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Fe(II) - Fe(III) electron transfer in a clay mineral with low Fe content

Drew E. Latta^{1,}, Anke Neumann², W.A.P.J. Premaratne³, Michelle M. Scherer¹*

¹ Department of Civil and Environmental Engineering, 4105 Seamans Center, The University of Iowa, Iowa City, IA 52242 USA

² School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, NE1 7R, UK

³ Department of Chemistry, University of Kelaniya, Kelaniya, 11600 Sri Lanka

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*Corresponding author:

Drew E. Latta, Ph.D.

Department of Civil and Environmental Engineering

4105 Seamans Center

The University of Iowa

Iowa City, IA 52242

USA

Ph. +1-319-936-0034

Email: drew-latta@uiowa.edu

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ABSTRACT

Iron-containing clay minerals are ubiquitous in soils, sediments, and water and provide a significant source of redox-active Fe that is known to influence metal sorption, contaminant fate, and nutrient cycling. While biological reduction of clay minerals has been known for some time, it has only recently been shown that Fe(II) can abiotically reduce Fe(III) in clay minerals. Here we used Mössbauer spectroscopy to show that Fe(II) reduces an extensive amount of Fe(III) in a low Fe clay mineral (Wyoming montmorillonite SWy-2, 2.3 wt% Fe). The extent of reduction ranges from 12 to 78% over a pH range of 4.0 to 7.5 and Fe(II) concentration from 0.4 to 2.2 mM and increases as the amount of sorbed Fe(II) increases until about half of the mineral is reduced. It is unclear how such extensive reduction occurs in an Fe-bearing clay mineral with such a low Fe concentration. With only 2.3 wt% Fe in SWy-2, Fe atoms in the clay mineral are spatially isolated and electron conduction or hopping between neighboring Fe atoms seems unlikely and is also supported by Mössbauer spectroscopy collected over a range of temperatures. The lack of evidence for electron hopping in SWy-2 raises the intriguing question of how the electrons access the Fe deep in the clay mineral structure. Data from Mössbauer spectroscopy and chemical extraction suggest that electron transfer through the basal plane rather than edge sites may explain how such extensive reduction occurs in SWy-2. Electron transfer through the basal plane would provide access to the Fe atoms throughout the structure without requiring electrons to move in the structure via hopping or conduction. Our work demonstrates that Fe(II) reduction of clay minerals can occur across a range of geochemically relevant conditions and that extensive reduction can occur in low Fe clay minerals possibly via electron transfer through the basal plane.

INTRODUCTION

Iron-containing clay minerals are ubiquitous in Earth's environments, and provide a significant source of reactive Fe that can influence metal adsorption, contaminant fate, and nutrient cycling in soils, sediments, and water.¹⁻⁹ Clay minerals can contain a range of Fe contents, from trace impurities of Fe to comprising the majority of the octahedral layer cations (e.g., nontronites with up to 30 wt% structural Fe).¹⁰ The redox state of iron (either Fe(II) or Fe(III)) and the total amount of Fe in clay minerals has been extensively studied because it alters the properties and behavior of clay minerals in soils and sediments through changes in cation exchange capacity, hydration and swelling, and the ability to react with contaminants through reduction and oxidation.^{2,3,5,11-17} Changes in cation exchange capacity, redox properties, and textural behavior of clay minerals can significantly influence metal mobility in the subsurface.

While metal mobility in the subsurface is known to be influenced by sorption of metals onto clay minerals, most of the metals studied (e.g., Cd, Pd, Zn, Ni, Cu, Co) are not redox-active like Fe.^{1,18,19} Redox cycling between Fe(III) and Fe(II) within clay minerals has typically been attributed to the enzymatic activity of Fe reducing bacteria,²⁰⁻²² however, more recent evidence suggests that abiotic reactions between aqueous Fe(II) and structural Fe(III) within clay minerals might also be important reactions in Fe cycling in clay minerals.²³⁻²⁵ Both dithionite and aqueous Fe(II) have been shown to chemically reduce Fe(III) within clay minerals.²³⁻²⁶ Uptake of Fe(II) by clay minerals is influenced by pH, Fe(II) concentration, and electron transfer reactions between Fe(II) and the clay mineral Fe(III).^{23-25,27,28} Electron transfer between aqueous and sorbed Fe(II) and the clay mineral Fe(III) results in significantly more uptake of Fe(II) relative to other divalent cations, and has been shown to correspond to the redox properties of the clay mineral.^{25,29} While reduction of Fe-bearing clay minerals by Fe(II) has been shown, the mechanism of electron transfer remains unclear.

Several mechanisms for electron transfer, however, have been proposed as evidence of both biotic and abiotic Fe redox cycling in clay minerals continues to accumulate. Electron transfer at the basal plane surfaces of smectites to structural Fe(III) has been suggested to occur during chemical reduction of structural Fe(III) by dithionite, based on visible absorption spectroscopy and Mössbauer spectroscopic evidence.^{26,30-32} Mössbauer data also indicated electron transfer could occur through the basal surfaces during Fe(II) reduction of a nontronite at low pH.²⁴ At high pH, however, Mössbauer data indicated electron transfer occurred predominantly through edge sites. Electron transfer through clay mineral edges was also suggested for biological reduction of Fe-rich smectite and nontronite,^{9,32} leading to a conceptual model of microbial clay mineral Fe reduction that involves a redox front moving inward from the edges rather than a spatially random process.^{9,30,32} In addition, the physiology of the microbes may also affect clay mineral reduction, with electron-shuttle producing *Shewanella* species reducing more Fe(III) than direct-contact requiring *Geobacter* species under the same conditions.¹⁷ Electrochemical measurements have further revealed that complete cycling of Fe between Fe(II) and Fe(III) within the clay mineral structure of several smectites is possible when a strong enough potential is applied.³³⁻³⁵

To investigate the mechanism of electron transfer from Fe(II) to clay minerals as well as the extent and prevalence of this reaction in soils and sediments, we explored the effect of pH and Fe(II) concentration on Fe(II) sorption and electron transfer to a low Fe content clay mineral. We chose a clay mineral with a low Fe content (Wyoming montmorillonite, SWy-2, 2.3% wt) as it is more environmentally relevant than the iron-rich nontronites we and others have previously used.^{23,24,36} We also chose conditions that represent environments undergoing extensive Fe reduction where release of mmol/L level concentrations of Fe(II) would be expected.^{37,38}

MATERIALS AND METHODS

Preparation of clay mineral SWy-2. The Wyoming montmorillonite clay mineral SWy-2 was purchased from the Source Clays Repository of The Clay Minerals Society (www.clays.org) and size-fractionated and Na⁺-homoionized according to previously published procedures.²⁴ The <0.5 μ m size fraction was freeze-dried, ground, and sieved (100 mesh), and checked for impurities with infrared (IR) and Mössbauer spectroscopies. Dithionite-reduced SWy-2 was prepared through a modified dithionite-citrate-bicarbonate method.³⁹ Briefly ~500 mg SWy-2 was added to 250 mL of a solution containing 9 mM sodium citrate, 220 mM sodium bicarbonate, and was heated under stirring to 70 °C. Reduction was accomplished by adding 1 g of sodium dithionite (technical grade) to the heated suspension. Reduction was followed by 3 washes with 1 M NaCl, 2 washes of DI water, and final suspension in 50 mM NaCl.

Fe(II) sorption experiments. Anoxic conditions were maintained for all Fe(II) sorption experiments and sequential extractions by using an anoxic chamber (N₂/H₂: 93:7) and N₂-purged solutions.

To determine the effect of pH value on Fe(II) sorption to SWy-2, we monitored the aqueous Fe(II) concentration in non-buffered suspension of 2 g/L SWy-2 over the pH range of 4.0 to 8.0 to 4.0, as previously described in detail.^{24,40} In short, the suspension was adjusted to a starting value of pH 4.0 and Fe(II) solution was added to yield an initial Fe(II) concentration of 2 mM. The pH value was readjusted in steps of 0.5 pH units using 0.05 M HCl or 0.05 M NaOH and at each pH value a sample of 3 mL was withdrawn, filtered (0.2 μ m nylon filter), and acidified (concentrated HCl) once the pH value remained within 0.02 pH units over 10 minutes. The aqueous samples were analyzed for Fe(II) and Fe(total) using the 1,10-phenanthroline method.⁴¹ The amount of sorbed Fe was determined as the difference between initially added Fe(II) and final Fe(II), taking into account changes in suspension volume and mass loss due to sampling.

For Fe(II) sorption experiments that were analyzed with Mössbauer spectroscopy, batch reactors containing 25 mL of 25 mM PIPPS (piperazine-N,N'-bis(3-propanesulfonic acid, pK_{a1} 3.79) buffer, MES (2-(N-morpholino)ethanesulfonic acid), pK_a 6.06) buffer, or MOPS (3-(N-morpholino)propanesulfonic acid, pK_a 7.20) buffer were adjusted to pH values of 4.0, 6.0, and 7.0 or 7.5 with 1 M NaOH, respectively. Ionic strength was maintained with 50 mM NaCl. All buffers hereafter are referred to by their abbreviated name, and all contain 50 mM NaCl electrolyte and 25 mM organic buffer. An aliquot of 100 mM ⁵⁶Fe(II)Cl₂ was added to provide approximately 2

mM $^{56}\text{Fe(II)}$ in solution, and 50 mg Na^+ -homoionized SWy-2 was added to solution, vigorously mixed by hand and placed on an end-over end rotator in the dark. The reactors were sampled by centrifugation (18,500×g, 15 min) and the supernatant was decanted, filtered, and acidified with 5 M HCl for Fe(II) and Fe(total) analysis using the 1,10-phenanthroline method.⁴¹ Reaction times were 18, 22, and 26 days for pH 4.0, 6.0, and 7.5, and 57 days for pH 7.0 reactors, respectively. To ensure that the longer reaction times did not affect the results obtained, one experiment at pH 7.5 was also carried out for 2 h. We note that there was no significant difference between spectra for samples reacted for 2 hours or up to 57 days (**Figure S-1**).

For experiments that involved varying concentrations of Fe(II), batch reactors containing 25 mL MOPS with a pH value of 7.5 were prepared. Fe(II) concentrations were varied by changing the volume of 100 mM $^{56}\text{Fe(II)Cl}_2$ added to each reactor. All other variables were maintained as described above. Reaction times for the 0.3 mM and 1 mM $^{56}\text{Fe(II)}$ experiments were approximately 2 hours.

