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REDUCTION OF NITROAROMATIC COMPOUNDS BY IRON(II) REDUCED
CLAY MINERALS

by
Tyler Lee Olson

A thesis submitted in partial fulfillment
of the requirements for the Master of
Science degree in Civil and Environmental Engineering
in the Graduate College of
The University of Iowa

August 2014

Thesis Supervisor: Professor Michelle M. Scherer

Graduate College
The University of Iowa
Iowa City, Iowa

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's thesis of

Tyler Lee Olson

has been approved by the Examining Committee
for the thesis requirement for the Master of Science
degree in Civil and Environmental Engineering at the August 2014
graduation.

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Michelle M. Scherer, Thesis Supervisor

David M. Cwiertny

Drew E. Latta

To my parents and my brother

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Background

Clay minerals are the most abundant and chemically active parts of the surface mineral world of Earth (Velde, B., 1995). Many types of clay minerals are ubiquitous in the environment and often contain iron in their structure. Structural Fe(II) resulting from chemical and microbial reduction of iron-bearing clay minerals has been shown to reduce a variety of contaminants (Buerge et al, 1999; Neumann et al., 2009; Hofstetter et al, 2006). Understanding how reduced clay minerals could impact environmental contaminants may lead to improved methods regarding contaminant monitoring and remediation.

Clay minerals are classified as clays. However not all clays are clay minerals. The term “clay” is generally referring to the small fine grained particles of some type of earth material. However the term “clay mineral” is more specific in that it refers to a clay that originated from the weathering of rocks. Most clay minerals are found near the surface of the Earth such as in river beds, soils, and ocean floors. There are several types of clay minerals that exist. Among the most common groups classified as clay minerals are kaolinite, illite, and smectite. Kaolinite group includes the clay mineral kaolin which is a major component used in pottery. Illite group is generally found amongst marine environments. The smectite group includes the classes of clay mineral such as bentonite, nontronite, and montmorillonite. These classes of the smectite group are known for their expansion in volume due to sorption of water (sometimes referred to “swelling”). Many water bodies that are made artificially are lined with clay such as bentonite to expand and seal the liners more efficiently.

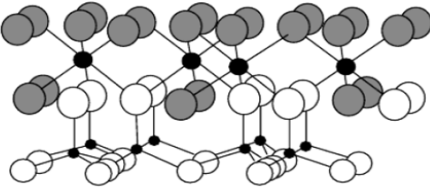
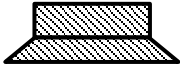
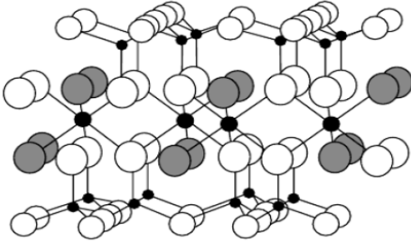
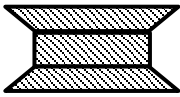
Clay Mineral Chemistry

The clay mineral class of nontronite in the smectite group is the clay mineral focused on within this research. Nontronite is a ferric mineral with minor substitutions of either aluminum or magnesium cations within the clay mineral structure (Velde, B., 2005). Like all smectite clay minerals, nontronite has an overall low charge which allows polar ions (including hydrated) to be absorbed between different sheets of clay mineral structures (Velde, B., 2005). This characteristic is observable as the clay mineral can “swell” in size when hydrated with water. In the smectite group, it should be noted that there are two types of structural form. The two types of structural form are 1:1 and 2:1 layer types as illustrated in Figure 1-1. The 1:1 layer type consists of one tetrahedral plane adjacent to an octahedral plane. A 2:1 layer type consists of an octahedral plane between two tetrahedral planes. In the tetrahedral plane, the majority of the layer is built of interlinked tetrahedral units of a central silicon ion with bonded oxygen atoms with minor presence of a metal ion in place of the silicon ion (Velde, B., 1995). The octahedral layer is mostly made of octahedral units of a central metal ion bonded to either oxygen atoms or hydroxyl groups (Velde, B., 1995).

Contaminate Removal Mechanism by Structural Iron

The metal cation within the octahedral layer of the smectite group can be an iron cation. This iron can either exist as Fe(III) or Fe(II) where the Fe(II) form is considered the reduced form of the complexed iron and the Fe(III) is the oxidized form. It has been shown in previous studies that reduced clay (containing structural Fe(II)) can reduce environmental contaminants (Buerge et al, 1999; Neumann et al., 2009; Hofstetter et al, 2006). In the environment an oxidized clay mineral (containing structural Fe(III)) can be reduced by microbial action. (Stucki et al, 1987). Once the clay mineral is reduced it has

the capacity to reduce an environmental contaminant. Thus, the iron can then be reduced again and continue to reduce other environmental contaminants. The iron has the ability to be considered a renewable electron donor for a variety of contaminants. As a theoretical example, shown in Figure 1-2, some forms of microbial respiration can reduce clay minerals in which the clay mineral can reduce a variety of environmental contaminants.

Smectite Layer Types		
Layer Classification	Structural Form	Representative Figure
1:1 Layer Type		
2:1 Layer Type		

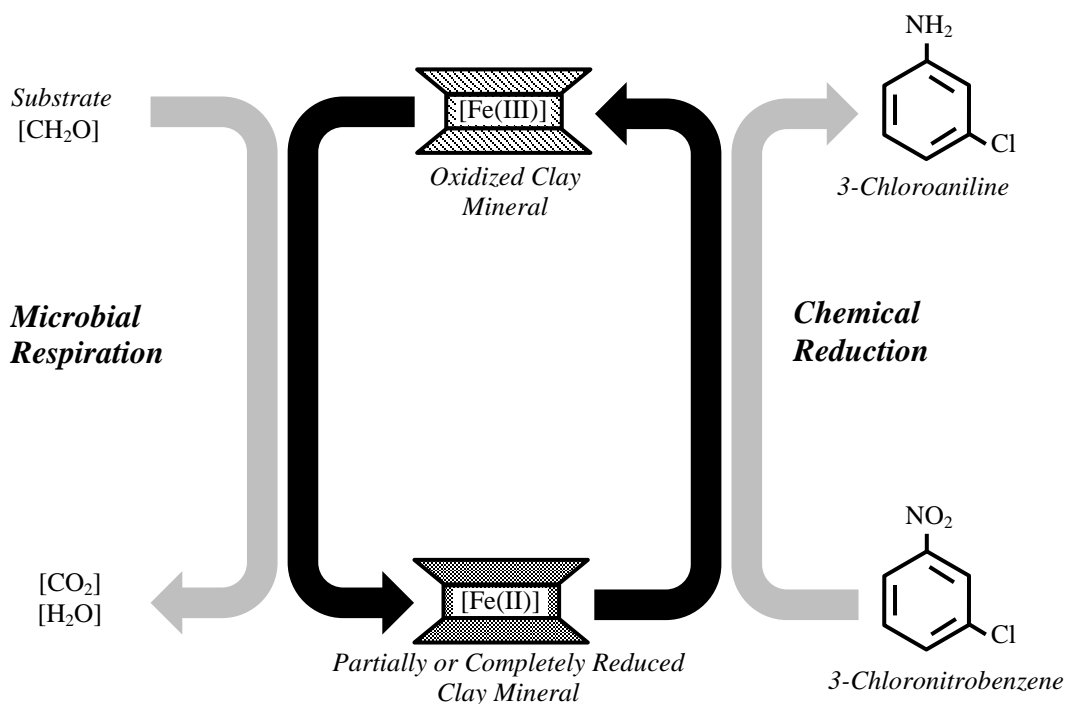
Adapted from Sposito, Garrison (2008)

Figure 1-1. Smectite group layer types with respect to its “ball and stick” molecular form.

The small hollow circles represent oxygen atoms, the large filled circles represent the hydroxyl groups, the small filled circles are indicating central tetrahedral ion, and the medium sized filled in circles indicate the octahedral central metal ion. The representative figures are simple illustrations used to symbolize either a 1:1 or 2:1 layer type.

Iron Biogeochemical Cycle

-A Theoretical Example with Clay Minerals and Nitroaromatic Compounds-



Adapted from Klausen et al. (1995) ES&T

Figure 1-2. Iron reduction and oxidation cycle with biological reduction of the clay mineral and reduction of a contaminant (nitroaromatic compound presented for an example)

However, growing microorganisms in the laboratory may not be a good experimental model as microbes could grow and respire at different rates within a testing time frame. Therefore, many studies utilize chemical reducing agents such as sodium dithionite to reduce clays to maintain a consistent testing environment (Hofstetter et al, 2008; Stucki et al. 2006, Neumann et al. 2008). Using chemical reducing agents can result in a more controlled reduction of the clay minerals.

Previous research has shown that using aqueous Fe(II) (dissolved iron in the Fe(II) form) which sorbes to a nontronite clay mineral, can reduce the iron within the clay mineral structure (Neumann, 2013; Schaefer et al, 2011). In this study, the reductant aqueous Fe(II) is used to reduce the clay mineral at different pH values. It was determined that at pH values between 4.0 and 6.0 the aqueous Fe(II) sorbed to the basal planes of the clay mineral NAu-1 (basal planes are the outer surface layer of the clay mineral structure, predominately adjacent to the tetrahedral layers). At higher pH values such as 7.5 the aqueous Fe(II) sorbes to both the OH-edge hydroxyl groups and basal planes (See Appendix A for figures and more details). With more Fe(II) sorbed to the clay mineral at higher pH values, the clay mineral was reduced more than compared to the same clay mineral at lower pH values (Appendix A).

Hypotheses

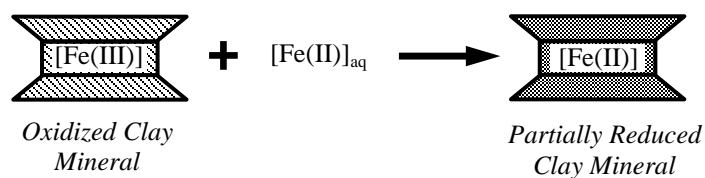
It has been reported that clay minerals can be reduced at different pH values and can exhibit different extent of reduction (Neumann, 2013). It has also been shown that pH effects the efficiency of contaminant reduction by reduced clay minerals (Grundl et al., 2000). However, it is unclear if a nontronite N_{Au}-1 could be reduced by Fe(II) sorbed to the clay mineral could affect the reduction of nitroaromatic compounds. Furthermore, does the aging of the reduced clay mineral (aging refers to the length of time a reduced clay mineral has to equilibrate with its surrounding) affect the reduction rate of the nitroaromatic compound? To address this knowledge gap, several hypotheses are formulated to investigate:

Hypothesis 1: An Fe(II)-reduced clay mineral is capable of reducing nitroaromatic compounds (Figure 1-3).

Hypothesis 2: The rate of reduction of nitroaromatic compounds by Fe(II)-reduced clay minerals is pH dependent.

Hypothesis 3: Extent of time a clay mineral is “aged” in an Fe(II)-free solution will impact the rate of nitroaromatic compound reduction by Fe(II)-reduced clay mineral.

