites and must be of different valence (Hunter and Bertsch, 1994; Komadel et al., 1990). Fe(II)-O-Fe(II) entities were postulated to form as soon as

all Fe(III)-O-Fe(III) groups are partly reduced to Fe(II)-O-Fe(III). The reduction process is accompanied by the uptake of protons and cations from solution as well as by the migration of Fe(II) ions within the octahedral sheet yielding trioctahedral Fe(II) clusters which are separated by domains of vacancies. This mechanism of Fe(III) reduction was proposed only for *trans*-vacant smectites, i.e., for smectites exhibiting octahedral hydroxyl groups on opposite sides with respect to the octahedral vacancy (Figure 1b). In contrast, *cis*-vacant smectites, i.e., smectite with octahedral hydroxyl groups on the same side of the vacancy (Figure 1a), did not tend to form trioctahedral domains due to higher activation energy for the involved structural rearrangements (Drits and Manceau, 2000). This hypothesis was supported by IR-spectroscopic studies which report trioctahedral domains in reduced iron-rich smectites whereas neither Fe(II)-Fe(III) nor Fe(II)-Fe(II) entities could be identified (Fialips et al., 2002a,b).

The extent to which Fe in clay minerals participates in redox reactions and the kinetics of Fe oxidation and reduction are, in contrast, not well understood. While microbes can reduce a large share of the structural Fe in phyllosilicates (Kostka et al., 1999b), most studies concerned with Fe redox reactivity addressed Fe(II) oxidation and concomitant reduction of contaminants, that is nitroaromatic compounds (Hofstetter et al., 2003, 2006; Neumann et al., 2008), polychlorinated ethanes (Neumann et al., 2009), uranium (Ilton et al., 2004), technetium (Peretyazhko et al., 2008). Few general trends describing Fe reactivity have been established to date, for example, that rates of contaminant reduction were almost pH independent over a narrow, ambient range (pH 6.5–8). Quantitative models for the reduction kinetics of organic compounds revealed the presence of two distinct and interconvertable Fe(II) sites, which exhibit high and low reactivity, in iron-rich smectites (total Fe content of 12–13 wt%) (Neumann et al., 2008). If, in contrast, the total Fe content was low (3 wt%), pseudo-first order kinetics of contaminant reduction pointed towards the presence of one type of reactive Fe(II) of even lower reactivity. Structure reactivity relationship of different organic probe compounds further showed that, within a compound class, the mechanisms of structural Fe(II) oxidation is identical, regardless of the structural Fe content of the smectite.

While such kinetic models enable a good quantitative description of structural Fe(II)

93 reactivity, the model outcome provide no information on the mineralogical nature of the
94 different reactive Fe(II) sites. Conversely, it remains unclear which of the spectroscopically
95 identified structural Fe(II) entities are responsible for the distinct Fe(II) reactivities observed
96 during organic compound reduction and how they can be identified in reduced iron-rich
97 smectites. Finally, it is also unclear if specific reactive Fe sites persist for more than one
98 reduction/re-oxidation cycle because Fe redox reactions may irreversibly change part of the
99 smectite's structure (Fialips et al., 2002a,b; Komadel et al., 1995).

100 The goals of this study were (1) to identify the different structural Fe(II) species in
101 reduced smectites that were responsible for the reductive transformation of organic com-
102 pounds and (2) to assess the factors that influence the extent of reversibility of structural
103 alterations during changes in Fe redox state. To this end, we analyzed IR spectra of four
104 smectites, which differ with regard to total iron content, the configuration of octahedral hy-
105 droxyl groups (*trans-* vs. *cis*-vacant), and the location of the negative excess charge (i.e.,
106 Wyoming montmorillonite (SWy-2), ferruginous smectite (SWa-1), Ölberg montmorillonite,
107 and a synthetic nontronite). Wyoming montmorillonite (SWy-2) represents an example of
108 a predominantly octahedrally charged, *cis*-vacant smectite of moderate total iron content
109 (2.8 wt%), exhibiting isolated octahedral Fe cations (Vantelon, 2001; Vantelon et al., 2003).
110 Synthetic nontronite contains only Fe(III) as octahedral cation as well as some tetrahe-
111 dral substitution with Fe(III) and was used as the opposite end-member of a tetrahedrally
112 charged, iron-rich *trans*-vacant smectite (total iron content of 33.5 wt%). The main fac-
113 tor governing the formation of *cis*- and *trans*-vacant layers is the structural iron content
114 with iron-rich smectites (Fe content >0.6/unit cell) being predominantly *trans*-vacant while
115 those smectites containing lower amounts of iron (Fe content <0.6/unit cell) are *cis*-vacant
116 (Drits et al., 2006; Wolters et al., 2009). Thus, iron-rich ferruginous smectite (SWa-1) and
117 Ölberg montmorillonite (for unit cell composition see Table 1), which contain approximately
118 the same amount of total iron ranging in between the end-members (12-13 wt%), exhibit
119 both a *trans*-vacant configuration. They differ in the location of the negative excess charge
120 as ferruginous smectite is tetrahedrally charged while Ölberg montmorillonite contains a
121 predominantly octahedral excess charge.

Each smectite was studied as unaltered, non-reduced mineral, in its reduced state following chemical Fe(III)-reduction by dithionite as well as in a (partially) re-oxidized form, for which either air (20% oxygen), pure oxygen, or a nitroaromatic compound was used as oxidant. From the disappearance and re-appearance of characteristic IR absorption bands with changes in Fe redox state, the (ir)reversibility of structural changes in the smectites was inferred. The assignment of specific absorption bands to distinct Fe(II) and Fe(III) entities enabled the identification of potentially reactive structural Fe(II) arrangements. Finally, we discuss how information concerning spectroscopically identified Fe(II) species can be linked to the observable, *apparent reactivity* of structural Fe(II). To this end, we evaluated Fe(II) oxidation indirectly through analyses of reduction kinetics of sample oxidants (nitroaromatic compounds), which were used as probes for Fe(II) reactivity. Variable rates of oxidant disappearance and the reduction equivalents consumed were compared to the dynamics of IR-band appearance and disappearance during structural Fe oxidation and reduction. On the basis of this information, we propose predominantly reactive Fe(II) arrangements in the four clay minerals (synthetic nontronite, Wyoming montmorillonite, ferruginous smectite, and Ölberg montmorillonite).

1.1 Theoretical Background

To facilitate the unambiguous assignment of absorption bands to specific iron-containing entities, we studied five characteristic IR regions in the middle (MIR) and near infrared (NIR) region. The redox state and the structural environment of octahedral iron can be derived directly from the absorption bands of hydroxyl groups attached to two adjacent octahedral cations (denoted as MM–OH, M for metal).

Only those cation pairs sharing hydroxyl groups are observable with the IR technique (Figure 1). Bands corresponding to MM–OH bending vibrations (δ) are found between 720 and 950 cm^{-1} (region 'a' in Figure 2) and MM–OH stretching vibrations (ν) between 3500 and 3600 cm^{-1} (region 'b' in Figure 2 (Farmer and Russell, 1964; Farmer, 1974)). In the NIR region, the combination of MM–OH bending and stretching modes ($\delta+\nu$) appears at

149 4200–4600 cm^{-1} (region 'c' in Figure 2) and allows for a verification of the assignments in the
150 MIR region because the sum of the band positions of the MM–OH bending and stretching
151 equals the observed MM–OH combination band position (Petit et al., 1999; Post and Noble,
152 1993). Hydroxyl groups attached to three adjacent cations, i.e., trioctahedral domains, are
153 denoted as MMM–OH and also exhibit bending and stretching vibrations in the MIR region,
154 which give absorption bands between 600 and 700 cm^{-1} (bending, region 'd' in Figure 2)
155 and from 3600 to 3700 cm^{-1} (stretching, region 'b' in Figure 2 (Farmer and Russell, 1964)).
156 Additional though indirect information comes from the absorption bands of tetrahedral SiO
157 groups, which are linked to octahedral cations via the apical octahedral oxygen atom (O_{ap}).
158 So-called lattice deformation bands, which can be described by either M– O_{ap} stretching or
159 O_{ap} –Si bending vibrations (Farmer and Russell, 1964), are observed between 400 and 600
160 cm^{-1} (region 'd' in Figure 2). Stretching vibrations of the Si–O bonds correspond to bands
161 found between 900 and 1200 cm^{-1} (region 'e' in Figure 2).

162 2 Materials and Methods

163 2.1 Clay mineral reduction and re-oxidation

164 A complete list of chemicals used in this study can be found in the electronic annex (EA).
165 Ferruginous smectite (SWa-1) and Wyoming montmorillonite (SWy-2) were obtained from
166 the Source Clays Repository (Columbia, Missouri), fractioned to $< 2 \mu\text{m}$, and freeze-dried
167 prior to use. Ölberg montmorillonite (iron-rich montmorillonite from Ölberg (Petit et al.,
168 2002), $< 2 \mu\text{m}$ fraction) and synthetic nontronite (Decarreau et al., 2008) were used as
169 obtained.

170 Suspensions of reduced clay mineral were prepared under anoxic conditions according to a
171 modified citrate-bicarbonate-dithionite method (Stucki et al., 1984b). Suspensions contained
172 1.25 g of clay mineral and 66 mL of citrate-bicarbonate buffer (ratio 1:8 of 0.3 M citrate and
173 1 M bicarbonate solution) and were diluted with water to 250 mL. To ensure that the clay
174 mineral was finely suspended, the suspension was stirred overnight and then heated to 70

175 °C. Sodium dithionite salt (3.75 g), corresponding to three times the mass of clay mineral,
176 was added for maximal iron reduction and the reaction was stopped after 4 hours by filtra-
177 tion. Different Fe(II)/total Fe ratios were obtained by adding different amounts of sodium
178 dithionite to the suspension. All suspensions were homoionized by threefold ultrafiltration
179 with 1 M NaCl (76 mm ultrafiltration cell, 0.2 μ m Express plus membrane filters, Milli-
180 pore AG; Volketswil, Switzerland) and subsequently washed by ultrafiltration with deionized
181 water outside the glovebox under a N₂ pressure of 2 to 4 bar. Aliquots of reduced stock
182 suspensions were dried in the air lock of the anaerobic chamber overnight, and pulverized for
183 IR measurements.