Several experiment were also done with $^{57}\text{Fe(II)}$ from $^{57}\text{Fe(II)Cl}_2$. Reactors at pH 4.0 were constructed with reduced Na^+ -homoionized SWy-2 suspended in PIPPS buffer to which varying aliquots of 100 mM $^{57}\text{Fe(II)Cl}_2$ was added to reach ~0.3 and ~1 mM Fe(II). Similarly, reactors with ~2 mM $^{57}\text{Fe(II)}$ were prepared to study the products formed from the reaction between SWy-2 and aqueous Fe(II) in pH 6.0 (MES) and pH 7.5 (MOPS) buffers. All reactors containing $^{57}\text{Fe(II)}$ contained 15 mL buffer and 30 mg clay mineral. Reaction times were approximately 2 hours.

Mössbauer spectroscopy. For Mössbauer spectroscopy, solids were recovered from the experiments described above and were collected after centrifugation from the centrifugation tubes, packed into 3 mm thick plastic holders, and sealed in an anoxic chamber with two pieces of Kapton tape. Mössbauer spectra were collected at various temperatures in transmission mode with the a previously described Mössbauer system²⁴ and a MS4 Mössbauer spectrometer (SEE Co, Edina, Minnesota, USA) equipped with a closed cycle cryostat (SHI-850, Janis Research Co., Wilmington, Massachusetts, USA). All spectra were calibrated against 7 μm $\alpha\text{-Fe(0)}$ foil and fit using Recoil software applying Voigt-based fitting.⁴² Uncertainties of the fitted parameters are derived from the co-variance matrix used in the Levenberg-Marquardt algorithm implemented in the Recoil fitting routine and reported as 95% confidence errors.⁴³

Sequential extraction. Reactors containing ~2 mM Fe(II) were also prepared with Fe(II)Cl₂ having a natural isotope abundance and were subjected to a sequential extraction procedure as previously described.²⁴ The extracted reactors contained 15 mL of PIPPS (pH 4.0), MES (pH 6.0), or MOPS (pH 7.5) buffers and 30 mg Na^+ -homoionized SWy-2. One set of reactors containing SWy-2 reacted with 2 mM $^{56}\text{Fe(II)}$ at pH 4.0 was prepared for subsequent sequential extraction with 25 mL PIPPS buffer (pH 4.0) and 50 mg Na^+ -homoionized SWy-2. The larger volume and SWy-2 mass was needed to collect a Mössbauer spectrum of sufficient quality. Extraction with 1 M CaCl₂ (4 h, pH~7) was shown to selectively remove Fe(II) sorbed to clay mineral basal planes and subsequent extraction with 1 M NaH₂PO₄, (18 h, pH 5.0) targeted Fe(II) bound to clay mineral

edge OH-groups, as demonstrated previously²⁴ and further verified in the SI. Solid and aqueous phases were separated by centrifugation (18,500×g, 15 min). Subsequently, the supernatant was treated as described above and, where applicable, the solids were analyzed with Mössbauer spectroscopy.

RESULTS AND DISCUSSION

Fe(II) sorption on SWy-2. To characterize Fe(II) sorption on a low Fe clay mineral, we measured sorption of Fe(II) onto the iron-containing clay mineral SWy-2 (2.3 wt% Fe) as a function of pH and Fe(II) concentration. As pH increased, Fe(II) uptake from solution increased linearly from pH 4.0 until about pH 6.5 where a sharp rise in Fe(II) sorption was observed (**Figure 1, Table 1**). This S-shaped pH edge pattern is consistent with Fe(II) uptake onto negatively charged clay mineral basal planes (via cation exchange with Na⁺) at low pH values (< 6.0) and increased sorption at higher pH values due to increasing deprotonation of variable charge hydroxyl groups on SWy-2 edge sites.^{24,40,44-47} In general, Fe(II) sorption on clay minerals follows that of other divalent metals, but is larger in magnitude than for other divalent metals.^{1,25,45} Macroscopic sorption of Fe(II) to SWy-2 as a function of pH is markedly similar to what we previously observed for the high-iron nontronite clay mineral NAu-1 (22 wt% Fe),²⁴ and is consistent with high and low Fe Australian smectites (NAu-1 & 2, and MAu-1) recently studied by Tsarev, Waite and Collins²⁷ As with NAu-1,²⁴ we also observed hysteresis after adding acid to the suspension that had been previously adjusted to pH 8.0, possibly due oxidation of Fe(II) by structural Fe(III) within SWy-2. The S-shaped pH edge centered around pH 6.5 is also consistent with previous reports of Fe(II) sorption on SWy-2 at a much lower Fe(II) concentration than used here (0.03 μM compared to 2 mM).²⁵

Sorption of Fe(II) onto SWy-2 over a range of Fe(II) concentrations (at constant pH of 7.5) follows a steep sorption pattern similar to that observed previously for Fe(II) sorption to Wyoming montmorillonite and nontronites at near-neutral pH (**Figure 2**).^{28,45,48} The amount of Fe(II) sorbed on SWy-2 is similar to what we previously observed on NAu-1 despite differences in structural Fe(II) contents (2.3 wt% for SWy-2 versus 22 wt% for NAu-1).²⁴ Soltermann et al. also observed similar amounts of Fe(II) sorption on clay minerals with varying Fe contents (2.9 wt% Fe SWy-2 and 15.4 wt% Fe SWa-1).²⁵

Previous work on Fe(II) sorption on Fe-bearing clay minerals also showed that substantially less Fe(II) sorbed on reduced and Fe-free clay minerals compared to unreduced clay minerals.^{25,29} Soltermann et al.'s work was done at much lower Fe(II) concentration than we used here (0.03 μM compared to 2 mM) nonetheless we still observe a similar trend at pH 6.0 and 7.5 with dithionite reduced SWy-2 sorbing about 30% less Fe(II) than SWy-2 that was not reduced (**Figure 1**). The greater extents of Fe(II) sorption on Fe(III)-bearing clay minerals relative to reduced and Fe-free clay minerals are, as suggested by Soltermann et al., most likely due to electron transfer resulting in oxidation of sorbed Fe(II) and thus increasing the overall observed removal of Fe(II) from solution to an amount greater than observed for sorption alone. Note, however, at a lower pH of 4.0, we observed similar amounts of Fe(II) sorbed on reduced and unreduced SWy-2 (**Figure 1**

and **Table 1**). Because sorption of Fe(II) by Fe-bearing clay minerals involves Fe(II)-Fe(III) electron transfer²³⁻²⁵ it is difficult to interpret macroscopic Fe(II) sorption behavior without a thorough understanding of the factors controlling how and to what extent electron transfer occurs.

Fe(II)-Fe(III)_{clay} electron transfer. To investigate electron transfer between sorbed Fe(II) and the clay mineral SWy-2, we used the isotope specificity of ⁵⁷Fe Mössbauer spectroscopy in an approach similar to our previous work with the nontronite clay minerals NAu-1 and NAu-2.^{23,24} Because ⁵⁷Fe Mössbauer spectroscopy is specific to the ⁵⁷Fe isotope, we can react Mössbauer-invisible aqueous ⁵⁶Fe(II) with SWy-2 containing naturally abundant ⁵⁷Fe and track changes in the oxidation state of the ⁵⁷Fe(III) present within SWy-2.

Prior to reaction with ⁵⁶Fe(II), the Mössbauer spectrum of SWy-2 in pH 7.5 buffer shows that all of the Fe within the SWy-2 structure is Fe(III), and in octahedral coordination (center shift (CS) = 0.42 mm/s, quadrupole splitting (QS) = 0.97 mm/s) (**Figure 3, Table 2**).³⁵ A broad distribution of QS parameters (1σ = 0.83 mm/s) suggests Fe(III) is distributed in different chemical environments in the SWy-2 structure. Our observation of all the structural iron as Fe(III), within error, is consistent with a previous study of SWy-2, where 95% of the structural iron was identified as Fe(III).^{25,35,49}

After reaction of SWy-2 with ⁵⁶Fe(II), a second doublet, indicative of Fe(II), appeared in each spectrum over the whole range of pH and ⁵⁶Fe(II) concentrations explored (**Figures 3 and 4**). Appearance of an Fe(II) doublet indicates that electrons were transferred from sorbed or aqueous ⁵⁶Fe(II) to Fe(III) in the structure of the clay mineral, consistent with previous studies that observed electron transfer from Fe(II) to Fe(III) in nontronites,^{23,24} montmorillonites,²⁵ and the fine fraction of a clay-rich sediment.⁵⁰ The Fe(II) doublets for pH 6.0, 7.0, and 7.5 at all Fe(II) concentrations have Mössbauer CS values ranging from 1.27 to 1.28 mm/s and QS values ranging from 3.01 to 3.03 mm/s, consistent with structural Fe(II) within clay minerals (**Table 2**).^{32,51-55} Although the appearance of Fe(II) doublets in the Mössbauer spectra provides conclusive evidence of electron transfer to structural Fe(III) in the clay, there is the possibility that the newly reduced Fe(II) does not remain structural but rather dissolves and resorbs or precipitates as a secondary phase. Several lines of evidence, however, suggest that the Fe(II) does indeed remain in the structure including (i) the similarity of the Mössbauer parameters between Fe(II)-reduced SWy-2 and dithionite-citrate-bicarbonate (DCB) reduced SWy-2 (**Figure 5 and Table 2**) and (ii) if secondary precipitates of Fe, such as green rust formed in the dithionite-reduced SWy-2, they would dissolve in DCB solution rather than remain doublets in the spectrum.^{56,57}

At the low pH of 4.0, we were surprised that the Mössbauer values (CS = 1.36 mm/s, QS = 2.86 mm/s) were closer to structural Fe(II) rather than the basally sorbed Fe(II) we observed with nontronites (CS = 1.33 mm/s, QS = 3.43 mm/s).^{24,58} At low pH, basal plane sorption of Fe(II) dominates the Fe(II) uptake behavior and in our previous work we observed Mössbauer values similar to basally sorbed Fe(II) on Syn-1 when we reacted both ⁵⁶Fe(II) and ⁵⁷Fe(II) with NAu-1 at pH 4.0.²⁴ To check if Fe(II) sorbed to SWy-2 had Mössbauer parameters consistent with basally sorbed Fe(II) on NAu-1 and Syn-1, we sorbed ⁵⁷Fe(II) to chemically pre-reduced SWy-2 at pH 4.0.