Phase 1: Clay Mineral Reduction



Phase 2: Reduction of Nitroaromatic Compound

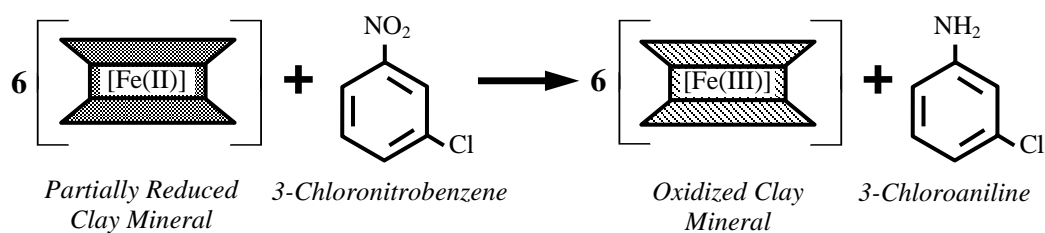


Figure 1-3: Theoretical depiction of the reduction of the structural Fe(III) in the clay mineral by aqueous Fe(II) (Phase 1). The partially reduced clay mineral can then reduce the nitroaromatic compound by a 6:1 (Fe(II) : nitroaromatic compound) ration based off of electron equivalence.

CHAPTER II

MATERIALS AND METHODS

Materials

Chemicals

Buffer solutions of 25 mM are made from buffer salts obtained from RPI Corporation. For the each pH buffer of 4.0 and 7.5 the buffer salts used were PIPPS and HEPES respectively. For the pH 6.0 buffer a buffer salt of MES is utilized. Buffered solutions are adjusted with either 1 M HCl or 1 M NaOH where HCl is a qualified trace metal grade provided by Fisher Scientific and the NaOH salt provided by Sigma Aldrich. The nitroaromatic compounds of 3-chloronitrobenzene and 3-chloroaniline are provided from Acros Organics. Aqueous Fe(II) natural abundance and aqueous $^{56}\text{Fe}(\text{II})$ isotopically fractionated are created with iron power certified by Isoflex. All other chemicals are either provided by RPI, Sigma Aldrich, and Fisher Scientific. All glassware is cleaned prior to use by soaking in 2M HCl for at least 18 hours and rinsed with de-ionized water. HDPE 30 mL tubes are also cleaned prior to use by soaking in 2M HCl for at least 18 hours and rinsed with de-ionized water with the added step of soaking the tubes in a dilute Contrad detergent solution for at least 24 hours in which followed a rising of de-ionized water.

De-ionized water is processed on site with a Barnstead di-ionization system in which the final product has a measured resistivity of at least 18.2 M Ω -cm to define its purity.

Environment

The kinetic experiments took place inside an anoxic glove box in which the environment within the enclosed glove box is maintained between 6% and 7% hydrogen gas and the remainder gas percentage was of nitrogen gas. All solutions utilized inside the anoxic environment are deoxygenated by purging the solutions with nitrogen gas. All solutions under 0.5 L are purged with nitrogen for at least one and a half hours and solutions between 0.5 L and 1.0 L in volume are purged for at least two hours. After purging, the solutions are immediately transferred to the anoxic environment without exposure to the atmosphere. Solid materials, such as the clay mineral, are allowed to equilibrate with the anoxic environment for at least 48 hours.

Clay and Clay Mineral Size Fractionation

The overall purpose for size fractionating the clay mineral is to purify the clay mineral, or more specifically, remove impurities such as kaolin, iron oxides, silica, and quartz. At smaller particle sizes, the presences of many of the impurities are removed during centrifuging. Centrifuging also removes particles that form less stable suspensions in comparison to the swelling clay minerals. The clay mineral of choice is Nontronite NAu-1 (a ferruginous smectite) which originated from the Uley Graphite Mine in the south central area of Australia. Clay mineral NAu-1 was provided by E. O'Loughlin of Argonne National Laboratory. The processes used to size fractionate the clay mineral was created by Anke Neumann of Newcastle University, UK after procedures outlined by Jackson, M.L., 1956. The process of clay mineral grinding is adapted from Keeling et al, 2000.

The raw clay mineral is first broken up with a hammer into small pieces. The broken up NAu-1 is then dried in an oven at 105°C for at least 12 hours. The clay mineral

is then ground into a fine power by using a tungsten carbide disc mill located in room 121 Trowbridge Hall of the University of Iowa. Grinding consists of loading 50 grams of clay mineral evenly into the clean grinding disk assembly. Grinding takes ten minutes to pulverize the clay mineral to a fine power. Cleaning of the tungsten carbide disc mill is done in-between clay mineral loadings to maintain cleanliness and to cool down the mill disks to prevent heat buildup. Cleaning consists of running the mill with a small volume of quartz sand to remove residual clay mineral particles in the mill, followed by wiping the tungsten carbide discs with de-ionized water and acetone to remove excess moisture.

To begin the size fractionation, 15 grams of N Au-1 is suspended in 1.0 L of 1.0 M NaCl and left to mix with a stir bar for at least 12 hours. The sodium chloride provides an electrolyte background to prevent a concentration gradient with the clay mineral and de-ionized water which otherwise may alter the clay mineral. Afterwards the clay mineral suspension is then centrifuged in 250 mL polypropylene Sorvall Dry-Spin centrifuge tubes with a Beckman J2-21M centrifuge at 10,000 rpm for 15 minutes with the temperature maintained at 10 °C. The solids are then re-suspended in 1.0 L of de-ionized water for at least 12 hours.

To separate the clay mineral particles by size, a Beckman GPKR centrifuge was utilized maintaining a constant temperature of 16 °C. According to equation 2-1 and Table 2-1 operating the centrifuge at 500 rpm for 8.5 minutes yields particle sizes less than 2 µm diameter particles in the supernatant. Continued centrifuging of the supernatant at 2000 rpm at 8.5 minutes yields a supernatant of clay mineral particles of less than 0.5 µm in diameter. The remaining solids are re-suspended and centrifuged again to recover any lost particles less than 0.5 µm in diameter.

$$T_m = \frac{[6.3 \times 10^9][\eta \log_{10} \left[\frac{R}{S} \right]]}{N^2 D^2 \Delta s} \quad \text{Equation 2-1.}$$

To homo-ionize the clay mineral, enough NaCl to yield 1 M concentration was added to the clay mineral suspension of particles of less than 0.5 μm in diameter and left to mix with a stir bar for at least 12 hours. The objective of homo-ionization is to substitute any cation sorbed to the basal planes of the clay mineral particles and replace them with sodium cations. After mixing, the suspension is centrifuged in 250 mL polypropylene Sorvall Dry-Spin centrifuge tubes with a Beckman J2-21M centrifuge at 10,000 rpm for 15 minutes with the temperature maintained at 10 °C. The solids are then

Table 2-1. Equation 2-1 variables and definitions

T_m	Time for sedimentation
η	Viscosity (in poise) 0.01111 for 16°C
R	Distance from axis of rotation to top of sediment
S	Distance from axis of rotation to top of suspension
N	Revolutions per minute (RPM)
D	Particle diameter desired
Δs	Difference in density between solvated particle (2.65 g/cm ³) and suspension liquid (0.999 g/cm ³)

re-suspended in 1.0 L of 1 M NaCl for at least 12 hours. This process is then repeated two more times. Finally the three times homo-ionized clay mineral is then suspended in 1 L of de-ionized water and centrifuged in 250 mL polypropylene Sorvall Dry-Spin centrifuge

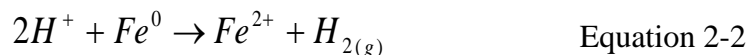
tubes with a Beckman J2-21M centrifuge at 14,000 rpm for 30 minutes with the temperature maintained at 10 °C. This step is repeated until the supernatant was clear in color.

Now with the clay mineral homo-ionized, the objective is to remove the impurities held within the clay mineral. The homo-ionized solids are re-suspended in 1 L of de-ionized water and left to mix with a stir bar for at least 12 hours. The suspension is then centrifuged in 250 mL polypropylene Sorvall Dry-Spin centrifuge tubes with a Beckman J2-21M centrifuge at 10,000 rpm for 5 minutes with the temperature maintained at 10°C. The solids are re-suspended in 1 L of de-ionized water and centrifuged again after mixing for at least 12 hours. The supernatant suspension are centrifuged three times in the same manner just described. Once the removal of impurities step is completed the cleaned suspension of N_{Au}-1 is then centrifuged in 250 mL polypropylene Sorvall Dry-Spin centrifuge tubes with a Beckman J2-21M centrifuge at 14,000 rpm for 60 minutes with the temperature maintained at 10 °C to completely remove all particles in suspension.

The processed clay mineral solids are then freeze-dried in small polypropylene petri dishes. The dried particles are then pulverized in an agate mortar and sieved to a fine power.

Reduction Agents

Aqueous Fe(II) (natural abundance or isotopically fractionated ⁵⁶Fe) is made from dissolving iron metal powder (of isotope choice) in 1.0 M HCl while mixing and heating inside an anoxic environment for two hours. The acid is required to oxidize the iron metal to Fe(II) according to equation 2-2 and also stabilize the formed Fe(II) in solution. The resulting solution is filtered with a nylon 0.22 μm nylon filter and enough de-ionized water was added to yield 0.1 M HCl solution of aqueous Fe(II).



Reduction of Nitroaromatic Compound Batch Experiment

All batch experiments are conducted in an anoxic environment in 20mL glass auto sampler vials. To reduce the clay mineral, enough aqueous Fe(II) and clay mineral N Au-1 were added to 15 mL of buffer solution to yield 2mM Fe(II) and 2g/L of N Au-1. The pH was adjusted with either 1.0 M HCl or 1.0 M NaOH to obtain the desired pH value within ± 0.05 with pH meter model AB15 manufactured by Fisher Scientific. The suspension is allowed to mix for at least 12 hours with no exposure to light. To remove the remaining aqueous Fe(II) from the clay mineral, the clay mineral suspension is centrifuged in 30 mL polypropylene Oakridge centrifuge tubes with a Thermo Scientific Heraeus Megafuge 16 centrifuge at 13,000 rpm for 15 minutes to remove all particles in suspension. The solids are suspended in 10 mL of de-ionized water and mixed for 30 minutes then the suspension is centrifuged in 30 mL polypropylene Oakridge centrifuge tubes with a Thermo Scientific Heraeus Megafuge 16 centrifuge at 13,000 rpm for 15 minutes to remove all particles in suspension. The solids are then suspended in 15mL of buffer solution and the pH is again adjusted and allowed to be continuously mixed until needed.

The batch reactor kinetic experiments begin with adding enough 3-chloronitrobenzene to make a 33.9 μM concentration in the reactor. Sampling from the reactors is done with glass syringes with a sample volume of 500 μL . Samples are filtered with a 0.22 μm PTFE filters into 2 mL auto sampler vials.

Analytical Methods

Clay Mineral Purity Characterization by FT-IR

The quality of the clay mineral is analyzed by a non-dispersive single beam Fourier transform infrared spectrometer (FT-IR) model type Nicolet iS10 manufactured by Thermo Scientific. Wavelength numbers explored are between 650 cm^{-1} and 4000 cm^{-1} which is the range of interest to identify the presence or absence of impurities. The absorbance between wavelengths $3700\text{-}3000\text{ cm}^{-1}$ and $1200\text{-}800\text{ cm}^{-1}$ are indicative of clay mineral-bound hydroxyl groups and Si-O bands (Wilson, M. J., 1994). The impurities such as kaolinite (located at 3700 cm^{-1}) can be identified as well as quartz (located at 800 and 780 cm^{-1}) (Wilson, M. J., 1994). The results shown in Figure 2-1 show that the presence of the impurities has been mitigated in each of the three batches of cleaned clay mineral N Au-1 because the detection of the impurities show less prominence.