184 For re-oxidation experiments with air (oxygen, 20%), pure oxygen (100%), or 4-acetyl-
185 nitrobenzene (4-AcNB), stock suspensions were diluted to yield between 2.5 and 8 g L⁻¹ of
186 reduced mineral (for details see Table 1) using anoxic solutions of 10 mM NaCl or MOPS
187 (morpholinopropanesulfonic acid) buffered at pH 7.5 $\pm$ 0.1. Reactors contained 20 mL smec-
188 tite suspension each and were kept in the dark on a roller apparatus at 25 $\pm$ 1 °C during
189 the experiments with 4-AcNB. Re-oxidation was achieved by bubbling the suspension with
190 pressed air or oxygen at 70 °C for 10 minutes to 20 hours. Then the gas was changed to ar-
191 gon and bubbling was continued for at least two hours before centrifugation and transferring
192 the reactors back into the anaerobic chamber. Experiments with 4-AcNB were initiated by
193 adding 20 to 250 μ L methanolic 4-AcNB stock solution resulting in initial 4-AcNB concen-
194 trations of 20 to 800 μ M. To terminate the experiment, suspensions were centrifuged at 4100
195 rpm for 15 min at 10 °C after addition of 1 M NaCl. Aqueous samples were withdrawn from
196 the supernatant and stored at 4 °C until HPLC analysis. The remaining clay pastes were
197 washed twice with deionized water, dried in the air lock overnight, and pulverized for IR
198 measurements. An overview of all experiments, the different clay minerals, and the applied
199 oxidants is given in Table 1.

200 For kinetic experiments with nitroaromatic compounds (NACs), homoionized synthetic
201 nontronite stock suspension was diluted to yield 0.5 g L⁻¹ of reduced mineral using anoxic
202 solution of 10 mM MOPS (morpholinopropanesulfonic acid) buffered at pH 7.5 $\pm$ 0.1. Reactors
203 contained 20 mL smectite suspension each and were kept in the dark on a roller apparatus

204 at 25 ± 1 °C during the experiments. All experiments were performed in duplicates. Kinetic
205 experiments were initiated by adding methanolic NAC stock solution to the anoxic reactors
206 resulting in initial NAC concentration of 50 μ M (methanol content $< 0.5\%$ v/v). In all
207 experiments samples were withdrawn at given time intervals, immediately filtered to stop
208 the reaction, and stored at 4 °C until HPLC analysis.

209 **2.2 Analytical procedures**

210 All samples containing NACs and reduction products (anilines) were analyzed by HPLC using
211 a reversed phase LC-18 column with eluents consisting of MeOH/H₂O or MeOH/H₂PO₄-
212 buffer mixtures and UV/vis detection. The measured 4-acetylaniline (4-AcAn) concentration
213 was used to calculate the Fe(II)/total Fe ratio after re-oxidation for the experiments with
214 4-AcNB. To this end, the number of Fe(II) equivalents needed for reduction of 4-AcNB to 4-
215 AcAn (i.e., 6) as well as the initial Fe(II) and total Fe concentrations were taken into account.
216 For all other experiments, total Fe and Fe(II) contents were measured directly according
217 to a modified 1,10-phenanthroline method (Amonette and Templeton, 1998; Stucki, 1981).
218 Briefly, a solution containing HF, H₂SO₄, and 1,10-phenanthroline (in the volumetric ratio of
219 1:12:2) was used to digest samples of the clay mineral suspensions. The reaction proceeded in
220 amber bottles at room temperature for one hour and was stopped by adding 10 mL B(OH)₃.
221 The resulting solutions were diluted with 50 mL deionized water. Aliquotes of 1 mL were
222 reacted in amber bottles overnight with either 10 mL citrate solution or 10 mL hydroxyl
223 ammonium solution for the subsequent colorimetric analysis for Fe(II) or total Fe content,
224 respectively.

225 Measurements in the mid-infrared (MIR) region were carried out on a Perkin Elmer
226 Spectrum One FTIR spectrometer using a custom-made attenuated total reflection (ATR)
227 unit equipped with a ZnSe crystal (7 reflections), which ensured strictly anaerobic conditions
228 during spectra acquisition. KBr pellets were prepared from a mixture of 150 mg of dry KBr
229 and 1.5 mg of dried smectite and analyzed on a Nicolet 510-FTIR spectrometer. Spectra
230 in the 250 to 800 cm^{-1} region were obtained immediately after pressing the pellet, whereas

spectra displaying the OH-stretching bands (3500 to 3800 cm^{-1}) were acquired after drying the pellet for 2 days at $110\text{ }^{\circ}\text{C}$ to evaporate smectite-bound water. In the near infrared (NIR) region, samples were analyzed using a Nicolet Magna 750 FTIR spectrometer with a diffuse reflectance (DRIFT) accessory 'Collector' from Spectra-Tech. All spectra represent the average of 64 scans at a resolution of 2 cm^{-1} (MIR) or 4 cm^{-1} (NIR). NIR spectra are displayed as obtained and MIR spectra were normalized to the Si-O stretching band. A validation of the structural stability of the dried samples over time and the comparability of the structural changes induced by reaction with oxygen or nitroaromatic compounds was carried out by means of IR spectroscopy and is given in the electronic annex (EA).

3 Results and Discussion

3.1 IR spectroscopic identification of reactive Fe(II) species and investigation of the reversibility of structural changes

To characterize the structural environment of redox-active Fe(II) within the smectite's lattice, the infrared (IR) absorption bands of hydroxyl groups linked to the octahedral cations were analyzed for specific structural arrangements of these cations (Fe(II), Fe(III), Al, Mg). Absorption bands were assigned to specific structural entities for each smectite by correlating observations in the hydroxyl bending and stretching region (regions 'a' and 'b' in Figure 2) with the corresponding combination bands (region 'c' in Figure 2). The use of the end-members Wyoming montmorillonite and synthetic nontronite as references further facilitated the assignment of observed bands to structural arrangements in the structurally more complex smectites Ölberg montmorillonite and ferruginous smectite. Additionally, samples with different Fe(II)/total Fe ratios were studied to determine the sequence of Fe(II) species oxidation and thus their reactivity as well as to assess the reversibility of the structural changes in each smectite during Fe reduction and re-oxidation. To this end, IR spectra were compared in the MM-OH bending region showing characteristic absorption bands for specific Fe containing entities and in the Si-O stretching region, which is diagnostic for changes affecting

the smectite's lattice. Reversibility was implied if absorption bands present in the original spectrum of unaltered sample changed in intensity and/or position upon Fe reduction and were restored at the same position after re-oxidation. For each smectite, all absorption band positions as well as the assigned cationic entities are summarized in Table 2.

3.1.1 Wyoming montmorillonite

Wyoming montmorillonite was studied in the unaltered (A), reduced (C), and re-oxidized (B) state (0, 75, and 40% Fe(II)/total Fe, respectively) and the corresponding IR spectra are shown in Figure 3. Spectra of individual samples are denoted in capital letters while subfigures are enumerated with small letters. In the MM-OH bending region (Figure 3a), the spectrum of the unaltered sample exhibits three sharp peaks at 917, 884, and 846 cm^{-1} . The intensity of the absorption band at 884 cm^{-1} decreased with higher structural Fe(II) content (spectra B, C) whereas the other two bands remained largely unchanged. Thus, only the band at 884 cm^{-1} is associated with iron. In agreement with the low iron and high aluminum content (Table 1) as well as with the assignments in previous IR spectroscopic studies of Wyoming montmorillonite (Gates, 2005; Vantelon, 2001), we therefore assigned the observed bands to AlAl-OH (917 cm^{-1}), AlFe(III)-OH (884 cm^{-1}), and AlMg-OH (846 cm^{-1}) entities. The peaks at 775 and 798 cm^{-1} (marked with an asterisk) are most likely due to quartz (Madejova and Komadel, 2001; Vantelon, 2001) and, therefore, small contributions due to Fe(III)Mg-OH groups previously proposed to be present in SWy-2 at 799 cm^{-1} (Gates, 2005) could not be observed.

A schematic representation of possible octahedral cation arrangements in unaltered Wyoming montmorillonite, which will be used throughout this study for comparison of results among different minerals and their oxidation states, is shown in Figure 4a. Wyoming montmorillonite is a *cis*-vacant smectite, i.e., two hydroxyl groups are on the same side of the vacancies (blank octahedra). The structure given in Figure 4a is representative of the cationic composition according to the structural formula (Table 1) with a ratio of Al:Mg:Fe of approximately 7:1:1. The representation takes into account that only those cation configurations sharing hydroxyl groups (depicted as filled circles) are observed as MM-OH entities in the

IR spectrum. Because only bending vibrations of hydroxyl groups linked to AlAl, AlFe(III), and AlMg entities were observed with IR spectroscopy, presumably only these entities share hydroxyl groups and are depicted in Figure 4a. In contrast, MgFe(III)–OH groups were not present or only in small amounts and are thus depicted without structural hydroxyl groups as suggested previously (Vantelon et al., 2003).

The complete disappearance of the AlFe(III)–OH band (884 cm^{-1}) at a Fe(II)/total Fe ratio of 75% (Figure 3a, C) in combination with the reappearance of the band at the same position with re-oxidation (B, 40% Fe(II)/total Fe) suggests that iron remained in the smectite lattice during reduction and was re-hydroxylated in a similar fashion as the unaltered sample upon re-oxidation. The increased width of the AlFe(III)–OH band in the re-oxidized sample (B) suggests that the OH-environment is distorted at a Fe(II)/total Fe ratio of 40% compared to the Fe(II)-free sample (A). In the IR spectrum of the reduced sample (C) we could not observe any additional absorption band, which would correspond to AlFe(II)–OH. The absence of a new band leaves room for speculation if the disappearance of the AlFe(III)–OH band was due to dehydroxylation to an IR-inactive AlFe(II) group or caused by a perturbation of the smectite structure leading to IR-inactive AlFe(II)–OH entities, or a combination of the two mechanisms. Because dehydroxylation of *cis*-vacant layers in low Fe(III)-containing Wyoming montmorillonite requires a high activation energy (Drits and Manceau, 2000), concomitant Fe(II) migration is probably limited and this mechanism seems unlikely. The comparably large shift of 10 cm^{-1} to lower wavenumbers observed for the Si–O stretching band (Figure 3e) and the narrowing of the MM–OH combination band (Figure 3c) with reduction rather support the hypothesis of structural perturbation. Although the intensity of the AlFe(III)–OH bending band (884 cm^{-1}) decreased during reduction (Figure 3a, C), the combination band (Figure 3c) seems to have lost intensity not only on the AlFe–OH side (lower wavenumbers) but also on the AlAl–OH side (higher wavenumbers, (Gates, 2005; Petit et al., 1999; Post and Noble, 1993)). These two observations indicate structural perturbation of the smectite’s lattice due to the reduction of iron-containing entities.