Sorption of Fe(II) onto reduced SWy-2 resulted in two Fe(II) doublets, one with parameters consistent with basally sorbed Fe(II) (CS = 1.40 mm/s, QS = 3.38 mm/s) and one with parameters (CS = 1.34 mm/s, QS = 3.01 mm/s) that were previously interpreted as frozen aqueous Fe(II) (CS = 1.36 mm/s, QS = 3.02 mm/s)⁵⁸ (**Figure 5** and **Table 2**). Neither set of parameters, however, match the parameters we found for ⁵⁶Fe(II)-reduced SWy-2 at pH 4.0 suggesting that despite what appears to be sorption of Fe(II) to the basal plane of SWy-2 at pH 4.0, reduction of the structural Fe is occurring.

It is interesting that electron transfer from basally sorbed Fe(II) on two different clay minerals results in Mössbauer parameters that indicate different clay mineral-Fe(II) binding environments. On SWy-2, it appears that structural Fe(II) is formed from electron transfer from sorbed Fe(II), whereas electron transfer from Fe(II) to NAu-1 generates basal Fe(II). In our work with NAu-1, we found that extraction with CaCl₂ could recover the basally sorbed Fe(II) and remove the basal Fe(II) doublet in the Mössbauer spectrum.²⁴ We used the same approach here and recovered 73% of the sorbed Fe(II) in the extraction with CaCl₂ (**Table 3**) but most of Fe(II) doublet remained in the Mössbauer spectrum (**Table 2** and **Figure 6**) providing further evidence that the reduced Fe(II) resulting from electron transfer remained as structural Fe(II) in SWy-2 as suggested by the Mössbauer parameters. Further sequential extraction of the SWy-2 with pH 5.0 NaH₂PO₄ removed a smaller portion of sorbed Fe (5.9%) and resulted in a Mössbauer spectrum with 8.1% of the Fe in SWy-2 as Fe(II) (**Table 2** and **Figure 6**). Furthermore, after extraction, the Mössbauer parameters of the SWy-2 Fe(II) are close to those of the dithionite reduced SWy-2 (**Table 2**). Although these parameters (CS = 1.31 mm/s, QS = 3.01 mm/s) are similar to frozen aqueous Fe(II)⁵⁸ (see above), given that aqueous Fe was added as ⁵⁶Fe(II) and 79% was extracted, we suggest that it is unlikely the post-extraction spectrum arises from aqueous Fe(II). The combined wet chemical and spectroscopic evidence indicates that the majority of the Fe(II) formed by electron transfer at SWy-2 at pH 4.0 is retained during extractions and confirms that the observed spectral features arise from clay mineral Fe(II) within the SWy-2 structure.

While electron transfer resulted in structural Fe(II) in SWy-2 over the range of pH and Fe(II) concentrations investigated, the extent of reduction of structural Fe(III) in SWy-2 varies significantly. As pH was increased from 4.0 to 7.5, the relative area of the Fe(II) doublet (red doublet in **Figure 3**) increased from 13% to 78% indicating that the amount of Fe(III) reduced in the clay mineral increased substantially as pH increased (**Figure 3**, **Table 2**). Similarly, the extent of clay mineral reduction also increased, from 52% to 78% as the Fe(II) concentration was increased from 0.4 to 2.2 mM at a constant pH of 7.5 (**Figure 4**, **Table 2**).

More clay mineral reduction with increasing pH and Fe(II) concentration may simply be due to more Fe(II) sorption. A plot of percent of clay mineral Fe reduced versus amount of Fe(II) sorbed shows that more clay mineral is reduced as more Fe(II) sorbs ranging up to almost 80% of the Fe(III) in the clay being reduced at high pH and Fe(II) concentration (**Figure S-2**). However, the amount of Fe(III) reduced as more Fe(II) is added levels off at higher amounts of sorbed Fe(II) as the structural Fe(II) extent exceeds 50% (**Figure S-2**). The amount of SWy-2 reduction observed

here at pH 6.0 is higher than the 26% SWy-2 reduction observed by Soltermann et al.²⁵ at pH 6.2, most likely because of the higher Fe(II) concentration used here.

To explore whether every Fe(II) that was sorbed participated in electron transfer, we estimated the apparent stoichiometry of the reaction between sorbed Fe(II) and structural Fe reduced in the clay mineral (**Figure 7**). We observed an apparent stoichiometry of 1:1 between Fe(II) uptake and structural Fe(III) reduction up until about 50% of the total Fe in SWy-2 was reduced. In other words, at pH 7.5, for every Fe(II) sorbed below the 50% threshold an Fe atom in the clay mineral is reduced. A 1:1 stoichiometry was also observed by Soltermann et al. for one point at a lower Fe(II) concentration of ~0.150 mM and pH 6.2.²⁵ Above this threshold of about 50%, Fe(II) continues to sorb, but electron transfer deviates from 1:1 stoichiometry indicating that electron transfer is inhibited and more Fe(II) sorbs than clay mineral Fe is reduced. In addition, at lower pH's (4.0, 6.0, 7.0) in SWy-2 and NAu-1²⁴ suspensions electron transfer deviated from 1:1 stoichiometry. In our previous work with a high Fe containing clay mineral (NAu-2), we observed a similar behavior at pH 7.5. With NAu-2, however, the deviation from 1:1 stoichiometry occurred at a much lower clay mineral Fe reduction extent (15%) compared to 50% in SWy-2.²³ A deviation from 1:1 stoichiometry also occurred for NAu-1 at pH 7.5 and ~2 mM Fe(II).²⁴ In all three cases, electron transfer appears to become inhibited at some threshold of mineral Fe reduction, but the thresholds, and the final clay mineral Fe reduction extents, are markedly different for the low Fe containing clay mineral (SWy-2) and the high Fe containing clay minerals (NAu-1/2).

We can envision several reasons why electron transfer might become inhibited at higher Fe(II) concentrations including charge balance limitations on removal of structural hydroxyl groups upon reduction, passivation of reactive sites by Fe(II) or newly-formed Fe(III) minerals, or thermodynamic limitations.²³ To evaluate which of these reasons might explain why electron transfer is inhibited, we compared absolute amounts of clay mineral reduction (as opposed to percent of clay mineral reduction) (**Figure 8**). SWy-2 has a significantly lower total Fe content compared to NAu-2 (2.3 wt% versus 22 wt%; i.e. 20.9 μ moles versus 200 μ moles in our experiments). Structural Fe reduction in SWy-2 plateaued at ~10 μ mol Fe(II) sorbed to SWy-2, whereas sorption of up to 35 μ mol Fe(II) to NAu-2 resulted in approximately quantitative electron transfer to clay mineral Fe (**Figure 8**). Similar to our findings for SWy-2, we also observed significantly lower absolute clay mineral Fe reduction for NAu-1²⁴ compared to NAu-2 (18 μ mol vs 35 μ mol clay mineral Fe(II), respectively). We examined several potential hypotheses to explain the differing behavior of the three clay minerals with increasing sorbed Fe(II) loading, including whether what we observed was driven by a difference in clay mineral redox potential³³ or due to competition between newly formed Fe(III) oxides and the clay mineral for sorption of aqueous Fe(II).^{23,25,27}

To determine whether differences in the clay mineral reduction potentials (E_H) could explain the observed variations in electron transfer extent for the investigated clay minerals, we calculated the E_H based on the fitted curves for NAu-1, NAu-2, and SWy-2 in Gorski et al.³³ We based our analysis on the extent of clay mineral reduction by Fe(II) observed at pH 7.5 and for 2 mM aqueous Fe(II), where all three clay minerals sorbed approximately the same amount of Fe(II) under these

conditions ($\sim 0.9 \text{ mmol g}^{-1}$), which should result in comparable reduction potentials of the added Fe(II) for all three clay minerals. In contrast to our expectation that the clay mineral-Fe(II) systems would equilibrate to similar redox potentials, all three clay minerals have different reduction potentials at their maximum extent of reduction by Fe(II), NAu-1 has the most reducing potential (-0.34 V), NAu-2 has an intermediate potential (-0.25 V), and SWy-2 has the most oxidizing potential (-0.15 V). Based on the similarities in Fe(II) uptake and concentration and the significant differences in reduction potentials of the clay minerals, it is difficult to explain the observed differences in electron transfer stoichiometry and clay mineral Fe reduction extent wholly by differences in clay mineral redox properties.

Alternatively, we considered whether Fe(III) oxides formed during the electron transfer process^{23,25,27} could contribute to the observed sorption of aqueous Fe(II) without subsequent electron transfer. Because the apparent stoichiometry between Fe(II) uptake and structural Fe(III) reduction is 1:1 at pH 4.0 and 6.0 and decreases at pH values above 6.0 (**Figures 7 and 8**), sorption most likely occurs to a mineral phase that exhibits a strong pH dependence. The pH value of the observed change in stoichiometry coincides with the pH range where sorption of Fe(II) to Fe(III) oxides becomes significant^{59,60} and additionally secondary mineralization of Fe(III) with Fe(II) may occur^{23,27,61,62}. Evidence for this secondary mineralization and sorption process comes from experiments with ⁵⁷Fe(II), where we observed formation of ferrihydrite and a potential green-rust like phase (**Figure S-6 and Supporting Information discussion**) with Mössbauer parameters distinct from Fe(II) in SWy-2. Further support for our hypothesis comes from recent biological experiments indicating lower electron transfer between Fe(II) and clay minerals in the presence of simultaneously present Fe(III) oxides.^{50,63} However, almost 80% of sorbed Fe(II) on NAu-2 was oxidized at pH 7.5, where we would expect competitive sorption of Fe(II) to impact electron transfer stoichiometry, indicating that besides sorbed Fe(II) and pH value additional factors such as clay mineral structural properties may determine the extent and possibly mechanism of electron transfer to clay mineral Fe.

Mechanism of structural Fe reduction in SWy-2 by sorbed Fe(II).

How does Fe(II)-Fe(III) electron transfer happen in SWy-2?