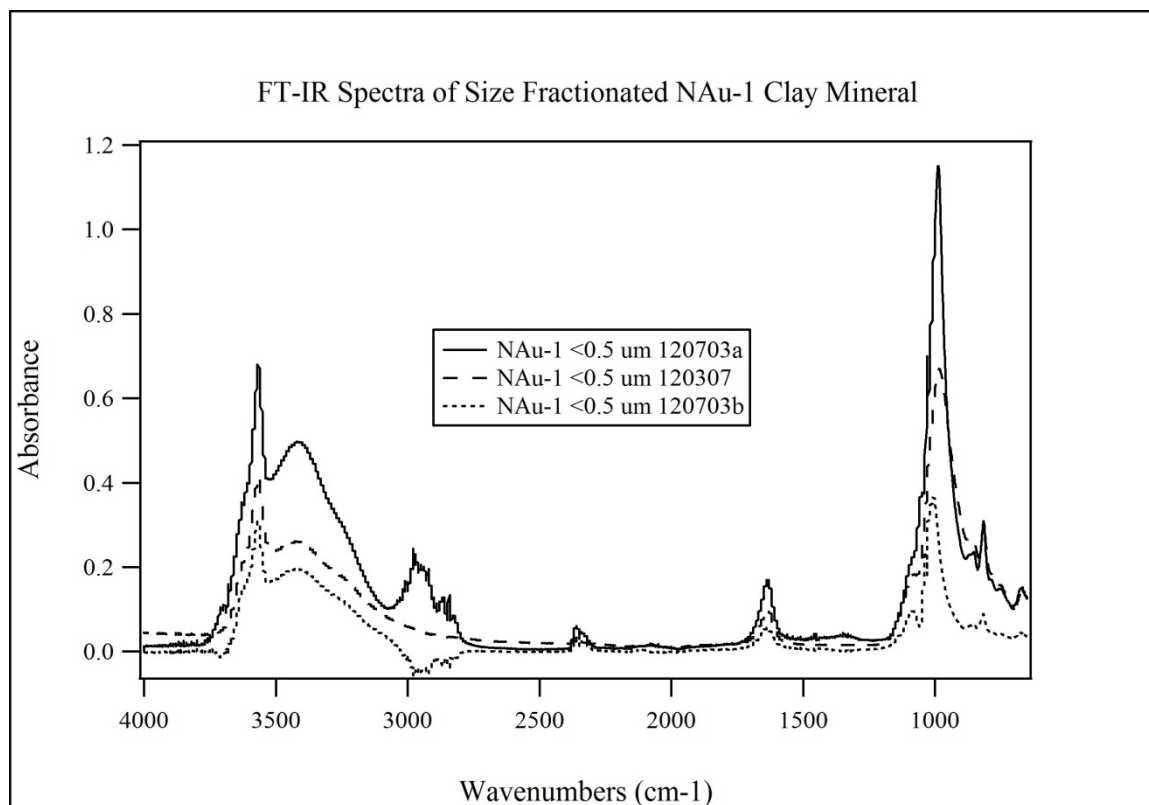


Figure 2-1. Fourier transform infrared spectras of three batches of size fractionated N Au-1 clay mineral (particles size $<0.5 \mu\text{m}$ diameter particles). Each spectra (indicated by solid, dash, and dotted lines) corresponds to a batch and date of testing. Wavenumbers range from 650 to 4000 cm^{-1} .

Iron Analysis

For aqueous ion samples, a modified 1,10 phenanthroline method is utilized using ferrous ammonium sulfate as a standard (Schilt, A.A, 1969). Samples are measured using a Spectronic Genesys 5 spectrometer with a wavelength of 510 nm. Iron within the clay mineral is measured using a Mössbauer Spectrometer at a temperature of 13 K using a ^{57}Co gamma ray source. 13 K is used as it returned a clearer spectra of the Fe(II) doublet in contrast to spectra collected at a higher temperatures such as room temperature. Visual inspection of the clay mineral is done using a JEOL JEM-1230 Transmission Electron Microscope with 300 grid holey carbon copper TEM grid (Figure 2-2). For TEM analysis a 2 g/L suspension of clay mineral was diluted to 0.5 g/L with ethanol (95% pure) and was sonicated for five minutes to break up clay minerals particles that may have coagulated. From this dilution, a 500 μL sample was placed on the TEM grid and the solvent was allowed to evaporate for a few minutes.

Nitroaromatic Compound Analysis

An Agilent 1100 High Pressure Liquid Chromatography (HPLC) is used to measure the concentrations of 3-chloronitrobenzene and 3-chloroaniline. A Supelcosil LC-18 reverse phase column of 5 μm particle size with dimensions 25cm x 4.6mm (length and interior diameter respectively) is utilized for the measuring of the concentration of the nitroaromatic compounds. The mobile phase was a 60:40 ratio of methanol (optima grade) and 5mM potassium phosphate buffer (pH adjusted to 7.0) respectively. A diode-array detector (DAD) is utilized to detect and measure the concentrations of the nitroaromatic compounds from a 40 μL sample.

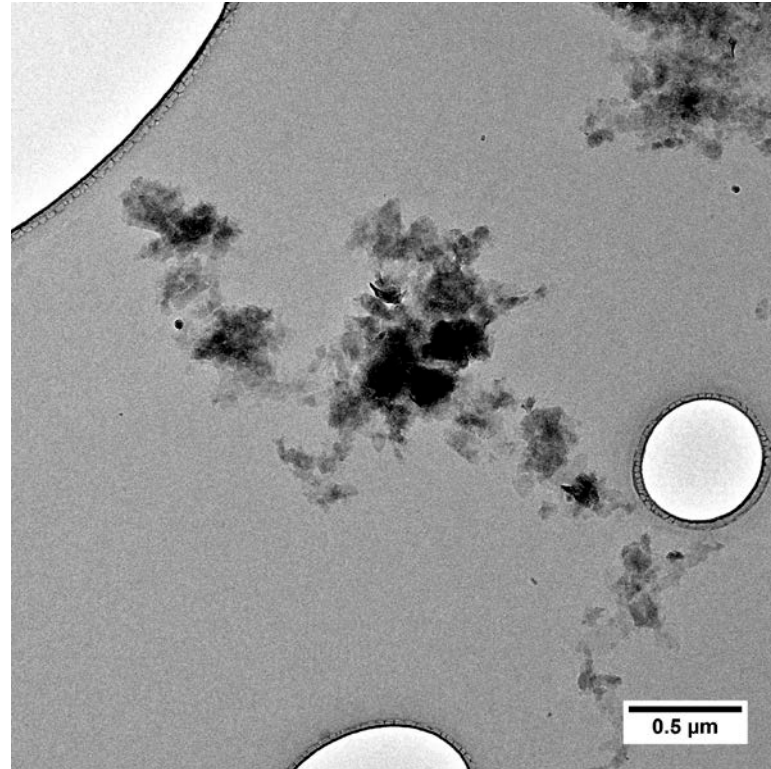


Figure 2-2: Visual inspection of clay mineral is done using a JEOL JEM-1230 Transmission Electron Microscope with 300 grid holey carbon copper TEM grid.

CHAPTER III

RESULTS AND DISCUSSION

Reduction of Nitroaromatic Compound by Fe(II) Reduced Clay Mineral

The size fractionated NAu-1 clay mineral batches described in chapter 2 were merged into a homogenous mixture to insure that the clay mineral used for each of the experiments discussed in this chapter to have the same characteristics. Transmission Electron Microscope (TEM) imagery was conducted on the merged batches of size fractionated clay mineral particles to investigate the particle size (see chapter 2 for more on the TEM imagery study). TEM images (including Figure 2-2) suggested that the separated particles were of particle diameter less than or equal to that of the desired <0.5 μm particle diameter. All of the clay mineral suspensions used in this chapter are made with a clay mineral concentration of 2 g/L in 15 mL volume of the appropriate buffer and electrolyte solution. Each suspension of clay mineral was capped and sealed inside an anoxic environment to prevent re-oxidation of the clay mineral. Suspensions of clay mineral were kept as a batch reactor for the duration of its corresponding experiment. The batch reactors were wrapped in aluminum foil to prevent the possibility of oxidation by light.

Reduction of Clay Mineral

To determine if a clay mineral could be reduced by aqueous Fe(II) with this experimental conditions, an iron oxidation measurement was conducted with a Mössbauer spectrometer where a 30 mg sample of clay mineral was partially reduced by aqueous $^{56}\text{Fe(II)}$ at pH 7.50 (± 0.05). An isotopically enriched ^{56}Fe solution was used as

the reductant rather than a natural abundant iron solution (“natural abundant” refers to the natural isotopic fraction of each isotope present in iron metal) because the Mössbauer spectrometer can only detect the iron isotope ^{57}Fe . Therefore the only source for detectable ^{57}Fe is in the structure of the clay mineral itself as its iron content has naturally abundant iron. As shown in Figure 3-1, the Mössbauer spectra of a partially reduced N Au-1 clay mineral suspension in a pH 7.5 system reveals that reduction has occurred as a small Fe(II) doublet appears (the peak at 2.5 mm/s and the shoulder at approximately -0.25 mm/s) where an unreduced clay mineral would only have the Fe(III) doublet (the two peaks between 0 and 2 mm/s). This demonstrates that aqueous Fe(II) can partially reduce the clay mineral N Au-1 with the conditions described in chapter 2 which are consistent with the results reported by Neumann (2013) for clay mineral N Au-1 and Schaefer et al. (2011) for clay mineral N Au-2 (a similar clay mineral to N Au-1 used in this chapter).