The combined IR spectroscopic evidence suggests that Fe(II) exists in only one structural environment in reduced Wyoming montmorillonite, i.e., as AlFe(II), which is re-oxidized in

the redox reaction with oxygen and NACs. Because the presence of Fe(III)Mg–OH groups as previously proposed for SWy-2 (Gates, 2005) could neither be confirmed nor discarded, small contributions by Fe(II)Mg groups cannot be ruled out. These groups are, however, IR-unobservable as no additional band was present in reduced SWy-2 and they contain Fe(II) as isolated cations in a similar structural environment as AlFe(II) groups. In the schematic representation of possible octahedral cation arrangements in reduced Wyoming montmorillonite (Figure 4b), the change in iron redox state (red for Fe(III); blue for Fe(II)) does not affect the overall octahedral cation arrangement.

Despite the small amount of Fe (2.8 wt%, Table 1) in the structure of Wyoming montmorillonite, Fe reduction affected the overall silicate structure, as became evident from the concomitant large shift of the Si–O stretching band (Figure 3e) and the complete disappearance of the AlFe(III)–OH bending band. After partial re-oxidation (B, 40% Fe(II)/total Fe) this bending band re-appeared at the same position and the silicate structure relaxed towards the initial state of the Si–O stretching modes. These observations suggest that structural changes during Fe reduction of Wyoming montmorillonite are reversible. However, complete re-oxidation was not achieved within one day of oxidation with pure oxygen at 70 °C, presumably due to the slow Fe(II) re-oxidation kinetics.

3.1.2 Synthetic nontronite

The IR spectrum of non-reduced synthetic nontronite (A, 0% Fe(II)/total Fe) exhibits two distinct peaks at 714 cm⁻¹ and 812 cm⁻¹ as well as a shoulder at 860 cm⁻¹ in the MM–OH bending region (Figure 5a). The absorption bands at 812 cm⁻¹ and 714 cm⁻¹ are characteristic for Fe(III) in the octahedral and tetrahedral sheet (Fe(III)Fe(III)–OH and Fe(III)^{IV}–O entities), respectively. This assignment is in agreement with the structural formula (Table 1), which denotes exclusively iron as octahedral cation and indicates some tetrahedral Fe(III) substitution (Decarreau et al., 2008). In addition, an indicative trend between the intensity of the band at 714 cm⁻¹ and the tetrahedral Fe content was recently observed (Andrieux and Petit, 2010), confirming the assignment of this band to tetrahedral Fe(III). The absorption band at 860 cm⁻¹ is typical for well-crystallized nontronites exhibiting a high level of octa-

hedral Fe(III) (Decarreau et al., 2008) and is therefore not assigned to a specific MM–OH entity. A schematic representation of the octahedral sheet configuration in unaltered nontronite is given in Figure 6a. All octahedral cation arrangements consist of Fe(III)Fe(III) entities and the hydroxyl groups (filled circles) are on opposite sides of the vacancy (blank octahedra), as is characteristic of *trans*-vacant smectites.

In the IR spectrum of reduced synthetic nontronite with a Fe(II)/total Fe ratio of 97% (F in Figure 5a) the absorption bands of the octahedral Fe(III)Fe(III)–OH and tetrahedral Fe(III) entities disappeared, indicating that both, octahedral and tetrahedral Fe(III)-entities were reduced. In the OH-bending region, two new bands were observed at 843 cm^{−1} (Figure 5a, low intensity) and at 646 cm^{−1} (Figure 5d). The latter is indicative of trioctahedral Fe(II)Fe(II)Fe(II)–OH arrangements (Fialips et al., 2002b; Manceau et al., 2000a; Wilkins and Ito, 1967), which is corroborated by the appearance of an additional stretching band at 3612 cm^{−1} in the spectrum of reduced synthetic nontronite (Figure 5b). Combining the wavenumbers of the bending (646 cm^{−1}) and stretching (3612 cm^{−1}) band yields an expected position for the Fe(II)Fe(II)Fe(II)–OH combination band of 4258 cm^{−1} (Petit et al., 1999; Post and Noble, 1993). In Figure 5c (for enlargement see Figure EA2b in EA), the spectrum of reduced synthetic nontronite (F) in the combination region shows a new band of low intensity at 4256 cm^{−1}, which further substantiates the identification of trioctahedral Fe(II) arrangements.

The assignment of the absorption band at 843 cm^{−1} is less certain. Owing to the large extent of Fe reduction (97% Fe(II)/total Fe, Table 1) and the absence of other octahedral components than Fe, this band is linked to Fe(II) and we suggest to tentatively assign this band to a Fe(II)Fe(II)–OH configuration. With the same reasoning the main OH stretching envelope observed at 3554 cm^{−1} (Figure 5b) occurs at a lower wavenumber compared to the unaltered sample (A), indicating that this band corresponds to dioctahedral entities. Owing to the large extent of Fe reduction (97% Fe(II)/total Fe, Table 1) and the strong intensity of the absorption band at 3554 cm^{−1}, this band is due to Fe(II)-containing entities, most likely Fe(II)Fe(II)–OH groups. Combining the positions of the Fe(II)Fe(II)–OH bending (843 cm^{−1}) and stretching (3554 cm^{−1}) band yields an estimated Fe(II)Fe(II)–OH combination band

position of 4397 cm^{-1} (Petit et al., 1999; Post and Noble, 1993). In the combination band region (Figure 5c, for enlargement see Figure EA2b), reduced synthetic nontronite (F) showed a second, asymmetric combination band at 4349 cm^{-1} . The calculated position is offset by 50 cm^{-1} to the observed combination band and cannot be explained by anharmonicity of unperturbed OH groups, which can account for shifts up to 10 cm^{-1} in dioctahedral smectites (Petit et al., 1999). Thus, the band at 843 cm^{-1} might rather be assigned to strongly perturbed Fe(II)Fe(II)–OH entities or even to dehydroxylated Fe(II)Fe(II) groups, to which the simple relationship between OH combination band position and OH bending and stretching band position (Petit et al., 1999; Post and Noble, 1993) cannot be applied. We hypothesize that the vibration modes of adjacent Fe(II)Fe(II)–OH and Fe(II)Fe(II)–O entities might yield the observed combination band.

From the investigation of non-reduced smectites with residual Fe(II) content the position of Fe(II)Fe(II)–OH bands in nontronites was previously deduced to be at 717 cm^{-1} (Gates, 2008). This band position is also in agreement with the general trend of the band position to decrease in wavenumber with decreasing valence of the MM–OH group in the spectra of natural samples (Besson and Drits, 1997; Gates, 2005). The absence of any new band around 720 cm^{-1} in the spectrum of reduced synthetic nontronite presented in our study (Figure 5a), however, does not support this position. Smectites containing residual Fe(II) can be investigated under aerobic conditions without observable Fe(II) oxidation (Gates, 2008), indicating that Fe(II) can be presumed to be in a stable configuration. In contrast, smectite samples studied in the work presented here contained Fe(II)/Fe(total) ratios between 0% and >90%, resulting in highly reactive Fe(II) configurations, which were not stable in the presence of oxygen. Thus, we suppose that these highly reactive Fe(II) entities in our samples cannot be treated in the same way as bands involving more stable Fe(II) configurations, e.g., as in the samples described in Gates (2008). Because Fe reduction is accompanied by deprotonation of octahedral MM–OH entities and simultaneous water molecule formation (Drits and Manceau, 2000), a charge deficit is induced on the newly formed bridging oxygen atom, which enhances its attractive forces on the neighboring OH group. This results in a changed orientation of the OH group and the strengthening of the $\text{O}\cdots\text{H}-\text{O}$ bond, thus shifting the expected absorption

band position to higher wavenumbers. A partial compensation of this effect by the charge deficit induced by the presence of tetrahedral Fe on the apical oxygen of the neighboring tetrahedron, however, cannot be ruled out. Fe reduction also results in Fe atom migration within the octahedral sheet and leads to the formation of trioctahedral Fe(II) entities, which are separated by domains of vacancies (Drits and Manceau, 2000; Manceau et al., 2000a), as schematically depicted in Figure 6b. Adjacent dioctahedral Fe(II)Fe(II)–OH groups might be strongly perturbed and thus exhibit absorption bands at a higher wavenumber. We therefore suggest that the high extent of reduction in our samples resulted in an increase in wavenumber (to 843 cm⁻¹) with decreasing valence of the Fe-containing MM–OH entities. In addition, the combination band position calculated from the proposed bending (717 cm⁻¹) and observed stretching (3554 cm⁻¹) band would be 4271 cm⁻¹, which deviates from the observed combination band position (4349 cm⁻¹) by 78 cm⁻¹, corroborating our finding that the proposed Fe(II)Fe(II)–OH band at 717 cm⁻¹ is absent in the spectrum of reduced synthetic nontronite. Because we already presented conclusive arguments for the assignment of the second observed combination band at 4256 cm⁻¹ to trioctahedral Fe(II) entities (see above), this band cannot be due to Fe(II)Fe(II)–OH groups. We therefore propose to assign the absorption band at 843 cm⁻¹ to perturbed Fe(II)Fe(II)–OH entities.

From the absorption bands of the like-valent Fe(III)Fe(III)–OH (812 cm⁻¹) and Fe(II)Fe(II)–OH (843 cm⁻¹) groups, the band position of the intermediary mixed-valent Fe(II)Fe(III)–OH configuration can be estimated to be 828 cm⁻¹ (Besson and Drits, 1997). In the spectra of partially re-oxidized samples D (69% Fe(II)/total Fe) and E (74% Fe(II)/total Fe) in the MM–OH bending region (Figure 5a) no additional band was observed at this position. This finding suggests that the Fe(II)Fe(III)–OH entities are either not IR-active or they cannot be detected due to overlap with the absorption bands of the like-valent Fe(III)Fe(III)–OH and Fe(II)Fe(II)–OH groups or due to fast electron transfer between adjacent Fe(II) and Fe(III) atoms in Fe(II)Fe(III)–OH entities, which was observed in partly reduced Fe-rich smectites with visible spectroscopy (Komadel et al., 1990; Lear and Stucki, 1987).

In the spectrum of partially re-oxidized sample E (74% Fe(II)/total Fe), the Fe(II)Fe(II)–OH bending band at 843 cm⁻¹ disappeared completely (Figure 5a) while the combina-

tion band at 4349 cm^{-1} (Figure 5c) remained largely unchanged in position and intensity. Because also the $\text{Fe(II)Fe(II)Fe(II)-OH}$ bending band at 646 cm^{-1} (Figure 5d) and the $\text{Fe(II)Fe(II)Fe(II)-OH}$ combination band at 4256 cm^{-1} (Figure 5c) were retained at slightly lower intensity, we hypothesize that the combination band at 4349 cm^{-1} corresponds to Fe(II)Fe(II)-OH entities which are closely linked to trioctahedral Fe(II) -groups. Consequently, the bending band at 843 cm^{-1} should be assigned to a different type of perturbed Fe(II)Fe(II)-OH group, which is separate from trioctahedral domains.