Despite the low Fe content of SWy-2 and the isolated nature of Fe atoms within its structure,⁶⁴ we observed significant reduction of SWy-2 by Fe(II). How electrons from aqueous or sorbed Fe(II) access up to 78% of the Fe in the structure of SWy-2 is an unresolved question. We can hypothesize several different mechanisms for reduction of the large amount of Fe(III) in SWy-2 by Fe(II) that include (i) reduction of structural Fe(III) via electron transfer at edge sites and subsequent reduction progression within the octahedral sheet, (ii) electron transfer through the basal planes of SWy-2, (iii) diffusion of Fe within the structure,⁶⁷ and (iv) partial dissolution of the clay mineral^{61,62} resulting in increased access of Fe(II) to the octahedral Fe(III) within the SWy-2.

Our previous work on nontronites suggested that electrons can be injected into the clay mineral lattice from Fe(II) sorbed to edge hydroxyl sites.²⁴ Because nontronites exhibit significant Fe-Fe clustering, with the most Fe(III)-rich nontronites having each octahedral Fe(III) atom in proximity of 3 other Fe(III) atoms,^{32,64-66,68} the injected electron(s) may move within the nontronite octahedral

sheet and away from the initial site of structural Fe reduction. Electron hopping between Fe(II) and Fe(III) in close proximity in $^{56}\text{Fe(II)}$ -reacted NAu-2 was supported by the observation of a $\text{Fe}^{2.x+}$ phase in temperature-dependent Mössbauer analysis and is supported by first-principle calculations.^{23,69,70} In contrast, infrared (IR) and X-ray absorption (EXAFS) spectroscopy indicate that Fe atoms within the SWy-2 structure are essentially isolated⁶⁴⁻⁶⁶ and temperature-induced intervalence charge transfer was absent for $^{56}\text{Fe(II)}$ -reacted SWy-2 (**Figure S-3, Table S-1**). It is, therefore, difficult to envision how a reduction front might propagate from edge sites to the interior of the SWy-2 clay mineral particles.^{32,68}

Similarly, we regard diffusion of Fe within the clay mineral as unlikely to result in the large amounts of electron transfer observed here. In our previous work focusing on Fe atom exchange in nontronites, we hypothesized that diffusion over the time scales of weeks to months might account for part of the atom exchange between dissolved Fe(II) and structural Fe(III).⁶⁷ However, here we observe significant reduction of SWy-2 Fe(III) within the time scale of 2 hours (**Figure S-1**), a time scale that is incompatible with the longer reaction times needed to facilitate significant diffusion through the clay mineral lattice.

Other lines of experimental and spectroscopic evidence have suggested that aqueous Fe(II) may induce partial dissolution of clay minerals and subsequent precipitation of Fe(II) and/or Fe(III) containing layered double hydroxides (LDHs).^{61,62} Although we cannot rule out this dissolution-precipitation mechanism, it is unlikely that significant precipitation of these mixed-valent phases would occur at pH values as low as 4.0 and 6.0.^{62,71} Our observation of greater than 50% reduction of structural Fe in SWy-2 at pH values between 6.0 and 7.0 suggests that dissolution-precipitation is not a dominant process. Furthermore, we found no evidence for precipitation of macroscopically ordered green rusts or other LDH's in XRD data for Fe(II)-reacted SWy-2 at pH 6.0 and 7.5 (**Figure S-5**), as the typical intense diffraction peaks owing to (00 l) planes and usually observed between 5-15 degrees 2-theta (Co K $_{\alpha}$) were absent in our diffraction patterns, and Fe or Al LDH phases are not precipitated at pH 4.0.^{72,73} We did, however, find tentative evidence for precipitation of a green rust-like phase from the greenish color of the suspension and from Mössbauer spectra of SWy-2 reacted with $^{57}\text{Fe(II)}$ (**Figure S-6** and Supporting Information discussion). Most importantly, the Mössbauer parameters for $^{56}\text{Fe(II)}$ -reacted SWy-2 are different from those of $^{57}\text{Fe(II)}$ -reacted SWy-2, which suggest formation of a separate phase, likely through recrystallization of neoformed Fe(III) with aqueous Fe(II), as discussed above.

This leaves electron transfer through the basal planes of SWy-2 as the most promising of the four alternative hypotheses we proposed for how Fe(II) reduces so much of SWy-2 (i.e., reduction through edge surfaces, reduction through basal surfaces, Fe diffusion, dissolution and LDH precipitation). Electron transfer through clay mineral basal planes, however, has been shown to be energetically unfavorable based on *ab initio* computational calculations of Fe(II) adsorbed to nontronite-like ferripyrophyllite silanol sites,⁶⁸ despite experimental evidence for electron transfer through the basal planes of NAu-1 at low pH values²⁴. We note, however, that SWy-2 exhibited significantly different redox behavior than nontronites during electrochemical investigation³³ suggesting that direct application of *ab initio* models for nontronite to Fe(III)-bearing

montmorillonites might not be feasible. Based on our analysis of the four alternative hypotheses, we propose that electron transfer through basal planes is the most likely explanation for how Fe(II) is able to reduce so much of the structural Fe(III) in SWy-2.

Evidence for Fe(II)-Fe(III) electron transfer through the SWy-2 basal planes

In our previous work, we used two lines of evidence to demonstrate electron transfer from basal plane sorbed Fe(II) to structural Fe(III) in clay mineral NAu-1. The first line of evidence was based on the pH dependence of Fe(II) sorption and our ability to use selective chemical extractions (CaCl_2 and NaH_2PO_4) to remove basal plane and edge hydroxyl group sorbed Fe(II). The Fe(II) sorption behavior and the selective chemical extractions both indicated that Fe(II) sorption to basal planes occurred at low pH values (at and below 6.0) while sorption to edge hydroxyl groups dominated at higher pH values. The second line of evidence came from a combination of the distinct Mössbauer parameters exhibited by the Fe(II) doublet that had resulted from electron transfer at low pH values and that the doublet was removed when extracted with CaCl_2 which targets basal plane sorbed Fe(II).²⁴

Here, we used a similar approach and measured Fe(II) sorption at pH values of 4.0, 6.0 and 7.5, and extracted the sorbed Fe(II) with CaCl_2 followed by NaH_2PO_4 to distinguish between basal plane and edge hydroxyl sorbed Fe(II). Because we strongly rely on the selectivity of the extraction procedure, we included additional data in the SI to further support our previous method verification. For Fe(II) sorbed to SWy-2 at pH 4.0 and 6.0, 59-80% of the sorbed Fe(II) was removed using CaCl_2 extraction whereas only 5-6% of the sorbed Fe was subsequently extracted with NaH_2PO_4 (Table 3), suggesting that sorption at low pH values occurred predominantly at basal planes and sorption to edge hydroxyl groups was minimal. Although we observed a substantial increase of Fe(II) sorption from pH 4.0 to 6.0 (**Figure 1, Table 1**), the absolute amount of Fe(II) recovered in the NaH_2PO_4 extraction, and thus bound to edge hydroxyl groups, remained at the same low level of less than 1 $\mu\text{mol Fe}$ (**Table 3**). Despite extraction of basally-sorbed Fe(II), as discussed above, we obtained Mössbauer data consistent with structural Fe(II) before and after extraction at pH 4.0.²⁴ The resistance of structural Fe(II) in SWy-2 to extractions targeting sorbed species can thus be interpreted that electrons transferred to structural Fe in SWy-2 become trapped in the structure as structural Fe(II), and suggests a different behavior of Fe(II) in SWy-2 than the more weakly bound Fe(II) formed on NAu-1 at pH 4.0.²⁴

In contrast to pH 4.0 and 6.0, after reaction of Fe(II) with SWy-2 at pH 7.5, only a small proportion (12%) Fe(II) sorbed to SWy-2 was released in the CaCl_2 extraction whereas 61% of sorbed Fe(II) was recovered in the subsequent NaH_2PO_4 extraction (Table 3) suggesting that Fe(II) sorption to deprotonated edge hydroxyl groups of SWy-2 dominated at pH 7.5. We note that we cannot distinguish whether Fe(II) was sorbed to clay mineral or Fe(III) oxide hydroxyl groups using the NaH_2PO_4 extraction. However, the increase in sorbed Fe(II) at pH 7.5 (**Figure 1**) did not lead to an equivalent increase in structural Fe reduction extent (**Figure 7**), suggesting that either a considerable fraction of aqueous Fe(II) sorbed to the newly-formed Fe(III) oxide or the isolated nature of structural Fe in SWy-2⁶⁴⁻⁶⁶ prevented electron hopping within the octahedral sheet and

thus limited the extent of structural Fe reduction that can arise from edge hydroxyl group bound Fe(II).

We previously estimated the extent to which Fe(II) sorbed to edge hydroxyl groups could contribute to structural Fe reduction by calculating the unit cells exposed directly to solution in idealized particles of $(0.5 \times 0.5) \mu\text{m}$ and $(0.05 \times 0.05) \mu\text{m}$.⁶⁷ Using the unit cell formula of SWy-2 $(\text{Na}_{0.37}(\text{Al}_{1.53}\text{Mg}_{0.24}\text{Fe}_{0.23})(\text{Si}_{3.87}\text{Al}_{0.13})\text{O}_{10}(\text{OH})_2)$,⁷⁴ we estimated the *a*- and *b*-parameters of the unit cells⁷⁵ and calculated the number of unit cells in the circumference of the particles. We used the ratio of unit cells in the circumference, which are exposed to solution, to unit cells in the entire particle as an estimate of the maximum contribution to structural Fe reduction that can occur from Fe(II) sorbed to edge hydroxyl groups. For particles of $(0.5 \times 0.5) \mu\text{m}$ we estimate that only 0.5% structural Fe reduction would be due to electron transfer via edge hydroxyl groups, while 5% of the structural Fe would be exposed to solution in the $(0.05 \times 0.05) \mu\text{m}$ particles. Our estimate of 0.5 to 5% reduction of structural Fe through exposed edge sites is much lower than the 78% reduction observed. We thus suggest that despite predominant sorption of Fe(II) to edge hydroxyl groups at pH 7.5, Fe(II) sorbed to basal surfaces of SWy-2 must be invoked to explain the large extent of structural Fe(III) reduction.