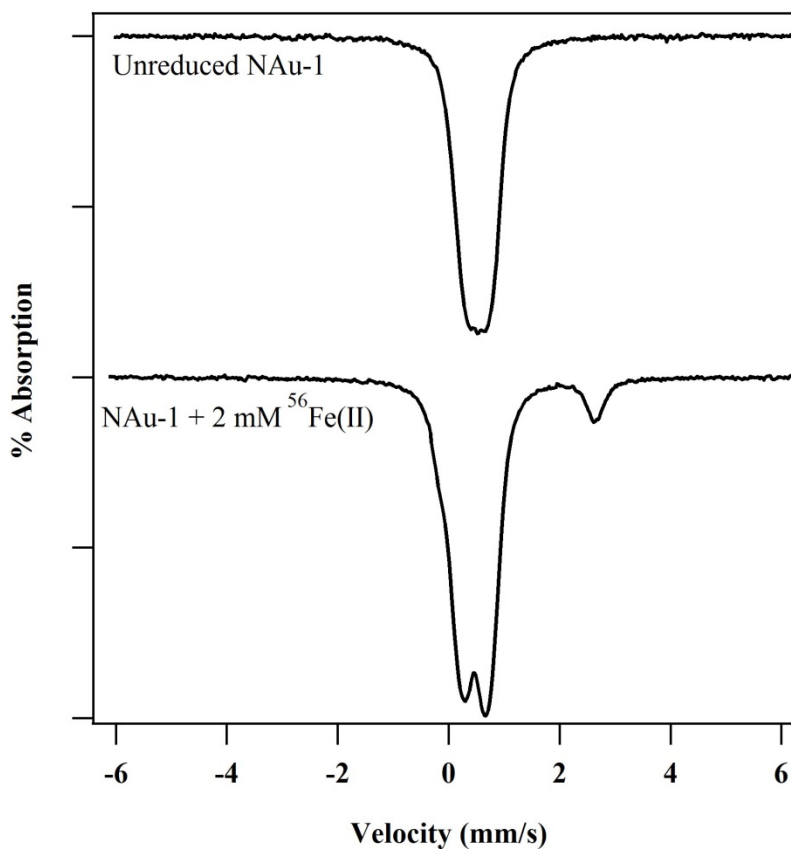


Figure 3-1. NAu-1 clay mineral unreduced in no buffer solution compared to a NAu-1 clay mineral partially reduced by 2 mM Fe(II) in 25 mM HEPES buffer and 50 mM NaCl background solution with a pH value of 7.50 (± 0.05)

To determine if there was enough available sorbed iron on the clay mineral to reduce the clay mineral's structural iron to Fe(II) (which in turn could be then used to reduce the nitroaromatic compound to its corresponding aniline), the aqueous iron molar concentration was measured with a modified 1,10 phenanthroline method before reduction and after reduction has took place. The difference between the molar concentration before reduction and after reduction identifies how much Fe(II) is sorbed to the clay mineral structure. Recall from chapter 2 that there is negligible iron initially sorbed to the clay mineral as the clay mineral itself was homo-ionized with sodium cations.

As shown in table 3-1, the moles of sorbed Fe(II) increases as the pH increases. For pH 7.5, 6.0, and 4.0 the Fe(II) sorbed to the clay mineral structure is 32.7 μmol , 9.3 μmol , and 5.4 μmol , respectively. The observation of Fe(II) sorption to the clay mineral was also noted in Neumann (2013) where at a higher pH, the Fe(II) has the potential to sorb to the edge OH-groups and the basal planes of the clay mineral structure such as at pH 7.5. However at lower pH values, such as 6.0 and 4.0, sorption is more likely to be significant at the basal planes and sorption to the edge OH-groups is minor (Neumann, 2013).

From the known concentration of initial nitroaromatic compound of 33.9 μM in a 15 mL volume (for a 0.51 μmoles of nitroaromatic compound), an electron balance (R) can be calculated between the amount of electrons potentially available from sorbed Fe(II) for reducing the clay mineral to the total amount of electrons needed to fully reduce the nitroaromatic compound present ($6 \times 0.51 = 3.06 \mu\text{moles}$). As shown in Table 3-1, the electron balance comparing amount of structural Fe(II) available to reduce the nitroaromatic compound for pH 4.0, 6.0 and 7.5 are 1.8, 3.0, and 10.7 respectively. This shows that at all pH values, there is enough reduced Fe(II) within the clay mineral structure to reduce all of the nitroaromatic compound.

Table 3-1. Sorbed Fe(II) to nitroaromatic compound with respect to pH

pH	[Fe(II)] _{t = 0 hrs.}	[Fe(II)] _{t = 12 hrs.}	[Fe(II)] _{sorbed}	R
4.0	34.1 μmol	28.7 μmol	5.4 μmol	1.8
6.0	32.7 μmol	23.4 μmol	9.3 μmol	3.0
7.5	34.1 μmol	1.4 μmol	32.7 μmol	10.7

Reduction of Nitroaromatic Compound and pH Dependence

To determine whether an Fe(II)-reduced clay mineral can reduce a nitroaromatic compound, a comparative study was conducted with NAu-1 and 3-chloronitrobenzene batch reactors made with a reduced clay mineral and unreduced clay mineral. The kinetic experiments began with adding enough 3-chloronitrobenzene to make a 33.9 μM in each reactor. The reactors were then mixed on a rotating machine to insure a well-mixed suspension during the length of the experiment. At predetermined time intervals, a 500 μL sample was taken via a glass syringe and needle. The glass syringe was used since the sample may sorb to a polypropylene syringe.

As shown in figure 3-2, at pH 7.5 with no aging (the significance of pH and aging will be discussed later in this chapter), there was no observable reduction of 3-chloronitrobenzene in the reactor that contained the unreduced clay mineral. The reduced product of 3-chloronitrobenzene, 3-chloronitroaniline was also not detected. In the

reduced clay system, a decrease was observed in the concentration of 3-chloronitrobenzene and an increase of 3-chloroaniline was also observed. This demonstrates that an Fe(II)-reduced clay mineral can reduce a nitroaromatic compound. Similar findings were also reported in studies by Grundl et al. (2000) at pH 7.5 using another ferruginous nontronite clay mineral SWa-1 with 4-chloronitrobenzene. In this same study by Grundl et al. (2000), discussed that aqueous Fe(II) is not thermodynamically favorable to reduce a nitroaromatic compound without first forming an inner sphere complex on a surface that is capable of transferring the first electron. Therefore aqueous Fe(II) alone is not expected to reduce the nitroaromatic compound in this chapter's study.

In addition to the experiment at pH 7.5, pH values of 4.0 and 6.0 were also investigated. At both of these two pH values there was no observed reduction of the nitroaromatic compound as shown in Figures 3-3 and 3-4. Data in Figure 3-4 was aged for seven days.

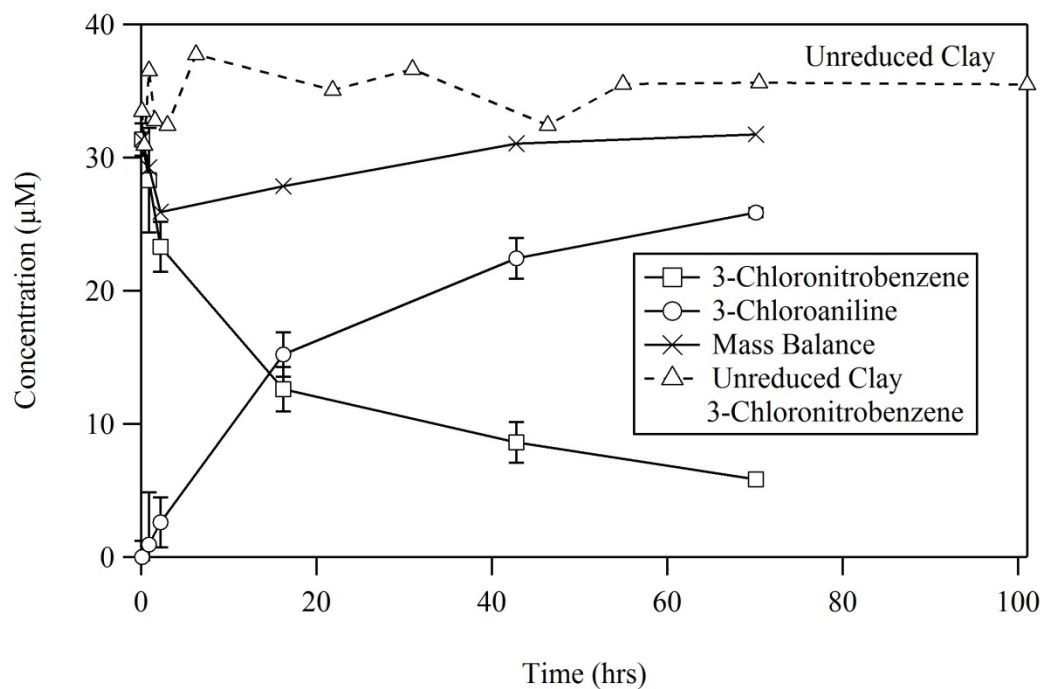


Figure 3-2. Reduction of 3-chloronitrobenzene (squares) to 3-chloroaniline (circles) by Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM HEPES buffer and 50 mM NaCl with a pH value of 7.50 (± 0.05). Solid line indicates a mass balance of 3-chloronitrobenzene and 3-chloroaniline. Dashed line indicates concentration of 3-chloronitrobenzene in control (system with unreduced clay mineral).

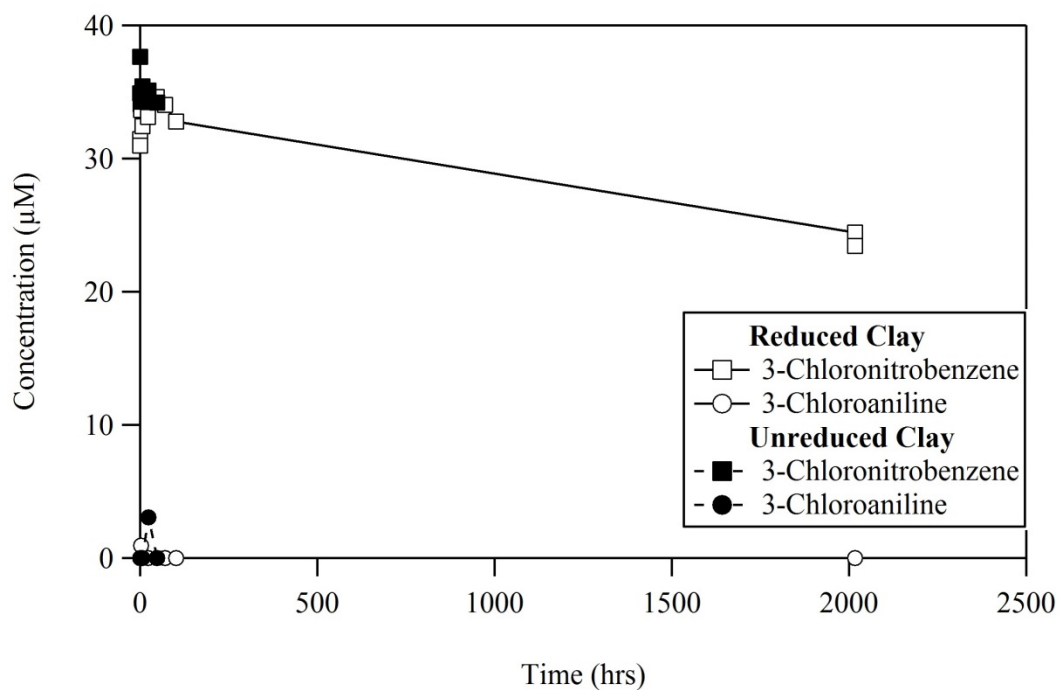


Figure 3-3. Reduction of 3-chloronitrobenzene (squares) to 3-chloroaniline (circles) by Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM PIPPS buffer and 50 mM NaCl with a pH value of 4.0 (± 0.05). Solid line indicates reduced clay system while the dashed line indicates the unreduced clay mineral suspension.