In Figure 6b, a schematic representation of the octahedral cation arrangements in reduced synthetic nontronite is given. The hydroxyl groups (filled circles) attached to three Fe(II) cations (blue octahedra) represent trioctahedral $\text{Fe(II)Fe(II)Fe(II)-OH}$ configurations, which enclose a domain of four vacancies (blank octahedra). The dioctahedral Fe(II)Fe(II)-OH configuration above this domain of vacancies is adjacent to trioctahedral groups, whereas the Fe(II)Fe(II)-OH entity below retained its original dioctahedral character. Due to cation rearrangement within the octahedral sheet some structural hydroxyl groups were transformed to water (open circles) to form domains of vacancies (Drits and Manceau, 2000).

In reduced synthetic nontronite (F), also tetrahedral Fe(III) was reduced, considering the high degree of iron reduction (97% $\text{Fe(II)}/\text{total Fe}$) in combination with the disappearance of the characteristic absorption band at 714 cm^{-1} (Figure 5d, for enlargement see Figure EA2a). To date it has been presumed that Fe(II) cannot exist in a tetrahedral coordination sphere and will be ejected from the silicate lattice (Russell et al., 1979). However, in the spectra of re-oxidized samples C (11% $\text{Fe(II)}/\text{total Fe}$) and B (7% $\text{Fe(II)}/\text{total Fe}$), the characteristic absorption band associated with tetrahedral Fe(III) at 714 cm^{-1} (Figure 5d, for enlargement see Figure EA2a) re-appeared, indicating that tetrahedral iron remained within the reduced nontronite's structure. Further evidence that tetrahedral Fe was not ejected from the structure of synthetic nontronite during reduction comes from the determination of Fe(II) and total Fe (Amonette and Templeton, 1998; Stucki, 1981), in which no Fe could be detected in the reduction and wash solutions and all structural Fe was recovered in synthetic nontronite after reduction and re-oxidation. Additionally, the Si-O stretching bands (Figure 5e) showed an unusual behavior with increased $\text{Fe(II)}/\text{total Fe}$ ratio. The

spectrum of unaltered synthetic nontronite (A, 0% Fe(II)/total Fe) was characterized by one broad band at a comparably low wavenumber of 945 cm^{-1} , indicative of a high amount of tetrahedral Fe(III) (Decarreau et al., 2008). For reduced synthetic nontronite (F, 97% Fe(II)/total Fe), at least three distinct Si–O absorption bands were observed at 994, 950, and 914 cm^{-1} , suggesting a strong influence of different octahedral arrangements and/or different tetrahedral environments. Especially the Si–O stretching component at the very low wavenumber of 914 cm^{-1} might be indicative for the presence of tetrahedral Fe(II) within the smectite’s structure as the Si–O stretching band is shifted to lower wavenumbers with increasing tetrahedral Fe content (Decarreau et al., 2008). Furthermore, in the spectra of re-oxidized samples C (11% Fe(II)/total Fe) and B (7% Fe(II)/total Fe), one single Si–O stretching band was restored at 960 cm^{-1} , which is at similar position as the absorption band in unaltered synthetic nontronite (A, 945 cm^{-1}). These observations support that tetrahedral Fe indeed remained within the reduced nontronite’s structure and was present as Fe(II).

Combined evidence suggests that three types of Fe(II)-species were present in the structure of reduced synthetic nontronite, i.e., tetrahedral Fe(II), octahedral Fe(II) in trioctahedral and (perturbed) dioctahedral arrangements. All Fe(II) species were oxidizable by oxygen or NACs. Due to the low intensity of the octahedral Fe(II)Fe(II)–OH bending band and the lack of a band for tetrahedral Fe(II) entities, it cannot be inferred unambiguously which of the Fe(II)-species was most readily oxidized.

Concerning the reversibility of structural changes in the mineral, Fe reduction affected both, the Fe(III)-containing entities, indicated by the disappearance of the characteristic bending bands (Fe(III)Fe(III)–OH at 812 cm^{-1} and Fe(III)^{IV}–O at 714 cm^{-1} , Figure 5a), and the overall silicate structure, as the one broad Si–O stretching band split into at least three individual bands (Figure 5e). Additionally, an overall decrease of OH-absorption band intensity in the bending, stretching, and combination region (Figures 5a-5c) was observed. In the spectra of re-oxidized synthetic nontronite (B, 7% Fe(II)/total Fe and C, 11% Fe(II)/total Fe) the Fe(III)Fe(III)–OH and tetrahedral Fe(III) absorption bands were restored at slightly shifted positions (Figure 5a, $817, 710\text{ cm}^{-1}$, respectively) and the OH-absorption band inten-

sity increased in all regions (Figures 5a-5c) but not to the same magnitude as in the unaltered sample (A). In the Si–O stretching region (Figure 5e) one broad peak was restored in the re-oxidized samples (B, C) at a slightly higher wavenumber compared to the non-reduced sample A (960 vs. 945 cm^{-1} , respectively). We therefore conclude that structural changes during Fe reduction are only partially reversible in case of synthetic nontronite.

3.1.3 Fe(II) species in ferruginous smectite (SWa-1)

The IR spectrum of unaltered ferruginous smectite (A, 0% Fe(II)/total Fe) exhibits three MM–OH bending bands at 918 cm^{-1} (Figure 7e), 874 cm^{-1} , and 819 cm^{-1} (Figure 7a). In analogy to the band assignment for the two end-members discussed above and in agreement with a previous study (Fialips et al., 2002a), we identified these bands as AlAl–OH, AlFe(III)–OH, and Fe(III)Fe(III)–OH entities, respectively. In Figure 8a, the octahedral sheet of unaltered ferruginous smectite is depicted schematically, showing the three observed cation arrangements as well as the *trans*-vacant hydroxyl configuration. This representation also reflects the cationic composition according to the structural formula (Table 1) with a ratio of Fe:Al:Mg of approximately 17:7:1.

In the combination band region (Figure 7c), the spectrum of unaltered ferruginous smectite (A) shows two absorption bands at 4464 cm^{-1} and 4362 cm^{-1} . For AlFe(III)–OH groups, the estimated position of the corresponding combination band (4474 cm^{-1}), which was calculated from the bending (874 cm^{-1}) and stretching (3600 cm^{-1}) bands, agrees well with the observed combination band at 4464 cm^{-1} . The same procedure gives a calculated band position of 4392 cm^{-1} for the Fe(III)Fe(III)–OH combination band (bending: 819 cm^{-1} , stretching: 3573 cm^{-1}), which differs from the position of the observed band at 4362 cm^{-1} by 30 cm^{-1} . Discrepancies as high as 30 cm^{-1} between calculated and observed positions for combination bands have been reported by several authors (Bishop, 2002; Gates, 2005; Madejova, 2005) for natural samples of dioctahedral smectites and might be related to next nearest neighbor effects. Another possible reason for the encountered discrepancy might be the imprecise determination of the Fe(II)Fe(II)–OH stretching band position due to remaining smectite-bound water and other overlapping components. However, our assignment of the combination

bands, i.e., AlFe(III)-OH at 4464 cm^{-1} and Fe(III)Fe(III)-OH at 4362 cm^{-1} , is supported by the corresponding bending bands (Figure 7a), which show the same relative positions, i.e., $\delta(\text{AlFe(III)-OH}) > \delta(\text{Fe(III)Fe(III)-OH})$, as the bands in the combination region. Additionally, a previous study of unaltered ferruginous smectite reported similar combination band positions and the assignment to the same octahedral arrangements (Gates, 2005). In this study an additional band at 4570 cm^{-1} corresponding to AlAl-OH combination vibrations was suggested, which may be present as a very small shoulder in the spectrum of unaltered ferruginous smectite (Figure 7c, A).

In the spectrum of partially reduced ferruginous smectite (D, 46% Fe(II)/total Fe) the intensity of the iron-associated bending bands (874 cm^{-1} , 819 cm^{-1} , Figure 7a) decreased while shoulders appeared at 865 cm^{-1} and 830 cm^{-1} . Both $\text{Fe(III)-containing}$ bending bands completely disappeared in the reduced sample (G, 90% Fe(II)/total Fe) whereas the two new bending bands increased in intensity and were assigned to AlFe(II)-OH (865 cm^{-1}) and Fe(II)Fe(II)-OH groups (830 cm^{-1}). Because we also studied the IR spectra of reduced synthetic nontronite and Wyoming montmorillonite as references, we are able to re-interpret a previous study by Fialips et al. (2002a). We propose that instead of hypothesizing the observed changes to be entirely due to gradual shifts of the original bending bands, new absorption bands corresponding to Fe(II) environments as assigned above are also responsible for the changes in the spectra.

From the bending band positions of the like-valent Fe(III)Fe(III)-OH (819 cm^{-1}) and Fe(II)Fe(II)-OH (830 cm^{-1}) entities the absorption band of the mixed-valent iron species, Fe(II)Fe(III)-OH , would be expected to appear at 825 cm^{-1} (Besson and Drits, 1997). No additional band corresponding to mixed-valent Fe(II)Fe(III)-OH groups was found in any spectrum of Fe(II) containing ferruginous smectite samples, probably due to the same reasons as discussed for synthetic nontronite (overlap with like-valent bands, not IR-active, and/or not detectable).

Similar to findings for reduced synthetic nontronite, characteristic absorption bands for trioctahedral $\text{Fe(II)Fe(II)Fe(II)-OH}$ entities were observed in the OH bending ($\sim 658\text{ cm}^{-1}$, Figure 7d, for enlargement see Figure EA3a) and stretching regions (3625 cm^{-1} , Figure 7b)

in the spectrum of reduced ferruginous smectite (G, 90% Fe(II)/total Fe). Due to an overlap with the Si–O(Fe) out-of-plane vibration at around 680 cm^{-1} , the determination of the trioctahedral bending band’s exact position is impeded (Figure 7d). Estimating the position of the combination band from the bending (658 cm^{-1}) and stretching (3625 cm^{-1}) band (Petit et al., 1999; Post and Noble, 1993) yields an expected band position of 4283 cm^{-1} . In analogy to observations for synthetic nontronite, the Fe(II)Fe(II)Fe(II)–OH combination band should appear as a small shoulder in the spectrum of reduced ferruginous smectite (G, 90% Fe(II)/total Fe, Figure 7c; for enlargement see Figure EA3b). Instead, a broad and intense band at around 4250 cm^{-1} was observed, which likely corresponds to a combination band of OH stretching with lattice deformation vibrations (Farmer and Russell, 1964), and maybe overlapped any possible Fe(II)Fe(II)Fe(II)–OH combination band at the calculated position. Although the relationship between OH-bending and stretching band and the corresponding combination band position of trioctahedral Fe(II) entities matched our observations in case of synthetic nontronite, it is not clear if this relationship can be generalized for trioctahedral arrangements in all smectites. Thus, more comprehensive studies evaluating the relationship between OH-bending, stretching and combination band position associated with trioctahedral Fe in smectites could clarify the present uncertainties.