CONCLUSIONS

We found that Fe(II) can reduce a large amount of structural Fe within the relatively low-Fe clay mineral SWy-2 over a range of pH and Fe(II) conditions. How such extensive reduction can occur when Fe atoms in the clay structure are isolated⁶⁴⁻⁶⁶ enough such that electron hopping between Fe atoms is unlikely (or at least slow) is a fascinating question. Both our Mössbauer and chemical extraction data suggest that a possible explanation for how such extensive reduction occurs is that electrons are transferred through basal planes rather than via edge sites. Electron transfers between basally-sorbed Fe(II) and structural Fe(III) in Fe-rich clay minerals are energetically uphill based on computational chemical models⁶⁸. However, our evidence for significant reduction of SWy-2 by Fe(II) is generally consistent with extensive reduction of SWy-2 by other chemical reductants such as dithionite, a host of soluble redox mediators,³³ and also by the soluble-mediator producing microbe *Shewanella putrefaciens*.¹¹ The experimental evidence suggests that computational models for Fe-rich clay minerals may not yet fully encompass the behavior of low-Fe clay minerals such as SWy-2, and further refinements, such as inclusion of realistic smectite layer charges, may be needed to apply these models to low Fe clay minerals.

The formation of structural Fe(II) in SWy-2 over a wide range of conditions and via reduction through the basal planes suggests that Fe(II)-mediated clay mineral reduction may be more prevalent than previously thought. In particular, significant reduction of clay minerals by Fe(II) at pH values below 6.0 may produce a significant pool of reactive Fe(II) at pH values where little Fe(II) sorbs to Fe(III) oxide minerals.^{60,76,77} Clay mineral Fe may thus be a currently underestimated source of redox equivalents in the environment where it may also act as a redox buffer,^{5,78} playing an important role in redox cycling of soils and sediments.

Associated Content

Supporting Information

Supporting information is available for this paper and includes:

A figure comparing the Mössbauer spectra of SWy-2 reacted with Fe(II) for 2 h and 57 d (Figure S-1), a figure of SWy-2 Fe(II):Fe(total) from Mössbauer spectral fitting versus sorbed Fe(II) (Figure S-2), a Mössbauer temperature profile of SWy-2 reacted with Fe(II) (Figure S-3 and Table S-1), a discussion of the methods and validation procedure used for sequential extractions (Figure S-4, Tables S-2 and S-3), and a discussion of the natural of secondary precipitates formed from reaction of Fe(II) with SWy-2 (Figures S-5 and S-6, Table S-4).

Author Declaration

The authors declare no competing financial interests.

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Figure 1. Fe(II) uptake on Wyoming montmorillonite (SWy-2, 2.3 wt% Fe) as a function of pH. The pH-titrations were carried out in non-buffered solutions containing 2 g/L SWy-2, 2 mM initial aqueous Fe(II), and 50 mM NaCl background electrolyte. The red arrows indicate the direction of titration for the two curves. Data points indicate repeat measurements from the same single reactor. Fe(II) uptake on dithionite reduced SWy-2 was measured with 1.2 mM aqueous Fe(II) at pH 4.0 and 2 mM aqueous Fe(II) at pH 6.0 and 7.5 in the presence of 25 mM buffer pre-adjusted to the selected pH value and 50 mM NaCl background electrolyte. Data points represent single reactors.

Figure 2. Fe(II) uptake on Wyoming montmorillonite SWy-2 (2.3 wt% Fe) as a function of aqueous Fe(II) concentration. Experiments were conducted at constant pH of 7.5 and at 2 g L⁻¹ mineral loading in 25 mM MOPS buffer and 50 mM NaCl electrolyte. Data points represent single reactors.

Figure 3. Mössbauer spectra of SWy-2 collected before reaction (A) and after reaction with 2.2 mM aqueous ⁵⁶Fe(II) (B-E) as a function of pH, with (B) pH 4.0, (C) pH 6.0, (D) pH 7.0, and (E) pH 7.5. Spectra are modeled with Fe²⁺ (green) and Fe³⁺ (red) doublets, with the sum of modeled components shown as the solid black line. Mössbauer spectral fitting parameters are reported in Table 2.

Figure 4. Mössbauer spectra of 2 g/L SWy-2 after reaction with (A) 0.4 mM $^{56}\text{Fe(II)}$, (B) 1.2 mM $^{56}\text{Fe(II)}$, and (C) 2.2 mM $^{56}\text{Fe(II)}$ in 25 mM MOPS (pH 7.5) and 50 mM NaCl. Spectra are modeled with Fe^{2+} (green) and Fe^{3+} (red) doublets, with the sum of modeled components shown as the solid black line. Data are collected at 13 to 19 K. Mössbauer spectral fitting parameters are reported in **Table 2**.

519

520 **Figure 5.** Mössbauer spectra of (A) chemically reduced SWy-2 and (B) dithionite-reduced SWy-
521 2 reacted with 0.3 mM $^{57}\text{Fe}(\text{II})$ in 25 mM PIPPS buffer (pH 4.0) and 50 mM NaCl. Mössbauer
522 spectral fitting parameters are reported in **Table 2**.

523

Figure 6. Comparison of SWy-2 reacted with 2 mM $^{56}\text{Fe(II)}$ at pH 4.0 before and after extraction with 1 M CaCl₂, and sequential extraction with 1 M CaCl₂ followed by 1 M NaH₂PO₄, pH 5.0. Conditions: 2 g/L SWy-2 in 25 mM PIPPS (pH 4.0) and 50 mM NaCl. Mössbauer spectral fitting parameters are reported in **Table 2**. Data are from 3 reactors treated to each of the extraction end points (including a no-extraction sample).

Figure 7. Apparent stoichiometry of the reaction between Fe(II) sorbed to SWy-2 and structural Fe within SWy-2 and NAu-2 (Schaefer et al., 2011).²³ The blue cross marker for SWy-2 at pH 6.2 represents a datum from Soltermann et al. (2014).²⁵ The blue triangles represent data for NAu-1 from Neumann et al. (2013).²⁴ The relative scales are based on Mössbauer-derived Fe(II) area and the ratio of sorbed Fe(II) to total Fe in the clay mineral, expressed as percent (**Figures 3 and 4; Table 1**). Data points represent single reactors.

Figure 8. Apparent stoichiometry of reaction between Fe(II) sorbed to SWy-2 and structural Fe within SWy-2. Absolute scale with structural Fe(II) calculated from the relative Mössbauer-derived Fe(II) area multiplied by the Fe content of 50 mg SWy-2 (20.9 μ moles, heavy dotted line) (Figures 3 and 4; Table 1). The amount of sorbed Fe(II) was determined from the difference between initial aqueous Fe(II) and final aqueous Fe(II) concentrations. Previously published SWy-2 data (blue cross: Soltermann et al., 2014),²⁵ NAu-1 (Neumann et al., 2013),²⁴ and NAu-2 (Schaefer et al., 2011)²³ are scaled to the same mass of clay mineral as the present study. The total Fe of NAu-2 is off the scale of the graph ($\sim 200 \mu$ moles Fe). Data points represent single reactors.

549 **Table 1.** Fe(II) sorption on native SWy-2 and reduced SWy-2

Experiment	pH	Buffer	Fe isotope	[Fe(II)] _{initial} , mM	[Fe(II)] _{final} , mM	Fe(II) _{sorb} , μ moles	Fe(II) _{sorb} , mmol g ⁻¹	Fe(II) uptake, %	Fe(II)/Fe _{total} ¹ , %	Fe(II) _{clay} , μ moles ²	Fe(II) _{sorb} :Fe _{clay} ³ , %	Fe(II) _{clay} :Fe(II) _{sorb} ⁴ , %	⁵⁷ Fe _{sorb} : ⁵⁷ Fe _{total} ⁵ , %
Vary pH													
Na ⁺ - SWy-2	4.0	PIPPS	⁵⁶ Fe(II)	2.29	2.01	7.10	0.142	12.4	12.6	2.65	33.7	37.3	n.a. ⁶
Na ⁺ - SWy-2	6.0	MES	⁵⁶ Fe(II)	2.25	1.52	18.2	0.363	32.3	56.7	11.9	86.3	65.7	n.a.
Na ⁺ - SWy-2	7.0	MOPS	⁵⁶ Fe(II)	2.29	1.12	29.2	0.584	51.0	70.3	14.8	139	50.7	n.a.
Na ⁺ - SWy-2	7.5	MOPS	⁵⁶ Fe(II)	2.27	0.364	47.7	0.954	84.0	77.7	16.4	227	34.3	n.a.
Vary Fe(II)													
Na ⁺ - SWy-2	7.5	MOPS	⁵⁶ Fe(II)	0.382	0.017	9.29	0.186	97.2	51.8	10.9	44.2	117	n.a.
Na ⁺ - SWy-2	7.5	MOPS	⁵⁶ Fe(II)	1.16	0.212	23.6	0.472	81.7	67.1	14.1	112	59.8	n.a.
Na ⁺ - SWy-2	7.5	MOPS	⁵⁶ Fe(II)	2.27	0.364	47.7	0.954	84.0	77.7	16.3	227	34.3	n.a.
⁵⁷Fe(II) experiments													
Na ⁺ - SWy-2 ⁸	6.0	MES	⁵⁷ Fe(II)	2.30	1.56	11.2	0.225	32.5	55.6 ⁷	n.a.	53.4	n.a.	97.5
Na ⁺ - SWy-2 ⁸	7.5	PIPPS	⁵⁷ Fe(II)	2.41	0.419	29.8	0.596	82.6	65.0 ⁷	n.a.	142	n.a.	99.1
Reduced SWy-2 ⁸	4.0	PIPPS	⁵⁷ Fe(II)	0.348	0.270	1.16 ⁸	0.046	22.2	92.6/100 ⁹	12.6 ⁸	9.2	n.a.	80.6
Reduced SWy-2 ⁸	4.0	PIPPS	⁵⁷ Fe(II)	1.24	0.870	5.52 ⁸	0.221	29.7	92.6/100 ⁹	12.6 ⁸	43.9	n.a.	95.2

550 ¹ Mössbauer spectral area of Fe(II) derived from fitting.

551 ² Structural Fe(II) calculated from Mössbauer Fe(II) area multiplied by the total Fe content of SWy-2 (21.0 μ moles).

552 ³ Ratio of Fe(II) taken up by SWy-2 clay mineral to that of the total Fe content of SWy-2.