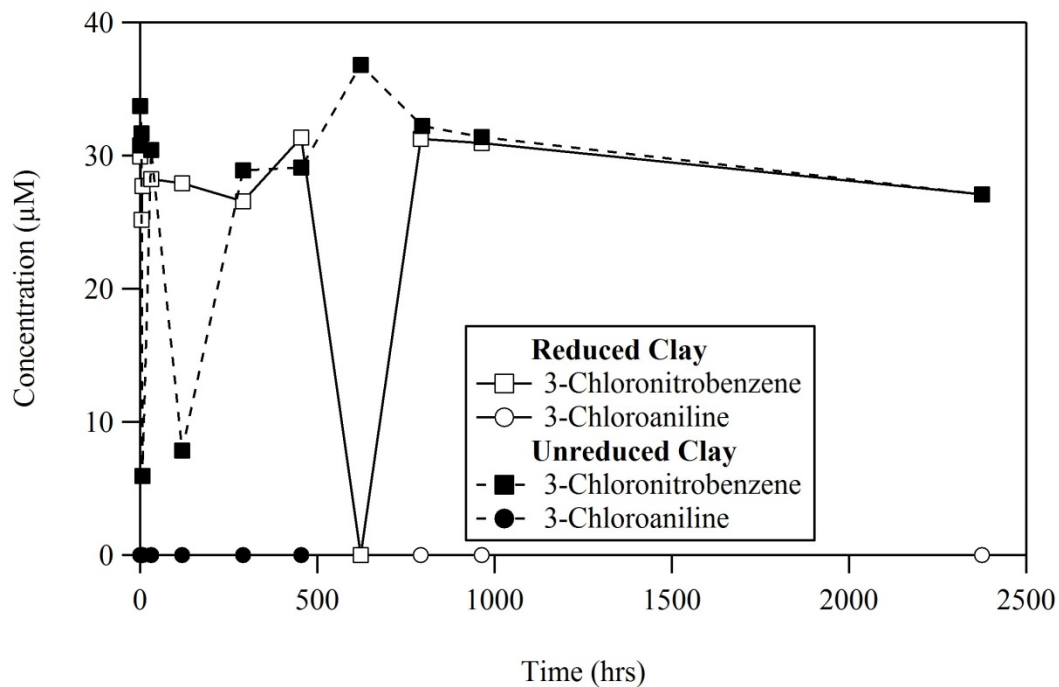


Figure 3-4. Reduction of 3-chloronitrobenzene (squares) to 3-chloroaniline (circles) by Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM MES buffer and 50 mM NaCl with a pH value of 6.0 (± 0.05). Solid line indicates reduced clay system while the dashed line indicates the unreduced clay mineral suspension. Note that 3-chloroaniline concentration in both unreduced and reduced clay mineral suspensions overlap.

Effect of Equilibration Time on Reduction of Nitroaromatic
Compounds

Aging Characteristics

To determine if equilibrium time has an impact on the rate of reduction of a nitroaromatic compound, a series of reactors were left to age for a predetermined time span. It should be noted, that the term “aging” refers to the time in which a clay mineral is equilibrated in a buffered solution after which the clay mineral has been previously reduced and the aqueous Fe(II) has been removed by a de-ionized water rinse. As shown in figure 3-5, at the pH values of 4.0 and 6.0 and zero aging time there is no observable reduction of the 3-chloronitrobenzene while the pH 7.5 system clearly shows a reduction 3-chloronitrobenzene.

In contrast, a series of reduced clay mineral suspensions were left to equilibrate with a fresh buffer solution for 92 days after the reduction of the clay mineral had taken place. As shown in Figure 3-6, for a pH 7.5 system the rate of reduction decreased with increased equilibrium time. Furthermore, at pH 4.0 for the equilibrium time of 92 days, there was no observable formation of 3-chloroaniline which was similar to what was observed at zero day equilibrium (Figure 3-7). These findings suggest that as equilibrium time increases, the slower the reduction rate of 3-chloronitrobenzene by a reduced clay mineral would occur.

The particles size distribution prior to clay mineral aging appeared to be not different from the clay mineral particles after aging. If the batch reactor ceases to mix, larger particles will settle to the bottom while the smaller particles remain in suspension for long periods of time. The settled particles did not appear visually to change in volume and particle size before and after aging.

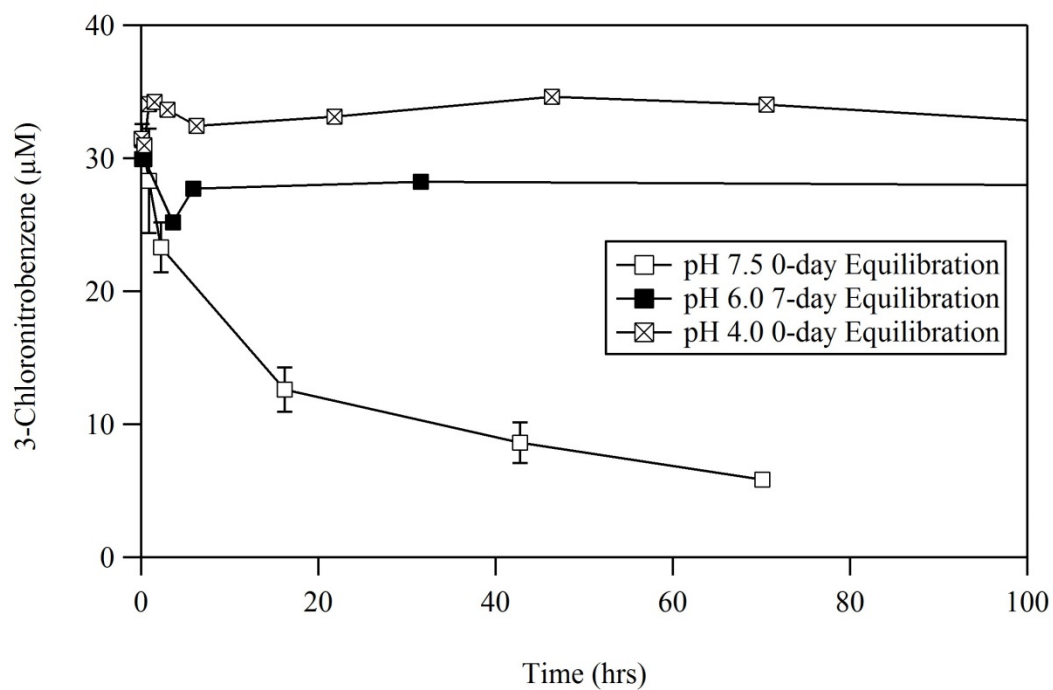


Figure 3-5. Effect of pH on 3-chloronitrobenzene reduction by Fe(II)-reduced NAu-1 for short equilibration time. Conditions for each pH system include Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM buffer solution and 50 mM NaCl. For pH systems of 7.5, 6.0, and 4.0 the buffer salts utilized are PIPPS, MES, and HEPES, respectively. Each buffered suspension of NAu-1 was adjusted to the target value within (± 0.05).

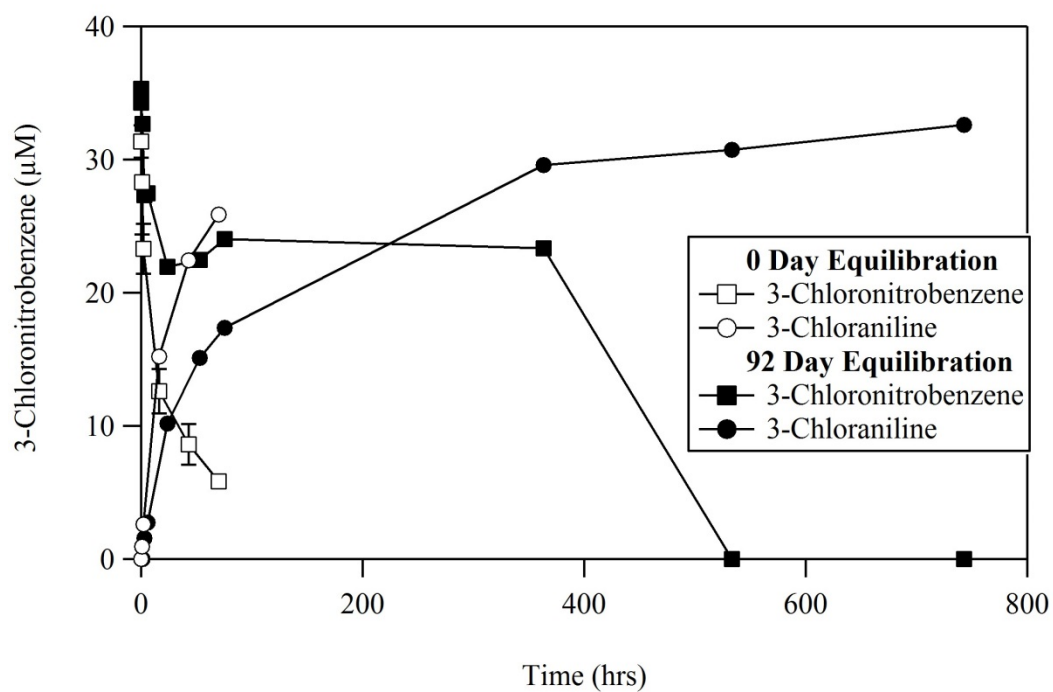


Figure 3-6. Effect of pH on 3-chloronitrobenzene reduction by Fe(II)-reduced NAu-1 for long equilibration time. Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM HEPES solution and 50 mM NaCl with pH 7.5 (± 0.05).

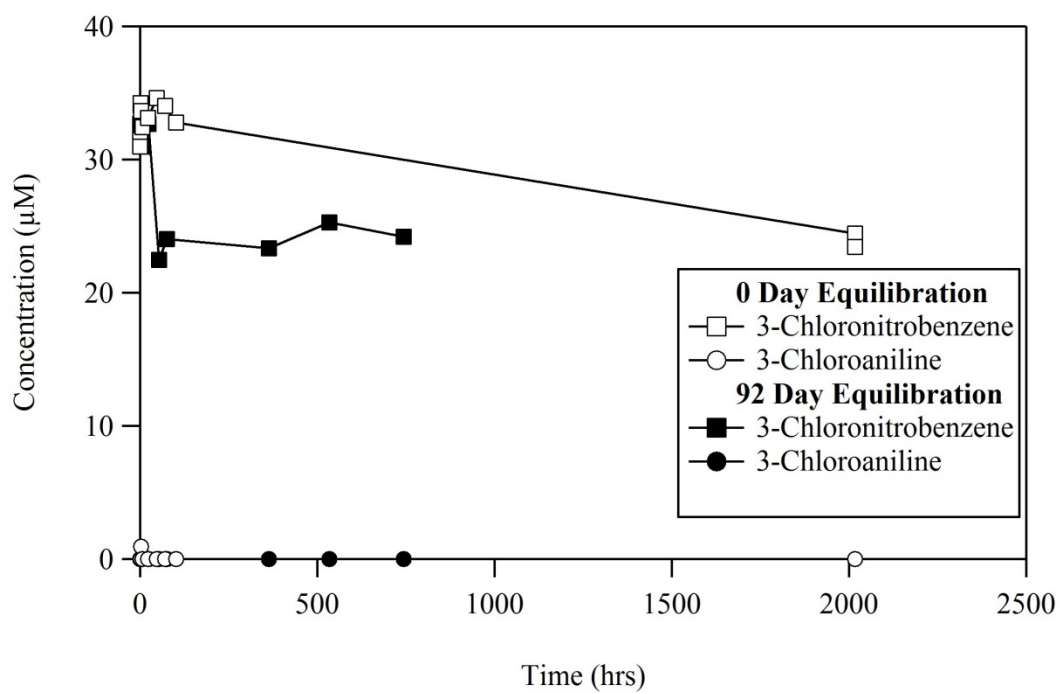


Figure 3-7. Effect of pH on 3-chloronitrobenzene reduction by Fe(II)-reduced NAu-1 for long equilibration time. Nau-1 clay mineral reduced by 2 mM Fe(II) in 25 mM PIPPS solution and 50 mM NaCl with pH 4.0 (± 0.05).