The spectrum of reduced ferruginous smectite (G, 90% Fe(II)/total Fe) in the combination region (Figure 7c) showed two absorption bands (4511 cm^{-1} , 4435 cm^{-1}) in the typical region for Al-containing entities. The absorption band at 4435 cm^{-1} falls well within the expected combination band position for AlFe(II)–OH groups ($4465\text{--}4405\text{ cm}^{-1}$), which was calculated from the assigned AlFe(II)–OH bending band (865 cm^{-1}) and observed stretching envelope ($3600\text{--}3540\text{ cm}^{-1}$). The second absorption band at 4511 cm^{-1} , which was low in intensity, might have appeared due to the overall decreased intensity of all other bands and could be assigned to an AlAl–OH combination band and is likely to correspond to the observed small shoulder at 4570 cm^{-1} in the unaltered sample (A).

Combining the bending band position (830 cm^{-1}) and stretching band envelope ($3600\text{--}3540\text{ cm}^{-1}$) of the Fe(II)Fe(II)–OH vibration, the corresponding combination band is expected between 4430 and 4370 cm^{-1} (Figure 7c). In the spectrum of reduced ferruginous smectite

(G, 90% Fe(II)/total Fe), no distinct absorption band was found in this region while in the partially reduced sample D (46% Fe(II)/total Fe) a band at 4330 cm^{-1} was observed. One possibility would be to assign this absorption band to a Fe(II)Fe(III)–OH group but for this entity no further evidence was found in the bending region (Figure 7a). Alternatively, the band could be assigned to a Fe(II)Fe(II)–OH band. The difference between the positions of the Fe(III)Fe(III)–OH band (4362 cm^{-1}) and the new band (4330 cm^{-1}) of around 30 cm^{-1} is very similar to the difference observed for synthetic nontronite (25 cm^{-1} , Table 2, Figure 5c), further suggesting an assignment of the band at 4330 cm^{-1} to a Fe(II)Fe(II)–OH group. As already discussed for reduced synthetic nontronite, the simple relationship between the position of observed bands in the OH combination region and the position of OH bending and stretching bands cannot be applied to all smectites, especially when they exhibit various octahedral cations and multiple bands. Many trioctahedral smectites and also other clay minerals such as talc or kaolinite have more complex pattern than dioctahedral smectites in the OH combination region, where OH combination band positions were observed which did not correspond to the sum of OH bending and stretching bands (Petit et al., 1999; Madejova et al., 2010). It was hypothesized that combination bands observed in these samples additionally involved stretching components of other bonds such as Al–O, Fe–O or Si–O.

Our assignments of Fe(II) containing bands (Table 2) indicate that three different octahedral Fe(II)-species, i.e., AlFe(II)□, Fe(II)Fe(II)□, and Fe(II)Fe(II)Fe(II), were oxidized by both, oxygen and NACs. The characteristic bending band for Fe(II)Fe(II)Fe(II)–OH at 658 cm^{-1} (Figure 7d) disappeared in the partially re-oxidized sample E (68% Fe(II)/total Fe), whereas the AlFe(II)–OH (865 cm^{-1}) and Fe(II)Fe(II)–OH bending bands (830 cm^{-1} , Figure 7a) only lost some of their intensity. This indicates that trioctahedral Fe(II) was the most reactive Fe(II) species in reduced ferruginous smectite.

Bending bands corresponding to both, AlFe(II)–OH (865 cm^{-1}) and Fe(II)Fe(II)–OH (830 cm^{-1} ; Figure 7a), lost some of their intensity in the partially re-oxidized sample E (68% Fe(II)/total Fe), and both disappeared at approximately the same Fe(II)/total Fe content of 19% (C). This suggests that both structural Fe(II) environments were re-oxidized presumably at equal rates. For sample C (19% Fe(II)/total Fe) neither the Fe(II)Fe(II)–OH

(830 cm^{-1}) nor the Fe(III)Fe(III)-OH (819 cm^{-1}) band were observed while the AlFe(III)-OH (874 cm^{-1}) band regained most of its intensity. This might indicate that restoring Fe(III)Fe(III)-OH groups involved structural rearrangements, which affected predominantly (former) Fe(II)Fe(II)- and $\text{Fe(II)Fe(II)Fe(II)-}$ entities and were less important for Al-containing arrangements. In Figure 8, schematic structures of unaltered ferruginous smectite (a) and reduced ferruginous smectite (b) are shown, which can be used to picture the suggested structural rearrangements. Retrieving the unaltered structure from the reduced one involves the migration of Fe cations from trioctahedral Fe(II) domains (three adjacent blue octahedra) back into the domain of vacancies (4 adjacent blank octahedra) to restore the majority of dioctahedral Fe(III) groups.

In the IR spectrum of the most re-oxidized sample (B, 7% $\text{Fe(II)}/\text{total Fe}$) both Fe(III)- containing bending bends, i.e., AlFe(III)-OH and Fe(III)Fe(III)-OH (Figure 7a), were present at the same position compared to the unaltered sample (A) but the Fe(III)Fe(III)-OH band (819 cm^{-1}) exhibited a much lower intensity. This finding suggests that the intense dehydroxylation at high $\text{Fe(II)}/\text{total Fe}$ ratios, which accompanies the formation of trioctahedral domains (Drits and Manceau, 2000), is only partly reversible during re-oxidation. The Si-O stretching envelope (Figure 7e) shifted from 1014 cm^{-1} in the unaltered sample (A) to 990 cm^{-1} in the reduced sample (G) and back to 1010 cm^{-1} in the re-oxidized sample (B), corroborating that partially irreversible structural changes occur during iron reduction in ferruginous smectite.

3.1.4 Fe(II) species in Ölberg montmorillonite

Figure 9 shows the IR-spectra of Ölberg montmorillonite, which contains a similar amount of total iron as ferruginous smectite as well as the same *trans*-vacant octahedral hydroxyl configuration (Table 1). The two smectites differ, however, in the location of the negative excess charge as Ölberg montmorillonite contains a significant higher fraction of octahedral Mg and thus exhibits an octahedral excess charge while ferruginous smectite is tetrahedrally charged. In the hydroxyl bending region (Figure 9a) we observed three bands at 867, 818, and 759 cm^{-1} in the spectrum of unaltered Ölberg montmorillonite (A, 0% $\text{Fe(II)}/\text{total Fe}$).

Because all three bands decreased in intensity in the spectrum of reduced Ölberg montmorillonite (G, 88% Fe(II)/total Fe), all three bands are associated with Fe(III). Hence, the bands were assigned to AlFe(III)–OH (867 cm^{-1}), Fe(III)Fe(III)–OH (818 cm^{-1}), and MgFe(III)–OH groups (759 cm^{-1}), in agreement with a previous study (Petit et al., 2002). A schematic representation of the octahedral structure of unaltered Ölberg montmorillonite is given in Figure 10a.

During Fe reduction, the intensity of all three bending bands decreased and two new bands appeared at a Fe(II)/total Fe ratio of 66% (F), which were assigned to AlFe(II)–OH (867 cm^{-1} , strong overlap with the Si–O stretching band) and MgFe(II)–OH entities (773 cm^{-1}). Increasing the Fe(II)/total Fe ratio to 88% (G), an additional band appeared at 835 cm^{-1} , which corresponds to Fe(II)Fe(II)–OH vibrations. From the study of natural clay mineral samples, the band positions were found to decrease in wavenumber with decreasing valence of the MM–OH groups (Besson and Drits, 1997; Gates, 2005), which contrasts the increased band positions observed in our study (835 cm^{-1} and 773 cm^{-1}). As was already discussed for reduced synthetic nontronite, deprotonation of octahedral MM–OH entities and simultaneous water molecule formation during Fe reduction (Manceau et al., 2000a) leads to a charge deficit on the newly formed bridging oxygen atom and enhances its attractive forces on the neighboring OH group. Thus, the orientation of the OH group is changed and the $\text{O}\cdots\text{H}-\text{O}$ bond is strengthened, shifting the expected absorption band position to higher wavenumbers.

Similar to the analysis of synthetic nontronite and ferruginous smectite, no IR-spectroscopic evidence for mixed-valent Fe(II)Fe(III)–OH groups was found in partially reduced samples. This observation made with all iron-rich smectites investigated here suggests that Fe(II)Fe(III) entities do not share hydroxyl groups, Fe(II)Fe(III)–OH groups are not IR active, or Fe(II)Fe(III) configurations are not detectable due to fast electron transfer between adjacent Fe(II) and Fe(III) atoms, which was observed in partly reduced Fe-rich smectites with visible spectroscopy (Komadel et al., 1990; Lear and Stucki, 1987).

In contrast to ferruginous smectite and synthetic nontronite, no characteristic bending band for trioctahedral Fe(II) domains ($\sim 650\text{ cm}^{-1}$) was observed in the spectrum of the most

659 reduced Ölberg montmorillonite sample G (88% Fe(II)/total Fe, Figure 9d, for enlargement
 660 see Figure EA4a). Because the spectra of unaltered (A) as well as reduced Ölberg mont-
 661 morillonite (G) exhibit an absorption band at 3618 cm^{-1} (Figure 9b), this band, although
 662 at a typical position for a trioctahedral Fe(II)Fe(II)Fe(II)-OH arrangement, was assigned
 663 to AlAl-OH groups (Petit et al., 2002). In Figure 9c (for enlargement see Figure EA4b),
 664 the combination spectrum of reduced Ölberg montmorillonite (G) shows a small shoulder at
 665 4260 cm^{-1} , which is at a similar position as the combination bands of trioctahedral Fe(II)
 666 entities in ferruginous smectite and synthetic nontronite (Table 2). Because no character-
 667 istic bending band for trioctahedral Fe(II) domains could be observed in the most reduced
 668 Ölberg montmorillonite sample G, this shoulder probably corresponds to a combination band
 669 of OH stretching with lattice deformation vibrations (Farmer and Russell, 1964). The same
 670 observation was made for the reduced sample of ferruginous smectite (Figure 7c; for enlarge-
 671 ment see Figure EA3b).