553 ⁴ Ratio of calculated moles of structural Fe(II) from Mössbauer Fe(II) area and Fe content of SWy-2 to the amount of Fe(II) taken up from solution by SWy-2.

555 ⁵ Ratio (expressed in percent) of ⁵⁷Fe(II) added through ⁵⁷Fe(II) spike to total system Fe(II), i.e. added ⁵⁷Fe(II)/(added ⁵⁷Fe(II) + SWy-2 ⁵⁷Fe)

556 ⁶ not applicable

557 ⁷ Fe(II)/Fe_{total} here reflects that of both the Fe(II) in the clay mineral as well as sorbed Fe(II), due to the addition of Mössbauer active ⁵⁷Fe(II)

558 ⁸ Experiment conducted in 15 mL buffer. Tabulated masses reflect the reduced volume.
559 ⁹ Fe(II)/Fe_{total} from Mössbauer spectral fitting before/after addition of ⁵⁷Fe(II)
560

561 **Table 2.** Mössbauer parameters for fitted spectra of 2 g/L SWy-2 reacted with $^{56}\text{Fe}(\text{II})$ or ^{57}Fe in
562 25 mM buffer and 50 mM NaCl.

Vary pH, 2.2 mM $^{56}\text{Fe}(\text{II})$

pH (buffer)	Site	CS ^a	(σ) ^b	QS ^c	(σ) ^d	Area	(σ) ^b	reduced χ^2
unreacted	Fe ²⁺	-		-		-		0.57
7.5 (MOPS)	Fe ³⁺	0.42 (0.01)		0.97(0.83)		100		
4.0 (PIPPS)	Fe ²⁺	1.36 (0.05)		2.86 (0.37)		12.6 (1.9)		0.70
	Fe ³⁺	0.46 (0.01)		0.90 (0.71)		87.4 (1.9)		
6.0 (MES)	Fe ²⁺	1.27 (0.004)		3.03 (0.08)		56.7 (1.2)		0.65
	Fe ³⁺	0.38 (0.03)		0.81 (0.48)		43.3 (1.2)		
7.0 (MOPS)	Fe ²⁺	1.28 (0.005)		3.01 (0.24)		70.3 (2.4)		0.59
	Fe ³⁺	0.38 (0.05)		1.57 (1.77)		29.7 (2.4)		
7.5 (MOPS)	Fe ²⁺	1.28 (0.002)		3.01 (0.07)		77.7 (0.8)		0.80
	Fe ³⁺	0.36 (0.03)		0.80 (0.48)		23.3 (0.8)		

Vary $^{56}\text{Fe}(\text{II})$, pH 7.5

Initial [Fe(II)] _{ao}	Site	CS ^a (mm/s)	(σ) ^b	QS ^c (mm/s)	(σ) ^d	Area (%)	(σ) ^b	reduced χ^2
0.4	Fe ²⁺	1.27 (0.00)		3.03 (0.04)		51.8 (0.5)		0.84
	Fe ³⁺	0.46 (0.00)		0.96 (0.69)		48.2 (0.5)		
1.2	Fe ²⁺	1.28 (0.00)		3.01 (0.11)		67.1 (0.9)		0.78
	Fe ³⁺	0.32 (0.03)		0.95 (0.59)		32.9 (0.9)		
2.2	Fe ²⁺	1.28 (0.002)		3.01 (0.07)		77.7 (0.8)		0.78
	Fe ³⁺	0.36 (0.03)		0.80 (0.48)		23.3 (0.8)		

Extractions of SWy-2 reacted with 2.2 mM Fe(II), pH 4.0

Treatment	Site	CS ^a	(σ) ^b	QS ^c	(σ) ^d	Area	(σ) ^b	reduced χ^2
CaCl ₂ extract	Fe ²⁺	1.32 (0.002)		2.92 (0.21)		10.6 (1.3)		0.74
	Fe ³⁺	0.48 (0.008)		0.94 (0.76)		89.4 (1.3)		
PO ₄ extract	Fe ²⁺	1.31 (0.02)		3.01 (0.10)		8.1 (1.0)		0.78
	Fe ³⁺	0.47 (0.05)		1.00 (0.82)		91.9 (1.0)		

Reduced SWy-2, pH 4.0

Treatment	Site	CS ^a	(σ) ^b	QS ^c	(σ) ^d	Area	(σ) ^b	reduced χ^2
Dithionite reduced	Fe ²⁺	1.27 (0.015)		3.01 (0.066)		92.6		0.84
	Fe ³⁺	0.52 (0.03)		0.63 (0.28)		7.4		
Reduced	Fe ²⁺	1.34 (0.00)		3.02 (0.28)		51.5		2.57
SWy-2+ Fe(II)	Fe ²⁺	1.40 (0.00)		3.38 (0.10)		48.5		

^aCenter shift relative to $\alpha\text{-Fe}^0$. ^b Standard deviation due to uncertainty.

^cQuadrupole splitting. ^d Standard deviation of QS from Gaussian distribution of QS parameter used in model.

565 **Table 3.** Fe(II) sorption and sequential extraction data for Fe(II)-reacted clay mineral SWy-2.

pH	aqueous			1M CaCl ₂ extract		1M NaH ₂ PO ₄ extracted (pH 5.0)					total recovery	
	initial Fe(II) (μmol)	final Fe(II) (μmol)	sorbed Fe(II) (μmol) ^a	Fe(II) (μmol)	% of sorbed ^b	Fe(II) (μmol)	Fe(III) (μmol) ^c	Fe(tot) (μmol)	% sorbed ^c	% of sorbed	% of sorbed	% of sorbed
4.0	34.1	28.1	6.03	4.82	80	0.036	0.298	0.335	5.5		85	
4.0, ⁵⁶ Fe ^d	33.3	29.0	4.30	3.13	73	0.042	0.211	0.253	5.9		79	
6.0	33.8	22.1	11.7	6.91	59	0.205	0.508	0.713	6.1		65	
7.5	33.6	13.2	20.4	2.49	12	11.9	0.545	12.4	61		73	

^a Calculated as the difference between initial Fe(II) and final Fe(II). ^bCalculated as the ratio of Fe(II) or Fe(tot) to the sorbed amount of Fe(II). ^cCalculated from the difference of Fe(tot) and Fe(II). ^dMeasured on 50 mg SWy-2 sample spiked with ⁵⁶Fe(II) in 25 mL buffer. The amounts of Fe were calculated from Fe concentrations in 15 mL volume to be consistent with other extractions shown here. Mössbauer data shown in **Figure 6**.

Low Fe
clay mineral

ET through
basal planes

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Supporting Information

Fe(II) - Fe(III) electron transfer in a clay mineral with low Fe content

Drew E. Latta^{1,*}, Anke Neumann², W.A.P.J. Premaratne³, Michelle M. Scherer¹

¹ Department of Civil and Environmental Engineering, 4105 Seamans Center, The University of Iowa, Iowa City, IA 52242 USA

² School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, NE1 7R, UK

³ Department of Chemistry, University of Kelaniya, Kelaniya, 11600 Sri Lanka

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*Corresponding author

CONTENTS.

Figure S-1. Comparison of Mössbauer spectra of SWy-2 reacted with 2 mM Fe(II) for 2 h and 57 days.

Figure S-2. Plot of Mössbauer spectra derived Fe(II):Fe(total) content of SWy-2 as a function of Fe(II) sorption.

Figure S-3. Mössbauer temperature profile of SWy-2 reacted with 2 mM Fe(II).

Table S-1. Mössbauer spectral fitting results for temperature profile data.

Section S-1. Discussion of the procedure used to verify the selectivity of the sequential extractions.

Table S-2. Sequential extractions of Fe(II) from Syn-1.

Figure S-4. Mössbauer spectra of Syn-1 + ⁵⁷Fe(II) subjected to sequential extractions.

Table S-3. Mössbauer spectral fitting results of Syn-1 + ⁵⁷Fe(II) from sequential extractions.

Section S-2. Discussion of the formation of secondary precipitates in the SWy-2 + Fe(II) system.

Figure S-5. X-ray diffraction data of SWy-2 before and after reaction with 2 mM Fe(II).

Figure S-6. Mössbauer spectra of SWy-2 reacted with 2 mM ⁵⁷Fe(II) showing the fate of added Fe(II) after electron transfer and secondary mineralization.

Table S-4. Mössbauer spectral fitting results of SWy-2 reacted with ⁵⁷Fe(II).

Figure S-1. Mössbauer spectra profiles for SWy-2 reacted with 2.2 mM $^{56}\text{Fe}(\text{II})$ for 2 hours (red) and 57 days (blue). Conditions are 2 g/L SWy-2 clay mineral in 25 mM MOPS (pH 7.5) and 50 mM NaCl.

Figure S-2. Plot of Mössbauer spectra derived Fe(II):Fe(total) content of SWy-2 as a function of Fe(II) sorption. Data from both varying pH and Fe(II) concentration experiments are plotted as one curve. The blue cross represents data on SWy-2 from Soltermann et al. (2014).¹

Figure S-3. Mössbauer spectroscopy temperature profiles for SWy-2 reacted with 2.2 mM $^{56}\text{Fe}(\text{II})$. Conditions are 2 g/L SWy-2 clay mineral in 25 mM MOPS (pH 7.5) and 50 mM NaCl. Mössbauer spectral fitting parameters are reported in **Table S-1**.

Table S-1: Mössbauer parameters for fitted spectra collected as a function of temperature for 2 g/L SWy-2 reacted with 2.2 mM $^{57}\text{Fe}(\text{II})$ in pH 7.5 25 mM MOPS and 50 mM NaCl.

Temperature (K)	Site	CS ^a (σ) ^b (mm/s)	QS ^c (σ) ^d (mm/s)	Area (σ) ^b (%)	reduced χ^2
140	Fe ²⁺	1.24 (0.00)	2.99 (0.09)	72.9 (0.7)	0.85
	Fe ³⁺	0.35 (0.02)	0.76 (0.49)	27.1 (0.7)	
77	Fe ²⁺	1.27 (0.00)	3.02 (0.06)	73.8 (0.9)	0.73
	Fe ³⁺	0.34 (0.03)	0.76 (0.48)	26.2 (0.9)	
13	Fe ²⁺	1.28 (0.00)	3.01 (0.10)	75.8 (0.8)	0.77
	Fe ³⁺	0.35 (0.03)	0.82 (0.51)	24.2 (0.8)	

^aCenter shift relative to $\alpha\text{-Fe}^0$. ^b Standard deviation due to uncertainty.