CHAPTER IV

SUMMARY

Summary

Mössbauer spectra of a partially reduced N Au-1 clay mineral suspension in a pH 7.5 system reveals that reduction has occurred as a small Fe(II) doublet appears at the spectra peak at 2.5 mm/s and a shoulder at approximately at -0.25 mm/s velocity in Figure 3-1, where as an unreduced clay mineral would only have the Fe(III) doublet which occurs between 0 and 2 mm/s velocity. Results from this work show aqueous Fe(II) can partially reduce the clay mineral N Au-1 with the conditions described in chapter 2 which are consistent with the results reported by Neumann (2013) for clay mineral N Au-1 and Schaefer et al. (2011) for clay mineral N Au-2.

No reduction of 3-chloronitrobenzene by an unreduced clay mineral at pH values 4.0, 6.0, and 7.5. The reduced product of 3-chloronitrobenzene, 3-chloronitroaniline was also not detected. At pH 7.5, Fe(II)-reduced clay mineral was able to reduce 3-chloroanilineto 3-chloroaniline. This demonstrates that an Fe(II)-reduced clay mineral can reduce a nitroaromatic compound. The electron balance comparing amount of structural Fe(II) available to reduce the nitroaromatic compound for pH 4.0, 6.0 and 7.5 are 1.8, 3.0, and 10.7 respectively. This shows that at all pH values, there should be enough reduced Fe(II) within the clay mineral structure to reduce all of the nitroaromatic compound.

Kinetic experiments performed on clay mineral N Au-1 showed a pH dependence on the ability for the clay mineral to reduce 3-chloronitrobenzene. In suspensions of N Au-1 at pH 4.0 and 6.0, there is no observed reduction of 3-chloronitrobenzene and no observed formation of 3-chloroaniline. At pH 7.5, there is evidence for reduction of 3-

chloronitrobenzene as a decrease was observed in the concentration of 3-chloronitrobenzene and an increase of 3-chloroaniline was also observed.

Kinetic experiments have shown that at pH 7.5 the rate of reduction decreased with increased equilibration time. The equilibration time refers to the time the clay mineral has equilibrated in a buffered solution after which the clay mineral has been previously reduced and the sorbed Fe(II) has been removed by a de-ionized water rinse. Furthermore, at pH 4.0 for the equilibrium time of 92 days, there was no observable formation of 3-chloroaniline which was similar to what was observed at zero day equilibration. These findings suggest that as equilibrium time increases, the slower the reduction rate of 3-chloronitrobenzene by a reduced clay mineral.

Significance of Clay Minerals Reduction Characteristics on Natural Environmental Systems

Clay minerals are the most abundant and chemically active parts of the surface mineral world of Earth (Velde, B., 1995). As a potential natural contaminant remediation compound, understanding its relevance to groundwater and soil interactions may lead to improved means of eliminating harmful compounds in our groundwater supply. To understand more on how equilibration time plays a critical role in the reduction potential of the clay mineral to reduce a nitroaromatic compound, further studies should focus on the pH stability over time and also average particle size within the suspension before and after reduction of the nitroaromatic compound. The mechanism that effects the aging of the clay mineral may be valuable in determining the effectiveness of remediation at a contaminated site.


APPENDIX

STUDY OF ELECTRON TRANSFER AT OH-EDGE GROUPS AND
BASAL PLANE SITES OF NAU-1 CLAY MINERAL WITH VARIOUS
PH VALUES

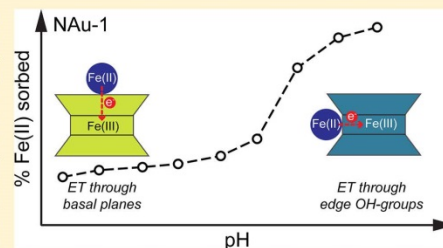
1 Spectroscopic Evidence for Fe(II)–Fe(III) Electron Transfer at Clay 2 Mineral Edge and Basal Sites

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5  Supporting Information

6 **ABSTRACT:** Despite the importance of Fe redox cycling in
7 clay minerals, the mechanism and location of electron transfer
8 remain unclear. More specifically, there is some controversy
9 whether electron transfer can occur through *both* basal and
10 edge surfaces. Here we used Mössbauer spectroscopy combin-
11 ed with selective chemical extractions to study electron
12 transfer from Fe(II) sorbed to basal planes and edge OH-
13 groups of clay mineral NAu-1. Fe(II) sorbed predominantly
14 to basal planes at pH values below 6.0 and to edge OH-groups
15 at pH value 7.5. Significant electron transfer occurred from
16 edge OH-group bound Fe(II) at pH 7.5, whereas electron
17 transfer from basal plane-sorbed Fe(II) to structural Fe(III) in
18 clay mineral NAu-1 at pH 4.0 and 6.0 occurred but to a much
19 lower extent than from edge-bound Fe(II). Mössbauer hyperfine
20 parameters for Fe(II)-reacted NAu-1 at pH 7.5 were consistent
21 with structural Fe(II), whereas values found at pH 4.0 and 6.0
22 were indicative of binding environments similar to basal plane-
23 sorbed Fe(II). Reference experiments with Fe-free synthetic
24 montmorillonite SYn-1 provided supporting evidence for the
25 assignment of the hyperfine parameters to Fe(II) bound to basal planes and edge OH-groups. Our findings demonstrate that
electron transfer to structural Fe in clay minerals can occur from Fe(II) sorbed to *both* basal planes and edge OH-groups. These
findings require us to reassess the mechanisms of abiotic and microbial Fe reduction in clay minerals as well as the importance of
Fe-bearing clay minerals as a renewable source of redox equivalents in subsurface environments.



26 ■ INTRODUCTION

27 Clay minerals are ubiquitously present in subsurface environ-
28 ments and contain a significant portion of Fe in soils.^{1,2} Struc-
29 tural Fe content in clay minerals varies widely from trace amounts
30 to up to more than 30 wt % in nontronite and biotite specimens.³
31 Both the amount and redox state of Fe in the structure of clay
32 minerals strongly affect the physical and chemical properties of
33 clay minerals. Affected clay mineral properties include ion
34 exchange and fixation capacity,^{4,5} surface hydration and swelling
35 in water,^{6–9} and reduction potential,¹⁰ which all influence reactive
36 interactions between clay minerals and water constituents.

37 Since the discovery that microbes can reduce structural Fe in
38 clay minerals,¹¹ numerous studies have confirmed this finding with
39 a variety of Fe-bearing clay minerals and microbial species.^{12–17} In
40 many laboratory studies chemical reductants have been used as
41 surrogates for naturally occurring reductants and were shown to
42 effectively reduce clay mineral Fe.^{4–6,8,9} Structural Fe(II) resulting
43 from microbial or chemical reduction can, in turn, reduce a variety
44 of pollutants, including chlorinated solvents,¹⁸ nitroaromatic
45 explosives,^{19,20} and metals.^{21–23} Different studies have empha-
46 sized that the binding environment of structural Fe(II) in clay
47 minerals will significantly impact clay mineral reactivity.^{10,20,24,25}

48 Despite the importance of Fe redox cycling in clay minerals,
49 both the mechanism of electron transfer as well as the resulting
50 Fe(II) speciation remains unclear. From spectroscopic studies

of dithionite-reduced smectites the hypothesis was formed that
51 structural Fe was reduced in a pseudorandom electron trans-
52 fer reaction, which can occur only via clay mineral basal plane
53 surfaces.^{26–28} Reduction from clay mineral edges, in contrast,
54 would progress through the octahedral sheet like a moving front²⁶
55 and was found to be consistent with observations made for micro-
56 bial Fe clay mineral reduction.²⁹

57 Differences between chemical and microbial Fe reduction
58 were also suggested for the fate of formed structural Fe(II). Some
59 have argued that formed Fe(II) remains in the clay mineral
60 structure, where subsequent solid-state electron transfer and
61 structural reorganization may yield a variety of reactive Fe(II)
62 entities.^{24,27–33} In other studies, microbial Fe reduction was
63 found to lead to partial reductive dissolution and Fe(II) release
64 into the aqueous phase.^{14,17,34,35} Once released into the aqueous
65 phase, it has been suggested that Fe(II) can either sorb to edge-
66 surface OH-groups, bind to basal surface planes via ion exchange,
67 or precipitate as a secondary mineral on the clay mineral
68 surface.^{35–38} Recently, we showed that sorption of Fe(II) to an
69

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70 Fe-containing smectite (NAu-2) resulted in structural Fe(III)
71 reduction,³⁹ but the involvement of basal planes vs edge OH-
72 groups was unclear.

73 Here, we investigated electron transfer from Fe(II) adsorbed
74 to basal planes and from Fe(II) complexed to edge OH-groups
75 to structural Fe(III) in nontronite NAu-1. To monitor the
76 extent of electron transfer from aqueous Fe(II) to structural
77 Fe(III) in NAu-1, we used ⁵⁷Fe isotope specific Mössbauer spec-
78 troscopy at low temperatures (13 K), similar to our previous
79 approach with clay mineral NAu-2.³⁹ We reacted NAu-1
80 with Mössbauer-invisible ⁵⁶Fe(II) at different pH values to
81 determine the relative contribution of Fe(II) sorption to the
82 two different surfaces to the overall electron transfer. A sequential
83 extraction targeting Fe(II) adsorbed to basal planes and Fe(II)
84 complexed to edge OH-groups was used to selectively recover the
85 adsorbed Fe(II). Reference sorption experiments were carried out
86 with Fe-free montmorillonite SYn-1 and aqueous ⁵⁷Fe(II) to
87 determine the Mössbauer hyperfine parameters for Fe(II) adsorbed
88 to basal planes and for Fe(II) complexed to edge OH-groups.

89 ■ MATERIALS AND METHODS

90 **Preparation of Clay Minerals.** Fe-free montmorillonite
91 SYn-1 and Fe-bearing nontronite NAu-1 were obtained from
92 the Source Clays Repository of The Clay Mineral Society
93 (www.clays.org) and subjected to a size-fractionation and Na⁺-
94 homoionization process (details on the clay minerals and the
95 treatment provided in the Supporting Information, SI). The
96 resulting <0.5 μm particles were freeze-dried, ground, and
97 sieved (100 mesh/150 μm), and the absence of impurities was
98 verified by infrared (IR) spectroscopy and Mössbauer spec-
99 troscopy.

100 **Fe(II) Sorption Experiments.** All experiments were carried
101 out in an anaerobic glovebox with a N₂/H₂ atmosphere (93/7),
102 maintained at <1 ppmv O₂. Solutions were purged at least 2 h
103 with N₂ prior to transfer into the glovebox.