672 In the combination region (Figure 9c, for enlargement see Figure EA4b) only one broad
 673 band was observed in the spectra of unaltered (A) as well as reduced (G, 88% Fe(II)/total
 674 Fe) Ölberg montmorillonite, which consequently included the individual bands of all dioct-
 675 ahedral cation arrangements. In the spectrum of reduced Ölberg montmorillonite (G), this
 676 combination band was found at a lower wavenumber (4337 cm^{-1}) compared to unaltered
 677 Ölberg montmorillonite (A, 4349 cm^{-1}). The observed difference of 12 cm^{-1} is comparable
 678 to what was found for Wyoming montmorillonite (14 cm^{-1} , Table 2), whereas a difference of
 679 $25\text{ to }30\text{ cm}^{-1}$ was observed for Fe reduction in synthetic nontronite and ferruginous smec-
 680 tite. This differentiation indicates that Fe reduction caused only structural perturbation in
 681 Ölberg montmorillonite and Wyoming montmorillonite, whereas more extensive structural
 682 rearrangements accompanied Fe reduction in synthetic nontronite and ferruginous smectite.

683 Drits and Manceau (2000) proposed that iron-rich *trans*-vacant dioctahedral smectites can
 684 form trioctahedral Fe(II)-entities enclosing domains of vacancies during Fe reduction while
 685 these structural rearrangements would be energetically unfavorable for *cis*-vacant smectites.
 686 The absence of trioctahedral domain formation for iron-rich *trans*-vacant Ölberg montmoril-
 687 lonite in combination with the small shift in the overall combination band envelope suggests

that not only a *cis*-vacant configuration but also an octahedral excess charge can efficiently hinder structural rearrangements during iron reduction. Combined IR spectroscopic evidence suggests that Fe(II) was present in three different octahedral environments in reduced Ölberg montmorillonite, i.e., AlFe(II)□, Fe(II)Fe(II)□, and MgFe(II)□. In Figure 10b the structure of reduced Ölberg montmorillonite is depicted schematically. It differs from unaltered Ölberg montmorillonite (Figure 10a) only with regard to the redox state of iron while the overall octahedral cation arrangement is unchanged.

Due to the overlap of the AlFe(II)–OH bending band (866 cm^{-1}) with the Si–O stretching band (977 cm^{-1}) in the spectrum of reduced Ölberg montmorillonite (G, Figure 9a), no conclusions concerning the reactivity of this Fe(II) containing group could be drawn. Also the identification of the relative reactivity of the Fe(II)Fe(II) and MgFe(II) entities was hampered because of the decreased overall intensity of the associated OH-bending bands in the reduced (G, 88% Fe(II)/total Fe) and partially re-oxidized samples E (56% Fe(II)/total Fe) and B (29% Fe(II)/total Fe). In the spectrum of partially re-oxidized sample E, the Fe(II)Fe(II)–OH bending band (835 cm^{-1} , Figure 9a) was at a similar position and of similar intensity compared to the most reduced sample (G), whereas the MgFe(II)–OH band (773 cm^{-1}) was found at a slightly higher wavenumber ($\sim 780\text{ cm}^{-1}$) but was still of similar intensity. At an even lower Fe(II)/total Fe ratio of 29% (B), the MgFe(II)–OH and Fe(II)Fe(II)–OH bands almost completely disappeared, suggesting that these Fe(II)-entities were re-oxidized presumably at a similar rate. While the Fe(III)Fe(III)–OH bending band re-appeared at a slightly higher wavenumber (821 cm^{-1}) compared to the spectrum of unaltered Ölberg montmorillonite (A, 818 cm^{-1}), the MgFe(III)–OH bending band was not present. Thus, the structural perturbation in Ölberg montmorillonite due to Fe reduction was extensive and, upon re-oxidation, only partially reversible.

We also checked whether the reversibility of structural alterations in Ölberg montmorillonite depended on the extent of initial Fe(III) reduction. To this end, we compared the spectra of dithionite-reduced samples with different Fe(II)/total Fe ratios to re-oxidized ones (i.e., D(52% Fe(II)/total Fe) $\rightarrow$ C(39%), F(66%), G(88%) $\rightarrow$ B(29%)) and the spectra of unaltered Ölberg montmorillonite (A) (Table 1). Comparison of unaltered sample A

with sample D (52% Fe(II)/total Fe) in the MM–OH bending region (Figure 9a) indicates a small decrease in intensity of the Fe(III)Fe(III)–OH (818 cm⁻¹) and MgFe(III)–OH bands (759 cm⁻¹) and the appearance of a small shoulder at 773 cm⁻¹ (MgFe(II)–OH). Increasing the degree of reduction to 66% (F) showed that, if more than 50% of the structural iron was reduced, structural changes included the disappearance of bands (Fe(III)Fe(III)–OH, MgFe(III)–OH), the occurrence of new bands (MgFe(II)–OH), as well as intense dehydroxylation. The re-oxidation of sample D to C (52% → 39% Fe(II)/total Fe) resulted in a very similar spectrum compared to the unaltered sample (A) but with lower overall absorption intensity. In contrast, spectrum B (29% Fe(II)/total Fe), which was generated from the re-oxidation of sample G (88% Fe(II)/total Fe), neither restored the Fe(III)Fe(III)–OH and MgFe(III)–OH bands at the same position nor of the same intensity as compared to the unaltered mineral (A). Our observations indicate that structural Fe reduction up to 50% of total Fe only induces largely reversible structural changes, whereas at higher degrees of reduction these structural alterations can become partially irreversible. These findings agree well with previous studies with iron-rich smectites (Fialips et al., 2002a,b; Komadel et al., 1995).

3.2 Linking spectroscopical observations with apparent reactivity of structural Fe(II) in smectites

To assess the implications of Fe(II) being present in various different structural environments in smectites for biogeochemical processes and pollutant dynamics, we compared our spectroscopic results (Table 2) to indirect measures for the *apparent* reactivity of structural Fe(II). Previous studies with dissolved oxidants as probes for reactive Fe(II) revealed that, depending on the total structural Fe content, several types of reactive Fe(II) species might exist (Ilton et al., 2004; Hofstetter et al., 2006; Neumann et al., 2008, 2009). Empirical models have been proposed that take into account not only the presence of Fe(II) entities of distinctly different reactivity but also the dynamics of Fe(II) site formation and “decay”. Such models, as shown in the equations below, were used to quantify the reactivity of struc-

744 tural Fe(II) as apparent pseudo-first order rate constants $k_{obs}^{J_n}$, which represent a weighted
 745 average of n different Fe(II) entities J_n exhibiting reactivity k_{j_n} (eq 1).

$$k_{obs}^{J_n} = \sum_{i=1}^n k_{j_n} \cdot [J_n] \quad (1)$$

746 Estimates for site-specific k_{j_n} were obtained from the quantification of the oxidants' dis-
 747 appearance kinetics and measurement of structural Fe(II) and Fe(III) contents to solve equa-
 748 tions (1–3) numerically (see Neumann et al. (2008, 2009) for details).

$$\frac{d[Ox]}{dt} = k_{obs}^{J_n} \cdot [Ox] \quad (2)$$

$$\frac{d[J_n]}{dt} = k_{j_n} \cdot [J_n] \cdot [Ox] - \sum_{i=1}^n k_{j_n \rightarrow j_m} \cdot [J_n] + \sum_{i=1}^m k_{j_m \rightarrow j_n} \cdot [J_m] \quad (3)$$

749 where $[Ox]$ and $[J_n]$ are oxidant and Fe(II) entities concentrations, respectively. $k_{j_n \rightarrow j_m}$
 750 and $k_{j_m \rightarrow j_n}$ are rate constants for structural re-arrangements of Fe(II) in the mineral, which
 751 account for the fact that Fe(II) oxidation also leads to concentration changes of reactive Fe(II)
 752 species upon structural rearrangements. This behavior is conceptualized as interconversion
 753 reactions between different structural Fe(II) species (eq 3).

754 Assessing the reactivity of Fe(II) with the above equations is most straightforward for
 755 Wyoming montmorillonite. The exclusive identification of Fe(II) in AlFe(II)-entities (Ta-
 756 ble 2) agrees with the previously made observation of pseudo-first order reduction kinetics
 757 of nitroaromatic compounds (NACs) arising from the oxidation of only one type of Fe(II)
 758 (Neumann et al., 2008). Iron-rich smectites, in contrast, showed more complex kinetics of
 759 nitroaromatic probe compound disappearance. This behavior is illustrated for the oxida-
 760 tion of Fe(II) in synthetic nontronite by NACs of very different electron transfer reactivity
 761 (4-acetylnitrobenzene, Figure 11a, and 4-methylnitrobenzene, Figure 11b). The biphasic ox-
 762 idant disappearance points towards the presence of at least two Fe(II) entities of distinctly
 763 different reactivity. Our spectroscopic data show that even three Fe(II)-containing entities
 764 are present in the structure of synthetic nontronite, i.e., octahedral Fe(II)Fe(II), trioctahedral

Fe(II)Fe(II)Fe(II) as well as tetrahedral Fe(II). Very similar conclusions regarding the comparison of spectroscopic vs. kinetic experiments can be drawn for ferruginous smectite and Ölberg montmorillonite. For both smectites, three types of structural Fe(II) arrangements were identified spectroscopically. In ferruginous smectite trioctahedral Fe(II) was found more reactive than Fe(II)Fe(II) and AlFe(II) groups while in Ölberg montmorillonite Fe(II)Fe(II)-, MgFe(II)-groups are presumably determining Fe(II) reactivity in contrast to AlFe(II) entities (Table 2). However, only two types of reactive Fe(II) are necessary to model the kinetics of Fe(II) oxidation.

In fact, the number of structural Fe(II) species found spectroscopically can exceed the number of reactive Fe(II) sites invoked from kinetic experiments. Owing to the experimental setup, the amount of Fe(II) oxidized for spectroscopic measurements encompassed more than 70% of the total Fe content (e.g., ferruginous smectite: 85% $\rightarrow$ 7% Fe(II)/total Fe, Table 1). Conversely, kinetic experiments were conducted to minimize perturbations of Fe(II) arrangements during their oxidation and only 3% of the structural Fe(II) were probed for (90% $\rightarrow$ 87% Fe(II)/total Fe). As illustrated in Figure 7, spectra G and F, such a small turnover of Fe(II) only gives rise to minor changes in smectite structure thus compromising the direct spectroscopic identification of Fe(II) arrangements responsible for probe compound reduction. Moreover, unless rates of Fe(II) oxidation can be determined during spectroscopic measurements, one cannot exclude that different structural Fe(II) entities exhibit similar reactivities.