^c Quadrupole splitting.

^d Standard deviation of QS from Gaussian distribution of QS parameter used in model.

^e Standard deviations of Fe²⁺ sites CS are < 0.003 mm/s.

Section S-1. Verification of the selectivity of the sequential extraction procedure

Methods

To verify the selectivity of the sequential extraction applied here and elsewhere,^{2,3} we used Fe-free montmorillonite Syn-1 (structural formula $\text{Na}_{0.024}(\text{Al}_{4.44}\text{Mg}_{0.04}\text{Fe}_{\text{tr}})(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_4$).⁴ We reacted 30 mg Na^+ -homoionized Syn-1 with 15 mL of approximately 1 mM $^{57}\text{Fe}(\text{II})$ solution buffered with 25 mM HEPES buffer at pH 7.5 and containing 50 mM NaCl. After centrifugation (swing bucket, 5000 rpm, 15 min), we subjected the solid to the sequential extraction procedure and analyzed all aqueous solutions and extracts for Fe(II) and Fe(tot) using the 1,10-phenanthroline method. After each centrifugation, we acquired a Mössbauer spectrum of the remaining solid. In addition, one set of reactors was prepared that additionally contained 0.5 M CaCl_2 . In this case, only the second extraction step (with NaH_2PO_4) was carried out.

Critically, we did not use any plastic (centrifuge) tubes during any of these experiments and the glass reactors were crimp-sealed with Teflon stoppers during reaction, extraction, and centrifugation. This procedure was intended to minimize Fe(II) oxidation by residual plastic-sorbed oxygen and/or oxygen intrusion during cycling of the glovebox' antechamber when transferring the reactors from the centrifuge into the glovebox.

The methods for clay mineral preparation, centrifugation, sequential extraction, 1,10-phenanthroline analysis, and Mössbauer sample preparation and analysis are described in the main manuscript.

Results and Discussion

In our previous work, we applied a sequential extraction procedure to selectively remove Fe(II) sorbed to clay mineral basal surfaces with CaCl_2 and, in a subsequent step, used NaH_2PO_4 to extract the remaining Fe(II) sorbed to clay mineral edge OH groups. We tested this extraction procedure using Fe-free montmorillonite Syn-1 to ensure that Fe(II) was sorbing to the clay mineral in the absence of interfacial electron transfer. We then combined Mössbauer spectroscopy and aqueous analysis of the extracts to demonstrate that CaCl_2 did indeed only remove basal Fe(II) and edge sorbed Fe(II) was quantitatively removed in the NaH_2PO_4 extraction.³

We note however, that the total Fe(II) recoveries after both extraction steps were reported previously as ranging from 54% to 169% (**Table S-2**), which might suggest to the critical reader that the overall procedure was not quantitative and/or selective. However, the very high recovery reported for Fe(II) sorbed at Syn-1 at pH 4 (169%) was mainly due to the very large variation in initial sorbed Fe(II) relative to the overall sorbed, small quantity of Fe(II) ($1.43 \pm 1.17 \mu\text{mol}$, **Table S-2**), which results in an uncertainty of the overall Fe(II) recovery of $\pm 86\%$. In all other experiments, much higher Fe(II) amounts sorbed and the variations were much smaller and usually $< 0.5 \mu\text{mol}$, suggesting that the reported Fe(II) recovery exceeding 100% was an outlier. In addition, no additional Fe was mobilized from the Syn-1 structure because Mössbauer analysis before Fe(II) sorption (as well as after the sequential extraction) demonstrated the absence of Fe in the clay mineral (**Figure S-1** in Neumann et al, 2013).³

In contrast, the low Fe(II) recoveries after reaction of Fe(II) with Syn-1 at pH 7.5 in combination with the high proportion of Fe(III) recovered in the NaH_2PO_4 extraction step indeed suggest problems with net oxidation of our sorbed and/or aqueous Fe(II). We noted in our previous manuscript that the most probable source of oxidation was the use of plastic centrifuge

tubes and repeated exposure of the centrifuge tubes to cycles of glovebox transfers. To confirm this hypothesis, we carried out the same experiments as described previously using sturdy glass vials that were sealed with Teflon lined rubber stoppers for both experiments and centrifugation. Indeed, the overall Fe(II) recovery in this study was $103 \pm 13\%$ (previously: $55 \pm 11\%$) and only minor amounts of Fe(III) were observed in the extracts ($0.16 \mu\text{mol}$, or 3.5% of sorbed Fe, **Table S-2**). Furthermore, the relative amount of oxidized Fe recovered (3.5%) is in agreement with the relative area of Fe(III) in the Mössbauer spectrum obtained after Fe(II) sorption to Syn-1 at pH 7.5 (1.5% , **Table S-3, Figure S-4A**), suggesting that the extraction procedure did not introduce net oxidation of Fe(II). Further confirmation for this conclusion comes from a mass balance calculation using both Mössbauer relative areas and measurements of recovered Fe of the CaCl_2 extracted Syn-1. Although the relative area of Fe(III) increased from 1.5% to 14.8% in the Mössbauer spectrum after CaCl_2 extraction (**Table S-3, Figure S-4B**), $2.9 \mu\text{mol}$ of Fe(II) were removed from the solid sample in this step (**Table S-2**). Thus, only $1.64 \mu\text{mol}$ Fe remained in the sample that was analyzed with Mössbauer spectroscopy. Taking into account the relative amount of Fe(III) in the CaCl_2 extracted sample (14.8%) and the remaining Fe content ($1.64 \mu\text{mol}$), we calculated the absolute amount of Fe(III) as $0.24 \mu\text{mol}$, which represents 5.3% of the initially sorbed Fe and is in agreement with the overall recovered 3.5% Fe(III) as well as the initially observed Fe(III) content of 1.5% . In conclusion, we are confident that our extraction procedure does not lead to net oxidation of Fe(II).

To verify the selectivity of the extraction procedure, we monitored the two distinctive Fe(II) components in the Syn-1 Mössbauer spectrum during the extraction procedure.³ We assigned the Fe(II) doublet with the unusual large center shift (CS) and quadrupole split (QS) which was absent after extraction with CaCl_2 to Fe(II) sorbed at basal surfaces (**Table S-3, Figure S-4**). Note that the basal plane sorbed Fe(II) needs to be fitted with two components (see pH 4.0 data in Table S-3), of which one has Mössbauer hyperfine parameters closer to edge-bound Fe(II), making it impossible to resolve this second basal component from the edge component at pH 7.5, where these two contributions overlap. We therefore do not compare the relative areas of basal and edge Fe(II) components at pH 7.5 directly to the wet chemical extraction data but rather use the Mössbauer data as direct evidence for the presence or absence of basal and edge sorbed Fe(II) at clay minerals. The Fe(II) doublet remaining after the CaCl_2 extraction was removed in the subsequent NaH_2PO_4 extraction and had values for CS and QS that were similar to those generally observed for Fe(II) on or in minerals. Due to the absence of structural Fe in Syn-1, we assigned this Fe(II) doublet to be indicative of Fe(II) sorbed to clay mineral edge OH groups.

Here, we also conducted an experiment, in which 0.5 M CaCl_2 was present during the reaction of Syn-1 with aqueous Fe(II) at pH 7.5. In the Mössbauer spectrum of the resulting solid (**Figure S-4D**), only the doublet for edge OH group bound Fe(II) was present, suggesting that Ca^{2+} outcompeted Fe(II) for sorption to Syn-1 basal planes. Similarly, we tested the NaH_2PO_4 extraction for its specificity for edge bound Fe(II) in experiments with Fe(II)-reacted Syn-1 at pH 7.5. Both aqueous extraction data (**Table S-2**) and Mössbauer spectrum (**Figure S-4E**) demonstrate that both basal and edge bound Fe(II) were removed in a one-step NaH_2PO_4 extraction. Basally bound Fe(II) was most likely exchanged for Na^+ , which was present in high concentrations compared to Fe(II) (1 M vs 0.44 mM , respectively). We thus conclude that our extraction procedure is selective when applied sequentially.

Table S-2. Sequential extraction data from Syn-1 reactors.

experiment	Aqueous			CaCl ₂ extracted				NaH ₂ PO ₄ extracted				Total recovery
	initial Fe(II)	final Fe(II)	Sorbed Fe(II) ^a	Fe(II)	Fe(III) ^b	Fe(tot)	% of sorbed	Fe(II)	Fe(III) ^b	Fe(tot)	% of sorbed	% of sorbed
	μmol	μmol	μmol	μmol	μmol	μmol	%	μmol	μmol	μmol	%	%
Syn-1, pH 4.0 (published ^c)	17.11(0.60)	15.68(0.57)	1.43(1.17)	2.39(0.05)	n.d.	2.37(0.05)	168	0.01(0.00)	0.06(0.01)	0.07(0.01)	1	169(86)
Syn-1, pH 7.5 (published ^c)	17.42(0.22)	8.06(0.18)	9.35(0.40)	2.65(0.06)	n.d.	2.64(0.07)	28	1.03(0.20)	1.43(0.77)	2.46(0.57)	26	55(11)
Syn-1, pH 7.5 (this study)	17.49(0.21)	12.95(0.20)	4.54(0.38)	2.90(0.12)	n.d.	2.80(0.02)	64	1.60(0.01)	0.16(0.19)	1.76(0.18)	39	103(13)
Syn-1, pH 7.5 (+CaCl ₂)	12.91	9.41	3.49									
Syn-1, pH 7.5 (this study)	13.10	6.52	6.58	N/A	N/A	N/A	N/A	6.62	n.d.	6.52	101	101

^asorbed Fe(II) was calculated as difference between initial and final Fe(II). ^bAmount of Fe(III) was calculated as the difference between the measured amounts of Fe(tot) and Fe(II). ^cData from publication Neumann et al., 2013.