104 Fe(II) stock solutions were prepared inside the glovebox by
105 reacting metallic Fe in its natural isotopic composition (or
106 natural abundance, n.a. Fe), or enriched in ⁵⁶Fe or ⁵⁷Fe isotope
107 (Isoflex, San Francisco, CA, USA) with 1 M HCl at ~60 °C
108 overnight. The resulting solution was filtered to remove any
109 residual Fe(0) and diluted with deionized (DI) water to the
110 desired concentration (~150 mM Fe(II), ~0.1 M HCl).

111 In one set of experiments, the aqueous Fe(II) concentration
112 in a suspension of clay mineral NAu-1 (2 g/L in 0.05 M NaCl)
113 was monitored as a function of pH value. After addition of
114 n.a. Fe(II) stock solution to yield 2 mM Fe(II) aqueous
115 concentration, the pH value of the suspension was adjusted to
116 either pH 4.0 or pH 8.0 using 0.05 M HCl or NaOH,
117 respectively. The stirred suspension was allowed to equilibrate
118 for at least 30 min before the pH was regularly adjusted until
119 the pH drift was <0.02 pH units per 10 min. This procedure
120 was repeated for steps of 0.5 pH units using HCl or NaOH to
121 adjust the pH value, taking one suspension through the pH-
122 range of 4.0 to 8.0 to 4.0 and the other through the
123 pH-range of 8.0 to 4.0 to 8.0. At each 0.5 pH-unit, 3 mL samples
124 were withdrawn from suspension, filtered (0.2 μm, nylon), and
125 acidified with concentrated HCl for subsequent Fe(II) and total
126 Fe analysis according to the 1,10-phenanthroline method.⁴⁴ The
127 amount of sorbed Fe(II) was calculated taking into account the
128 measured aqueous Fe(II) concentration at each pH step, the initial
129 aqueous Fe(II) concentration, the suspension volume remaining
130 in the reactor, and the clay mineral concentration.

For Fe(II) sorption experiments for subsequent Mössbauer
analysis, batch reactors containing 15 mL of 25 mM PIPPS
(Piperazine-N,N'-bis(3-propanesulfonic acid), pK_{a1} 3.79⁴⁵) buffer,
MES (2-(N-morpholino)ethanesulfonic acid, pK_a 6.06⁴⁶) buffer,
PIPES (piperazine-N,N'-bis(ethanesulfonic acid), pK_{a2} 6.78⁴⁵)
buffer, or HEPES (N-2-hydroxyethylpiperazine-N'-2-ethanesul-
fonic acid, pK_a 7.55⁴⁶) buffer were adjusted to pH 4.0, 6.0, 6.5,
and 7.5, respectively. The reactors also contained 0.05 M NaCl
to provide constant ionic strength and 2 mM aqueous ⁵⁶Fe(II)
(NAu-1) or 1 mM ⁵⁷Fe(II) (SYn-1). After adding 30 mg of clay
mineral to the solution, the suspension (2 g/L) was allowed to
equilibrate for 24–72 h in the dark. The reaction was stopped by
centrifugation (13'000 rpm, 15 min), and the supernatant was
decanted, filtered, and acidified with concentrated HCl for
subsequent Fe(II) and total Fe analysis according to the 1,10-
phenanthroline method.⁴⁴

Extractions. Additional reactors were set up and treated in
the same way as for Fe(II) sorption experiments. The resulting solids
were then subjected to a sequential extraction procedure selectively
targeting Fe(II) sorbed to clay mineral basal planes⁴⁷ using 1 M CaCl₂
(4 h, pH ~7) and Fe(II) bound to clay mineral edge OH-groups⁴⁸
using 1 M NaH₂PO₄ (18 h, pH 5). For each of the duplicate reactors,
10 mL extraction solution was used, the reactors were mixed end-
over-end for the appropriate time in the dark, and the extraction was
stopped and the supernatant treated as described for Fe(II) sorption
experiments. After each extraction step, a 30 min wash step with DI
water was carried out to remove any residual extractant. One set of
reactors was subjected only to the first extraction step, while another
set was taken through both extraction steps.

Mössbauer Analysis. Solids from Fe(II) sorption experi-
ments and resulting after each extraction step were resuspended
in 1–2 mL DI water, filtered, and sealed between two pieces of
Kapton tape to avoid oxidation during transfer to the Mössbauer
spectrometer. Mössbauer spectra were collected at 13 K with a system
described in the SI and were fit using the software Recoil (Ottawa,
Canada) using Voigt-based fitting⁵⁰ (for details see the SI).

131 ■ RESULTS AND DISCUSSION

Fe(II) Sorption to NAu-1. To quantify Fe(II) sorption to
NAu-1, we measured Fe(II) uptake from solution over a pH
range of 4.0 to 8.0. At pH values below pH 6.0, Fe(II) sorption
was relatively pH-independent ranging between 20–40%
(Figure 1). The lack of pH-dependence at lower pH values is
consistent with Fe(II) sorption to negatively charged basal
planes via an ion exchange reaction.^{37,40–43,51} Between pH
values of 6.5 and 7.0 a sharp increase in Fe(II) sorption was
observed that plateaued at pH 7.5 with nearly complete Fe(II)
removal from solution (Figure 1). The increased sorption at
higher pH values is consistent with additional Fe(II) binding to
edge OH-groups, which become deprotonated at pH values
above the point of zero net proton charge (PZNPC) and thus
available for cation complexation.^{37,41,51} Increased sorption at
pH values above 6.5 coincides well with the PZNPC of 7.2
estimated based on electrolyte titrations of clay mineral NAu-2,³⁷
a close structural relative of NAu-1.⁵² A slight hysteresis was
observed when starting the sorption experiment at pH 4.0
(20% vs 40% sorption at pH 4 for start and end, respectively,
Figure 1) compared to starting at pH 8.0. We hypothesize that
competition for basal plane adsorption between H⁺ and Fe(II)
is more pronounced when exposing the Na⁺-homoionized clay
mineral to Fe(II) at low pH values compared to when Fe(II) is
already sorbed to the basal planes and then slowly taken to low
pH values.

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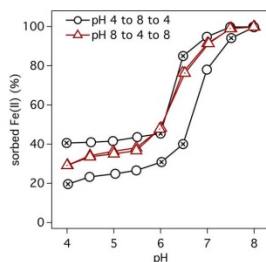


Figure 1. Adsorption of Fe(II) to clay mineral NAu-1 as a function of pH value for the pH-range 4.0 to 8.0. The pH-titrations from pH 4 to 8 to 4 (black circles) and pH 8 to 4 to 8 (red triangles) were carried out in nonbuffered suspensions (2 g/L NAu-1, 2 mM initial aqueous Fe(II)). Experiments for Mössbauer analysis and sequential extraction were carried out in buffered suspensions, marked with crossed symbols.

193 To assess whether Fe(II) sorbed primarily to basal planes at
194 low pH value (<6.0) and to edge OH-groups at higher pH
195 values, we used sequential wet chemical extractions to dis-
196 tinguish between Fe(II) bound via ion exchange and Fe(II)
197 complexed to OH-groups. Specifically, we subjected the Fe(II)-
198 reacted NAu-1 to a CaCl₂ extraction to recapture Fe(II)
199 sorbed to basal planes and to a subsequent NaH₂PO₄ extraction
200 to recover Fe(II) bound to edge OH-groups. CaCl₂ extraction
201 of NAu-1 reacted with 2 mM Fe(II) at pH 4.0 and 6.0
202 removed 95–119% of the initially sorbed Fe(II), whereas only
203 a small fraction was liberated in the subsequent extraction with
204 NaH₂PO₄ (Table 1). Recovery of most of the sorbed Fe(II)
205 with CaCl₂ corroborates that at pH values below 6.0 Fe(II) is
206 sorbed to negatively charged basal planes via an ion exchange
207 reaction and only minor sorption takes places at edge OH-
208 groups. In contrast, only 6% of the initially sorbed Fe(II) was
209 recovered in the CaCl₂ extraction of NAu-1 reacted at pH 7.5,
210 whereas the NaH₂PO₄ extraction step liberated about 64% of
211 the sorbed Fe(II) (Table 1). Significant Fe recovery only once
212 NaH₂PO₄ is used suggests that at pH 7.5 Fe(II) sorbs
213 predominantly to edge OH-groups and basal planes contribute
214 only to a minor extent to the overall observed Fe(II) sorption.
215 The participation of edge OH-groups in Fe(II) sorption at pH
216 7.5 is further corroborated by the cation exchange capacity
217 (CEC) at basal planes of 124.7 μmol/100 g as calculated from
218 the molecular formula of NAu-1 given in the SI. For our
219 experimental setup, we calculated from this CEC a maximum
220 uptake of 18.7 μmol Fe(II) at the basal planes, which is sig-
221 nificantly exceeded only at pH 7.5 (Table 1). At the inter-
222 mediate pH value of 6.5, sequential extraction of NAu-1
223 recovered significant Fe(II) amounts in both extractions steps
224 (71% and 41% with CaCl₂ and NaH₂PO₄, respectively), indicating
225 that at pH value 6.5 both clay mineral surfaces contribute to Fe(II)
226 sorption. We also note that the absolute amounts of Fe(II)
227 recovered in the CaCl₂ extracts were lower for the experiments
228 at pH 7.5 compared to pH 4.0, 6.0, and 6.5 (Table 1). We
229 hypothesize that our aqueous Fe(II) concentration was too low
230 to saturate all edge OH-groups, which are favored for cation
231 sorption at higher pH value,⁵³ and that unspecific sorption to
232 basal planes was thus limited at the higher pH value.

233 **Fe(II)–Fe(III) Electron Transfer at Clay Mineral NAu-1.**
234 To study electron transfer between sorbed Fe(II) and struc-
235 tural Fe(III) in clay mineral NAu-1, we used an approach

Table 1. Fe(II)–Clay Mineral Chemical Extraction Data^a

experiment	aqueous			CaCl ₂ extracted			NaH ₂ PO ₄ extracted			total recovery	
	initial Fe(II) (μmol)	final Fe(II) (μmol)	sorbed Fe(II) ^b (μmol)	Fe(II) (μmol)	Fe(III) ^b (μmol)	Fe(tot) (μmol)	Fe(II) (μmol)	Fe(tot) (μmol)	Fe(tot) (μmol)	% of sorbed ^c (%)	% of sorbed ^d (%)
SVn-1, pH 4.0	17.11(0.60)	15.68(0.57)	1.43(1.17)	2.39(0.05)	n.d.	2.37(0.05)	0.01(0.00)	0.06(0.01)	0.07(0.01)	1	169
SVn-1, pH 7.5	17.42(0.22)	8.06(0.18)	9.35(0.40)	2.65(0.06)	n.d.	2.64(0.07)	1.03(0.20)	1.43(0.77)	2.46(0.57)	26	54
NAu-1, pH 4.0	35.06(0.58)	28.03(0.19)	7.22(0.61)	6.23(0.05)	n.d.	6.20(0.09)	86				86
NAu-1, pH 4.0 ^e	31.29(0.10)	26.28(0.16)	5.18(0.05)	6.19(0.02)	n.d.	6.05(0.13)	119				119
NAu-1, pH 6.0	34.68(0.19)	26.39(0.42)	8.46(0.48)	7.42(0.00)	0.65(0.06)	8.07(0.06)	95	0.42(0.02)	2.48(1.56)	34	129
NAu-1, pH 6.5	33.50(0.21)	23.84(0.16)	9.82(0.37)	7.01(0.18)	n.d.	6.84(0.19)	71	2.10(0.06)	1.93(0.13)	41	112
NAu-1, pH 7.5	28.68(0.04)	1.26(0.05)	27.59(0.03)	1.57(0.09)	n.d.	1.52(0.09)	6	16.99(0.02)	0.71(0.12)	64	70

^a Calculated as difference of measured initial Fe(II) and final Fe(II). ^b Calculated as difference of measured Fe(tot) and Fe(II), taking the greater amount into account, to sorbed Fe(II). ^c Calculated based on the mass of NAu-1 added (30 mg) and the measured structural Fe content of 22.4%. ^d Data gained in experiments with ⁵⁷Fe(II). ^e Values in parentheses indicate standard deviations of replicate experiments, n.a. stands for not applicable, n.d. stands for not detected.