4 Conclusion

Our combined mid- and near infrared analysis of four smectites with different structural Fe content corroborate previous hypotheses that high structural Fe content is a prerequisite for the simultaneous occurrence of several reactive Fe(II) entities upon Fe reduction by dithionite. In contrast, smectites of low structural Fe content exhibit only one type of reactive Fe(II) species (Neumann et al., 2008). From the assessment of relative reactivities of the spectroscopically identified Fe(II)-containing entities, we can show that other mineral

properties than Fe content, such as the overall cationic composition and the location of the excess charge determine which Fe(II) species form during Fe reduction. The comparison of octahedrally charged, iron-rich Ölberg montmorillonite with tetrahedrally charged, iron-rich synthetic nontronite and ferruginous smectite shows that trioctahedral Fe(II) domains only form, if smectites contains a high amount of structural iron, exhibit *trans*-vacant configuration of the hydroxyl groups, and are tetrahedrally charged. These observations can be used to refine current models for structural Fe reduction (Drits and Manceau, 2000).

Infrared spectroscopy also indicated that reduction of iron-rich smectites was accompanied by intense dehydroxylation and structural changes, which were only partially reversible with re-oxidation. However, the overall silicate structure was preserved and structural iron dissolution during chemical reduction is usually small (i.e., less than 4% of the total iron (Ribeiro et al., 2009; Komadel et al., 1995; Stucki et al., 1984a)). Therefore, structural iron in smectites is considered to represent a renewable source of reduction equivalents for biogeochemical processes and the transformation of contaminants. However, the consequences of repeated reduction/re-oxidation cycles on irreversible structural changes needs to be addressed further. Future investigations should also assess the accessibility and reactivity of iron in structurally modified smectites.

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Figure 1: Schematic representation of octahedral cationic arrangement in a (a) *cis*-vacant and (b) *trans*-vacant smectite. The grey octahedra represent octahedral places filled with cations, whereas blank octahedra represent vacant sites. The hydroxyl groups (black filled circles) can either be on the same side (*cis*-vacant) or on opposite sides (*trans*-vacant) of the vacancies.

Figure 2: Overview of general absorption band positions of hydroxyl groups linked to octahedral cations, M, (marked in blue, regions a-c) and of the silicate lattice (marked in orange, regions d, e) in smectites in the middle and near infrared regions. Absorption bands of the octahedral hydroxyl groups result from fundamental bending (δ , region a) and stretching (ν , region b) vibrations as well as the combination of bending and stretching ($\delta + \nu$, region c) and differ for two or three adjacent octahedral cations (dioctahedral and trioctahedral OH, respectively). Absorption bands linked to the silicate lattice origin from lattice deformation vibrations (described as $\delta(\text{Si-O}_{\text{ap}})$ or $\nu(\text{M-O}_{\text{ap}})$, region d) and Si-O stretching vibrations (region e). The combination of lattice deformation bands with stretching vibrations of hydroxyl groups linked to octahedral cations can be observed in region c, but cannot be interpreted unambiguously.

Table 1: Names, acronyms, and total iron contents of the smectites used in this study. Smectite concentrations apply to the experimental reactors for re-oxidation with either oxygen (O_2) or 4-acetylnitrobenzene (4-AcNB). $Fe(II)/total\ Fe$ ratios refer to the conditions after re-oxidation. $Fe(II)$ concentration and total Fe content were determined by the phenanthroline method (Amonette and Templeton, 1998; Strucki, 1981) or were calculated from the measured 4-acetylaniline concentrations after re-oxidation with O_2 or 4-AcNB. Infrared spectra in the mid-IR region were obtained using the KBr pellet technique (KBr) as well as attenuated total reflection FTIR (ATR). Diffuse reflectance FTIR (DRIFT) was applied in the near-IR region.

Smeectite	Total Fe content [wt %]	Configuration of octahedral hydroxyl groups	Location of excess charge	smeectite concentration [g L ⁻¹]	Figure number and name	re-oxidation agent	Fe(II)/total Fe	IR method
Wyoming Montmorillonite SWy-2 ^a	2.8 ^b	<i>cis</i> -vacant	octahedral charge	–	3 A	–	–	ATR
				–	3 C	–	75	ATR
				–	3 B	O ₂	40	ATR
Ölberg	12.2 ^d	<i>trans</i> -vacant	octahedral	–	9 A	–	–	ATR
				–	9 D	–	52	ATR
				–	9 F	–	66	ATR
				–	9 G	–	88	ATR
Montmorillonite ^c			charge	5	9 E ^f 9 B ^f	O ₂ O ₂	56 29	ATR ATR
				2.5	9 C ^g	4-AcNB	39	ATR
				–	7 A	–	–	ATR
Ferruginous Smeectite, SWa-1 ^h	12.6 ^b	<i>trans</i> -vacant	tetrahedral charge	–	7 D	–	46	ATR
				–	7 G	–	90	ATR
				4.8	7 E ⁱ 7 C ^j 7 B ⁱ	O ₂ O ₂ O ₂	68 19 7	ATR ATR ATR
				4.9	7 F ^j EA1 A, B ⁱ	4-AcNB 4-AcNB	87 58	ATR ATR
				–	5 A	–	–	ATR
				–	5 F	–	97	ATR
Synthetic Nontronite ^k	33.5 ^d	<i>trans</i> -vacant	tetrahedral charge	2.6	EA1 C, 5 D 5 C ^l 5 B	O ₂ O ₂ O ₂	69 11 7	ATR ATR ATR
					EA1 D, 5 E	4-AcNB	74	ATR
								ATR

 $\text{R}_{0.74}^{+}(\text{Si}_{7.74}\text{Al}_{0.26})(\text{Al}_{3.06}\text{Mg}_{0.48}\text{Fe(III)}_{0.45})\text{O}_{20}(\text{OH})_4$ taken from (Mermut and Cano, 2001).
^b Determined as described in (Hofstetter et al., 2006).

^c $R_{0.38}^{+}(\text{Si}_{7.98}\text{Al}_{0.02})(\text{Fe(III)}_{2.22}\text{Mg}_{1.72}\text{Al}_{0.48})\text{O}_{20}(\text{OH})_4$ taken from (Petit et al., 2002).

^e IR spectra provided by Sabine Petit.
1998; Stucki, 1981).

^g Starting suspension for re-oxidation with 4-AcNB corresponds to sample 9 D. ${}^h R_{0.87}^{+}(\text{Si}_{7.38}\text{Al}_{0.62})(\text{Fe(III)}_{2.68}\text{Al}_{1.08}\text{Mg}_{0.23})\text{O}_{20}(\text{OH})_4$ taken from (Manceau et al., 2000b).

ⁱ Starting suspension for re-oxidation with oxygen and 4-AcNB corresponds was a sample with a Fe(II)/total Fe content of 85%, not shown here.

with oxygen and 4-AcNB corresponds to sample 7 G. $^k\text{R}_{1.5}^+(\text{Si}_{6.5}\text{Fe(III)}_{1.5})(\text{Fe(III)}_4)\text{O}_{20}(\text{OH})_4$ taken from (Decarreau et al., 2008).

Table 2: Peak position in cm^{-1} and possible assignments of bands in the near infrared (NIR) region ($4100\text{--}4600\text{ cm}^{-1}$) and middle infrared (MIR) region ($400\text{--}1200\text{ cm}^{-1}$) of Wyoming montmorillonite (SWy-2), Ölberg montmorillonite, ferruginous smectite (SWa-1), and synthetic nontronite. The data is presented according to increasing structural Fe content of the minerals (left to right) and the band positions are listed by decreasing wavenumber.

Type and (Region in Figure 2)	Reduction state	Assigned band	Wyoming montmoril- lonite (SWy-2)	Ölberg mont- morillonite	Ferruginous smectite (SWa-1)	Synthetic nontronite
OH- combination (‘c’)	unaltered	AlAl–OH	4534 ^a	4349 ^a	–	–
		AlFe(III)–OH			4464	–
		Fe(III)Fe(III)–OH			4362	4374
	reduced	AlAl–OH	4520 ^a	4337 ^b	–	–
		AlFe(II)–OH			(4511?), 4435	–
		Fe(II)Fe(II)–OH Fe(II)Fe(II)Fe(II)–OH			4330 4250	4349 ^c 4256
OH- stretching (‘b’)	unaltered	MM–OH	3627	3618 3590 3566 3545	3600 3573 – –	–
		AlAl–OH				–
		AlFe(III)–OH				–
		Fe(III)Fe(III)–OH				3566
		Fe(III)Mg–OH				–
	reduced	MM–OH	3620	3545	3600-3542	–
Fe(II)Fe(II)–OH Fe(II)Fe(II)Fe(II)–OH		3554 3612				
Si–O stretching (‘e’)	unaltered	Si–O	1012	1000	1013	945
	reduced	Si–O	1004 1024(s)	977	990	994 950(s) 914
OH- bending (‘a’)	unaltered	AlAl–OH	917	–	918	–
		AlMg–OH	846	–	–	–
		AlFe(III)–OH	884	867	874	–
		Fe(III)Fe(III)–OH	–	818	819	812
		Fe(III)Mg–OH	–	759	–	–
	reduced	AlFe(II)–OH	–	866 (s)	865	–
		Fe(II)Fe(II)–OH	–	835	830	843 ^c
		Fe(II)Mg–OH	–	773	–	–
		Fe(II)Fe(II)Fe(II)–OH	–	–	658	646
		–	–	–	–	–
tetrahedral cation		Fe(III) _{IV} –O	–	–	–	714
lattice bands (‘d’)	unaltered	M–O _{ap} stretching/ Si–O bending	621	685	681	669
			523	492	511	600
			465	451	496	490
			–	436	457	449
	reduced	M–O _{ap} stretching/ Si–O bending	621	677	– n.d.	– n.d.
			521	511	515	– n.d.
			465	453	463	490
			–	– n.d.	428	457
				428	422	

^a Only one broad absorption band was detected and no individual band positions can be assigned for the dioctahedral cation pairs. ^b Additionally to the broad band accounting for all dioctahedral cation pairs a shoulder at 4260 cm^{-1} was detected. The assignment remains unclear because in all other regions no band corresponding to trioctahedral Fe(II) was observed. ^c Combination and bending bands in reduced nontronite are hypothesized to correspond to two different types of perturbed Fe(II)Fe(II)-OH groups: the combination band presumably to groups closely linked to trioctahedral Fe(II) and the bending band to groups separate from trioctahedral domains. ^{n.d.} not detectable due to overlap with other bands or decrease in intensity.