Figure S-4. Mössbauer spectra of Syn-1 reacted with $^{57}\text{Fe}(\text{II})$ at pH 7.5, showing two Fe(II) doublets with characteristic parameters for basal (blue) and edge (red) sorbed Fe(II) (A). After extraction with CaCl_2 (B), the Fe(II) doublet for basal Fe(II) was removed, suggesting removal of basal sorbed Fe(II) in the extraction. The remaining edge bound Fe(II) was removed in the subsequent extraction with NaH_2PO_4 (C). The selectivity of CaCl_2 for basal planes is demonstrated in the experiment where CaCl_2 was present during the Fe(II) sorption step (D) and the complete removal of both Fe(II) doublets when the NaH_2PO_4 extraction was carried out without prior CaCl_2 extraction (E).

Table S-3. Mössbauer parameters for fitted Syn-1 spectra.

Sample name	Site	CS ^a mm/s	QS ^b (σ) ^c mm/s	Area(σ) ^d %	reduced χ ²
Syn-1, pH 4.0					
Fe(II)-reacted (published ^e)	basal Fe(II) 1	1.40	3.38(0.24)	75.7(9.0)	0.78
	basal Fe(II) 2	1.40	2.87(0.44)	24.3(9.1)	
refitted ^f	basal Fe(II)	1.40	3.25(0.37)	100	0.78
Syn-1, pH 7.5					
(published ^e) Fe(II)-reacted	basal Fe(II)	1.43	3.38(0.24)	36.1(0.3)	6.99
	edge Fe(II)	1.33	2.71(0.38)	61.7(0.3)	
	Fe(III)	0.33	0.77(0.09)	2.2(0.3)	
CaCl ₂ extracted	edge Fe(II)	1.28	2.67(0.35)	76.8(0.3)	6.41
	Fe(III)	0.33	0.75(0.40)	23.2(0.3)	
Syn-1, pH 7.5					
Fe(II)-reacted	basal Fe(II)	1.43	3.31(0.23)	29.3(0.3)	8.15
	edge Fe(II)	1.31	2.75(0.44)	69.2(0.3)	
	Fe(III)	0.36	0.69(0.04)	1.5(0.0)	
CaCl ₂ extracted	edge Fe(II)	1.28	2.64(0.36)	85.2(0.1)	8.26
	Fe(III)	0.31	0.77(0.21)	14.8(0.1)	
Syn-1, pH 7.5					
(+CaCl ₂) Fe(II)-reacted	edge Fe(II)	1.28	2.66(0.38)	93.5(0.1)	34.88
	Fe(III)	0.28	0.77(0.18)	6.5(0.1)	

^aCenter shift relative to α -Fe⁰. ^bQuadrupole splitting. ^cStandard deviation of QS from Gaussian distribution of QS parameter used in model. ^dStandard deviation due to uncertainty. ^eNeumann et al, 2013.³ ^fUsing a weighted average of the parameters of the two populations previously published.

Section S-2. Formation of secondary precipitates in SWy-2 + Fe(II) systems.

In order to test whether the observed SWy-2 Fe(II) doublets came from structural Fe(II) within SWy-2 or from secondary precipitates formed from the added Fe(II) we collected X-ray diffraction data on the Fe(II)-reacted SWy-2 (**Figure S-5**). We did not observe formation of any macroscopically ordered layered double hydroxide type phases or Fe(III) oxides, as have been shown to form upon reaction of Fe(II) with clay minerals.⁵⁻⁸ Furthermore, we did not observe peaks at 10-11 Å indicative of the transformation of smectite to illite.⁹

Because we did not observe macroscopically ordered Fe(II) or Fe(III) phases other than SWy-2 in XRD, we further characterized the products formed through sorption and electron transfer between Fe(II) and SWy-2 by using a spike of ⁵⁷Fe(II). Here, we added 2.2 mM ⁵⁷Fe(II) to a suspension of 2 g/L SWy-2 in pH 6.0 and pH 7.5 buffers. Addition of this spike resulted in 97.5% and 99.1% of the solid ⁵⁷Fe coming from the ⁵⁷Fe(II) through sorption and/or oxidation processes (**Table 1**). The observed Mössbauer spectrum therefore is highly dominated by the added ⁵⁷Fe, and we considered ⁵⁷Fe in the SWy-2 solids negligible during fitting.

The resulting Mössbauer spectra of SWy-2 + ⁵⁷Fe(II) were modeled as 4 separate spectral components, comprising an Fe(III) sextet, an Fe(III) doublet, and two Fe(II) doublets (**Figure S-6** and **Table S-4**). The Fe(III) sextet in both the pH 6.0 and pH 7.5 spectra has similar parameters (CS = 0.49 mm/s, 2ε = -0.10 mm/s, H = 38 to 41 T) and comprised 44 and 35% of the total area, respectively (**Table S-4**). The observed Mössbauer parameters are consistent with those of ferrihydrite,^{10,11} and are also consistent with the lack of a crystalline Fe(III) phase in the XRD pattern (e.g. lepidocrocite or goethite). The solids from the pH 6.0 and 7.5 reactors had different amounts of a paramagnetic Fe(III) doublet (10 and 17%, respectively) both having different Mössbauer parameters (**Table S-4**). The nature of these doublets is difficult to interpret given the multitude of Fe(III) phases that can have similar parameters.¹²

The two Fe(II) doublets of SWy-2 reacted with ⁵⁷Fe(II) at both pH 6.0 and pH 7.5 are both different from each other and from that of the ⁵⁶Fe(II) reacted SWy-2. The pH 6.0 Fe(II) doublets make up 46% of the total area, with one having a high CS = 1.40 mm/s and a high QS = 3.42 mm/s and comprising 32% of the total area. This doublet is similar to that of basally sorbed Fe(II) on Syn-1 that is removed by CaCl₂ as discussed above (**Table S-3**) and also similar to a doublet observed for pre-reduced SWy-2 reacted with ⁵⁷Fe(II) at pH 4.0 (**Figure 5**, **Table 2**). The second Fe(II) doublet (14% of the total area) in the pH 6.0 spectrum has a moderate CS = 1.36 mm/s and a moderate QS = 3.00 mm/s similar to one of the doublets of ⁵⁷Fe(II) sorbed to reduced SWy-2 at pH 4.0 (CS = 1.34 mm/s, QS = 3.02 mm/s, **Table 2**) and is tentatively assigned to frozen aqueous Fe(II).¹³

The Fe(II) doublets of the pH 7.5 samples include a very high CS (1.54 mm/s) and high QS (3.15 mm/s) doublet (4% of the total area) different from all other Fe(II) doublets overserved in this study, and of unknown character. The second doublet has parameters (CS = 1.27 mm/s, QS = 2.77 mm/s, **Table S-4**) that are close to edge-sorbed Fe(II) on Syn-1 (**Table S-3**) as well as comparable with chloride green rust (average CS = 1.30 mm/s, QS = 2.74 mm/s)¹⁴. Furthermore the Fe(III) doublet of the pH 7.5 sample (CS = 0.49 mm/s, QS = 0.45 mm/s) is similar to that of green rusts, and the Fe(II):Fe(III) ratio of 2.5 is close to the reported values for green rusts.¹⁴ Taken with the observed green color of the SWy-2 suspension after reaction with Fe(II) at pH 7.5 (only), we cannot rule out the formation of a green rust-like precipitate in these systems. However, given the difference in Mössbauer parameters of the ⁵⁶Fe(II) reacted SWy-2 and the parameters of ⁵⁷Fe(II)-reacted SWy-2, we conclude that we are observing different phases when the added Fe(II) is Mössbauer invisible (⁵⁶Fe(II)) compared to Mössbauer active (⁵⁷Fe(II)).

Therefore, given the difference in parameters observed based on the isotope of Fe(II) added and the similarity of $^{56}\text{Fe(II)}$ -reacted SWy-2 Mössbauer parameters to dithionite reduced SWy-2 parameters, we confirmed that the majority of Fe we observed in the $^{56}\text{Fe(II)}$ reacted SWy-2 systems is structural Fe(II). For the pH 7.5 data, we suspect that a green rust-like precipitate could form through a reaction between aqueous Fe(II) and Fe(III) produced from electron transfer between Fe(II) and SWy-2.

Figure S-5. X-ray diffraction patterns of hydrated SWy-2 suspended in (A) pH 7.5 MOPS buffer without Fe(II), (B) pH 7.5 MOPS buffer with 2 mM Fe(II), (C) pH 6.0 MES buffer with 2 mM Fe(II), and (D) a chloride green rust standard¹⁵. All samples were preserved in glycerol, giving the broad peak at ~30 degrees.

Figure S-6. Mössbauer spectra of 2 g/L SWy-2 reacted with 2.2 mM $^{57}\text{Fe}(\text{II})$ in (A) pH 6.0 25 mM MES and (B) pH 7.5 25 mM MOPS buffers with 50 mM NaCl.

Table S-4. Mössbauer parameters for fitted spectra of 2 g/L SWy-2 reacted with 2.2 mM $^{57}\text{Fe}(\text{II})$ in pH 6.0 25 mM MES and pH 7.5 25 mM MOPS and 50 mM NaCl.

Sample – Temp. (K)	Component	CS ^a (σ) ^b (mm/s)	QS ^c or 2 ϵ (σ) ^d (mm/s)	Hyperfine field, H (Tesla)	$\sigma(\text{H})$ ^e (Tesla)	Area (σ) ^b	χ^2
pH 6.0 – 17K	Fe ²⁺ site 1	1.40 (0.004)	3.42 (0.13)	-	-	32.0 (3.6)	1.2
		1.36 (0.007)	3.00 (0.28)	-	-	13.8 (4.0)	
	Paramagnetic Fe ³⁺	0.52 (0.02)	0.68 (0.37)	-	-	9.7 (1.2)	
		0.49 (0.01)	-0.10	40.5	11.5	44.4 (3.1)	
	Fe ³⁺ sextet						
pH 7.5 – 18K	Fe ²⁺ site 1	1.54 (0.008)	3.15 (0.12)	-	-	4.2 (0.2)	2.76
		1.27 (0.001)	2.77 (0.22)	-	-	43.3 (0.3)	
	Paramagnetic Fe ³⁺	0.49 (0.002)	0.45 (0.14)	-	-	17.4 (0.2)	
						35.0 (0.3)	
	Fe ³⁺ sextet	0.48	-0.10	37.8	14.3		

^aCenter shift relative to $\alpha\text{-Fe}^0$. ^b Standard deviation due to uncertainty.

^c Quadrupole splitting.

^d Standard deviation of QS from Gaussian distribution of QS parameter used in model.

^e Standard deviation of Gaussian distribution of hyperfine field.

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