Figure 3: Infrared spectra of Wyoming montmorillonite (SWy-2) in the (a) MM-OH bending, (b) MM-OH stretching, (c) MM-OH combination, (d) lattice vibration, and (e) Si-O stretching region for unaltered (A), reduced (B), and partially re-oxidized (C) samples with respective Fe(II)/total Fe contents of 0% (A), 75% (C), and 40% (B). Spectra in (a), (b), and (e) were obtained with a gas-tight ATR unit equipped with a ZnSe crystal, a DRIFT accessory was applied to acquire all spectra in (c), and samples for (d) were analyzed with the KBr pellet technique. The asterisks denote quartz impurities.

Figure 4: Schematic representation of octahedral cationic arrangement derived from IR spectroscopy in the structure of (a) unaltered and (b) reduced *cis*-vacant Wyoming montmorillonite (SWy-2). Only those cations sharing a hydroxyl group (black filled circle) can be investigated in the middle and near infrared regions.

Figure 5: Infrared spectra of synthetic nontronite in the (a) MM-OH bending, (b) MM-OH stretching, (c) MM-OH combination, (d) lattice vibration, and (e) Si-O stretching region for unaltered, reduced, and partially re-oxidized samples. Spectrum (A) is unaltered synthetic nontronite, (F) represents a reduced sample, and (B), (C), (D), and (E) are partially re-oxidized samples with respective Fe(II)/total Fe contents of 0% (A), 97% (F), 7% (B), 11% (C), 69% (D), and 74% (E). Spectra in (a) and (e) were obtained with a gas-tight ATR unit equipped with a ZnSe crystal, a DRIFT accessory was applied to acquire all spectra in (b), (c), and (d) were analyzed with the KBr pellet technique.

Figure 6: Schematic representation of octahedral cationic arrangement derived from IR spectroscopy in the structure of (a) unaltered and (b) completely reduced *trans*-vacant synthetic nontronite. During reduction, structural rearrangements lead to the formation of trioctahedral Fe(II) groups enclosing domains of vacancies and to the dehydroxylation of the octahedral sheet (indicated as open circle in (b)). Only those cations sharing a hydroxyl group (black filled circle) can be investigated in the middle and near infrared regions. Figure (b) only illustrates the types of Fe(II) entities present in reduced synthetic nontronite but does not reflect their relative abundance.

Figure 7: Infrared spectra of ferruginous smectite in the (a) MM-OH bending, (b) MM-OH stretching, (c) MM-OH combination, (d) lattice vibration, and (e) Si-O stretching region for unaltered, reduced, and partially re-oxidized samples. Spectrum (A) is unaltered ferruginous smectite, (D) and (G) represent to differing extents reduced samples, and (B), (C), (E), and (F) are partially re-oxidized samples with respective Fe(II) to total iron contents of 0% (A), 46% (D), 90% (G), 7% (B), 19% (C), 68% (E), and 87% (F). Spectra in (a) and (e) as well as spectra (A) and (B) in panel (b) were obtained with a gas-tight ATR unit equipped with a ZnSe crystal, a DRIFT accessory was applied to acquire all spectra in (c), and samples for (b), except spectra (A) and (B), and (d) were analyzed with the KBr pellet technique. The asterisks denote quartz impurities.

Figure 8: Schematic representation of octahedral cationic arrangement derived from IR spectroscopy in the structure of (a) unaltered and (b) completely reduced *trans*-vacant ferruginous smectite. During reduction, structural rearrangements lead to the formation of trioctahedral Fe(II) groups enclosing domains of vacancies and to the dehydroxylation of the octahedral sheet (indicated as open circle in (b)). Only those cations sharing a hydroxyl group (black filled circle) can be investigated in the middle and near infrared regions. The structural formula of ferruginous smectite (Table 1), which was used to generate this schematic representation, was derived from a sample containing a higher total iron content (20 wt% (Manceau et al., 2000b)) than given in Table 1. Thus, iron is slightly over-represented in this scheme.

Figure 9: Infrared spectra of Ölberg montmorillonite in the (a) MM-OH bending, (b) MM-OH stretching, (c) MM-OH combination, (d) lattice vibration, and (e) Si-O stretching region for unaltered, reduced, and partially re-oxidized samples. Spectrum (A) is unaltered Ölberg montmorillonite, (D), (F), and (G) represent to differing extents reduced samples, and (B), (C), and (E) are partially re-oxidized samples with respective Fe(II) to total iron contents of 0% (A), 52% (D), 66% (F), 88% (G), 29% (B), 39% (C), and 56% (E). Spectra in (a) and (e) as well as spectra (A), (C), and (D) in panel (b) were obtained with a gas-tight ATR unit equipped with a ZnSe crystal, a DRIFT accessory was applied to acquire all spectra in (c), and samples for (b), except spectra (A), (C), and (D), and (d) were analyzed with the KBr pellet technique. The asterisks denote quartz impurities.

Figure 10: Schematic representation of octahedral cationic arrangement derived from IR spectroscopy in the structure of (a) unaltered and (b) completely reduced *trans*-vacant Ölberg montmorillonite. Despite the high total iron content and the *trans*-configuration of the octahedral hydroxyl groups, no structural rearrangements occur during reduction of this octahedrally charged smectite, in contrast to observations for iron-rich, *trans*-vacant smectites exhibiting a tetrahedral excess charge. Only those cations sharing a hydroxyl group (black filled circle) can be investigated in the middle and near infrared regions.

(a) 4-acetylnitrobenzene

(b) 4-methylnitrobenzene

Figure 11: Typical reduction kinetics of (a) the most reactive nitroaromatic compound, 4-acetylnitrobenzene, and (b) the least reactive nitroaromatic compound, 4-methylnitrobenzene, in suspension of reduced synthetic nontronite (97% Fe(II)/total Fe). The solid lines represent the time course of the nitroaromatic compound concentration according to the two-site model developed previously (Neumann et al., 2008); the dashed lines correspond to a pseudo-first order kinetic model.

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Electronic Annex

Geochimica et Cosmochimica Acta

Evaluation of Redox-active Iron Sites in
Smectites using Middle and Near Infrared
Spectroscopy

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1 Materials

1.1 Chemicals

All chemicals were of analytical grade or higher purity and were used without further treatment.

4-acetylnitrobenzene (4-AcNB), 4-nitrotoluene (4-MeNB), HCl, NaCl, NaHCO₃, H₂SO₄ (95 – 97%), hydroxylammoniumchloride (NH₂OH·HCl), trisodiumcitrate-dihydrate (C₆H₅Na₃O₇ · 2H₂O), and ethanol (EtOH) were purchased from Merck AG; Dietikon, Switzerland. 4-acetylaniline (4-AcAn), 4-chloronitrobenzene (4-ClNB), 4-chloroaniline (4-ClAn), *o*-Phenanthroline, morpholino-propane sulfonic acid (MOPS), HNO₃ (65 %), HF (40 %), Mohr's salt (FeH₈N₂O₈S₃ · 6H₂O), boric acid (B(OH)₃), sodium dithionite (Na₂S₂O₄), and KCl were obtained from Fluka AG; Buchs, Switzerland. Methanol (MeOH) was obtained from Scharlau; Barcelona, Spain and O₂, N₂, N₂/H₂ and Ar (≥ 99.999%) from Carbagas; Rüm-
lang, Switzerland.

2 Results

2.1 Validation of the experimental setup

To ensure the structural stability of dried samples over time, the chosen experimental setup was validated for one infrared (IR) method, i.e. attenuated total reflection (ATR) IR spectroscopy, using partially re-oxidized ferruginous smectite (SWa-1). The MM–OH bending and stretching as well as the Si–O stretching region of partially re-oxidized ferruginous smectite at different time intervals after preparation are shown in Figure EA1 (a)-(c) (indicated as EA1 A, B in Table 1 of the main text). Comparison of spectrum (A) in Figure EA1 (a)-(c), corresponding to the sample directly after preparation, with spectrum (B), which was obtained for the identical sample 2 months after preparation, shows no or only minor changes. The differences in the MM–OH and Si–O stretching regions (Figures EA1b and EA1c) are due to differing amounts of adsorbed water or caused by different particle loadings on the surface of the ATR crystal, respectively. This indicates that the dried samples, which were stored in the anaerobic chamber, retained their structure within the timeframe necessary for IR-measurement (less than 2 weeks). Thus, changes in the IR spectra shown throughout this study can be ascribed to different structural Fe(II) configurations rather than to artifacts from structural rearrangements after sample preparation.

We verified whether two different oxidants, i.e. oxygen and 4-acetylnitrobenzene (4-AcNB), caused the same qualitative changes in the IR spectra as a consequence

Figure EA1: Infrared spectra in the (a) MM-OH bending, (b) MM-OH stretching, and (c) Si-O stretching region of samples of (A, B) ferruginous smectite (SWa-1) and (C, D) synthetic nontronite. Spectra (A) and (B) represent partially re-oxidized ferruginous smectite (58% Fe(II)/total Fe) directly after (A) and 2 months after (B) sample preparation. Spectra (C) and (D) show samples of synthetic nontronite, which were partially re-oxidized with oxygen (C, 69% Fe(II)/total Fe) or 4-acetylnitrobenzene (D, 74% Fe(II)/total Fe). Panels (a)–(c) show spectra obtained with a gas-tight ATR unit equipped with a ZnSe crystal and the KBr pellet technique was applied to acquire spectra (C, D) in panel (b).

of structural changes upon Fe(II) oxidation. As shown in Figure EA1, the IR spectra of partially re-oxidized synthetic nontronite, spectra C (69% Fe(II)/total Fe after oxidation with oxygen) and D (74% Fe(II)/total Fe after oxidation with 4-AcNB), are very similar for both samples. The observed rather small differences in MM–OH and Si–O stretching region (Figures EA1 (b) and (c)) were caused by the differing Fe(II)/total Fe ratio but were not due to the nature of the Fe(II)-oxidant. This result indicates that oxygen and 4-acetylnitrobenzene impose the same effects on the structure of smectites during Fe(II) oxidation. We conclude that spectra obtained from suspension treated with oxygen or 4-AcNB are equivalent.

2.2 IR spectroscopic identification of reactive Fe(II) species and investigation of the reversibility of structural changes

Figure EA2: Enlargements of the infrared spectra of synthetic nontronite in (a) the MMM-OH bending and (b) the MM-OH combination region.

Figure E/A3: Enlargements of the infrared spectra of ferruginous smectite in (a) the MMM-OH bending region and (b) the MM-OH combination region.

Figure EA4: Enlargements of the infrared spectra of Ölborg montmorillonite in (a) the MM–OH bending region and (b) in the MM–OH combination region.