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236 based on the isotope specificity of ^{57}Fe Mössbauer spectroscopy, similar to our previous work with NAu-2.³⁹ ^{57}Fe Mössbauer spectroscopy is sensitive to only the ^{57}Fe isotope and is transparent to all other isotopes of Fe as well as all other elements. Using aqueous Mössbauer-invisible $^{56}\text{Fe}(\text{II})$ enabled us to monitor changes in the oxidation state of ^{57}Fe present in the structure of clay minerals. We collected data at pH 4.0 and pH 7.5 in order to observe any differences when Fe was sorbed primarily to basal planes or edge OH-groups.

245 The Mössbauer spectrum of unreacted NAu-1 (Figure 2A) shows that all structural Fe in NAu-1 is present as Fe(III). We found that most of the structural Fe(III) exist as octahedral Fe(III) (95%, Oct₁ Fe(III)) and also found minor amounts (5%) present in an additional Fe(III) site with hyperfine parameters consistent with both octahedral and tetrahedral coordination (Table 2). Previous spectroscopic investigations of clay mineral NAu-1 have indicated the absence of tetrahedral Fe in the structure of this clay mineral.^{17,54} Thus, we assigned this minor component to a second octahedral Fe(III) site (Oct₂ Fe(III)).

255 Reaction of NAu-1 with aqueous $^{56}\text{Fe}(\text{II})$ at pH 7.5 yielded an additional peak in the Mössbauer spectrum at around 257 2.7 mm/s (Figure 2B), indicating the presence of an Fe(II) doublet (red shaded area). The hyperfine parameters of the Fe(II) doublet fall within the expected range for structural Fe(II) in clay minerals (CS: 1.23 mm/s, QS: 2.87 mm/s)^{17,28,29,55–59} and thus suggest that structural Fe(III) in clay mineral NAu-1 was reduced, similar to what we previously observed for clay mineral NAu-2.³⁹ The Fe(II) doublet comprises 9% of the spectral area, indicating that 9% of structural Fe in NAu-1 were reduced by adsorbed $^{56}\text{Fe}(\text{II})$ (Table 2), which amounted to 27.6 μmol or 23% of the structural Fe present (Table 1). The extent of structural Fe reduction observed for NAu-1 is slightly lower compared to what we found for NAu-2 (15%³⁹), which is probably due to subtle structural differences between the two clay minerals.⁵² Simultaneous with the appearance of the Fe(II) doublet the small component of Oct₂ Fe(III) disappeared, which is also evident from the change in the overall form of the Mössbauer spectrum from asymmetric to unreacted NAu-1 to symmetric for Fe(II)-reacted NAu-1. Oct₂ Fe(III) accounted for only 5% of unreacted NAu-1 structural Fe(III) and 9% structural Fe reduction was observed, suggesting that 276 Oct₂ Fe(III) was also susceptible to reduction. This is in contrast to results from our previous findings for NAu-2, in which only one octahedral component was reduced by sorbed Fe(II) and may have determined the maximum extent of structural Fe reduction.³⁹

280 Extraction of $^{56}\text{Fe}(\text{II})$ -reacted NAu-1 (pH 7.5) with CaCl_2 did not yield significant changes in the Mössbauer spectrum (Figure 2C). The relative amount of structural Fe(II) decreased negligibly from 9% to 8% (Table 2), and the amount of Fe(II) found in the CaCl_2 extract was equivalent to 6% of the adsorbed Fe(II) (Table 1). The combined evidence points toward minor Fe(II) sorption to basal planes at pH 7.5 and negligible contribution of this Fe(II) species to interfacial electron transfer. After subsequent extraction with NaH_2PO_4 , however, the Fe(II) doublet in the Mössbauer spectrum disappeared (Figure 2D), indicating removal or reoxidation of reduced structural Fe in NAu-1. Overall recovery of 70% of the initially sorbed Fe(II) in the two extraction steps (Table 1) further corroborates removal of most sorbed Fe(II), which was involved in the previous electron transfer reaction and which was predominantly complexed to edge OH-groups (64% recovery with NaH_2PO_4 , Table 1). These results are thus consistent with electron transfer from Fe(II) complexed to edge OH-groups and the formation of structural Fe(II) in NAu-1.

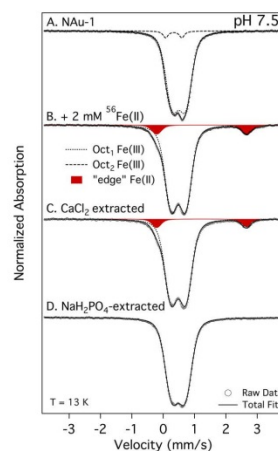


Figure 2. Mössbauer spectra of clay mineral NAu-1 at pH 7.5 before reaction (A), after reaction with Mössbauer invisible $^{56}\text{Fe}(\text{II})$ (B), after extraction with CaCl_2 (C), and subsequent extraction with NaH_2PO_4 (D). The Fe(II) doublet (red) in (B) is indicative for structural Fe reduction, and only minor changes are observed in (C). The absence of the structural Fe(II) doublet in (D) suggests that structural Fe(II) has been removed.

Fe(II) Sorption to Fe-Free Montmorillonite SYn-1. For 299 comparison, we reacted the Fe-free synthetic montmorillonite 300 SYn-1 with $^{57}\text{Fe}(\text{II})$ to determine whether sorbed Fe(II) in the 301 absence of interfacial electron transfer would yield an Fe(II) 302 doublet distinct from structural Fe(II) in NAu-1 at pH 7.5. 303 Before reaction with $^{57}\text{Fe}(\text{II})$, the Mössbauer spectrum of SYn-1 304 shows no features (Figure S1A), confirming the absence of structural 305 Fe in SYn-1. After reaction with aqueous $^{57}\text{Fe}(\text{II})$ at pH 7.5, 306 we observed two distinct Fe(II) doublets in the Mössbauer 307 spectrum (Figure 3A) as a result of nearly 50% sorption of the 308 aqueous $^{57}\text{Fe}(\text{II})$ (Table 1). The hyperfine parameters of the 309 inner Fe(II) doublet have slightly larger CS and narrower QS 310 (red, CS: 1.33 mm/s, QS: 2.71 mm/s, Table 2) but are still 311 reasonably similar to those of Fe(II)-reacted NAu-1 at pH 7.5. 312 In contrast, the values for the outer Fe(II) doublet (blue, CS: 1.43 313 mm/s, QS: 3.38 mm/s, Table 2) are rather unusual for day 314 mineral-bound Fe(II). The values are, however, very similar to what 315 was previously observed for Fe(II) adsorbed to bacterial cell walls⁶⁰ 316 and for basal plane exchanged Fe(II) at natural and synthetic Fe- 317 free montmorillonites,^{43,61} suggesting that Fe(II) sorbed to both, 318 basal planes and edge OH-groups of SYn-1 at pH 7.5. 319

To identify the two Fe(II) doublets, we subjected $^{57}\text{Fe}(\text{II})$ - 320 reacted SYn-1 to CaCl_2 and NaH_2PO_4 extraction. The CaCl_2 321 extraction removed the unusual outer Fe(II) doublet (Figure 3B), 322 and the spectral area of the removed Fe(II) doublet (36%, 323 Table 2) agrees well with the recovered fraction of sorbed 324 Fe(II) in the CaCl_2 extract (28%, Table 1), suggesting that this 325 doublet represents basal plane-bound Fe(II). Additional extrac- 326 tion with NaH_2PO_4 removed the second (inner) Fe(II) doublet 327 (Figure 3C), consistent with this doublet representing Fe(II) 328 bound to edge OH-groups as was found for Fe(II)-reacted 329 NAu-1 (pH 7.5). In the NaH_2PO_4 extract a slightly smaller Fe 330 amount was recovered than in the CaCl_2 extract (Table 1), 331 further corroborating our assignment of the Fe(II) doublet with 332

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Table 2. Mössbauer Parameters for Fitted Spectra

sample name (χ^2)	CS ^a (mm/s)	QS ^b (σ) ^c (mm/s)	area(σ) ^c (%)
NAu-1			
untreated(1.38)			
octahedral Fe(III) 1	0.50	0.46(0.28)	95.4(0.8)
octahedral Fe(III) 2	0.34	0.52(0.00)	4.6(0.7)
⁵⁶Fe(II)-reacted, pH 7.5(2.23)			
octahedral Fe(III)	0.48	0.48(0.28)	91.1(0.2)
"edge" Fe(II)	1.23	2.87(0.22)	8.9(0.2)
CaCl₂-extracted(2.23)			
octahedral Fe(III)	0.48	0.49(0.29)	92.2(0.2)
"edge" Fe(II)	1.22	2.86(0.19)	7.8(0.2)
CaCl₂-NaH₂PO₄-extracted(1.68)			
octahedral Fe(III)	0.49	0.47(0.29)	100.0(0.2)
⁵⁷Fe(II)-reacted, pH 4.0(6.08)			
octahedral Fe(III) 1	0.53	0.55(0.41)	42.9(0.1)
octahedral Fe(III) 2	0.36	0.62(0.12)	3.4(0.1)
basal Fe(II) 1	1.40	3.37(0.29)	47.8(0.1)
basal Fe(II) 2	1.38	2.52(0.29)	5.9(0.1)
CaCl₂-extracted(3.32)			
octahedral Fe(III) 1	0.48	0.58(0.47)	93.5(0.3)
octahedral Fe(III) 2	0.44	0.61(0.16)	6.5(0.2)
⁵⁶Fe(II)-reacted, pH 4.0(1.11)			
octahedral Fe(III) 1	0.49	0.43(0.33)	91.9(0.2)
octahedral Fe(III) 2	0.31	0.53(0.23)	6.8(0.1)
"basal" Fe(II)	1.33	3.43(0.15)	1.3(0.2)
CaCl₂-extracted(1.20)			
octahedral Fe(III) 1	0.49	0.43(0.34)	95.4(0.3)
octahedral Fe(III) 2	0.30	0.55(0.12)	4.6(0.2)
⁵⁶Fe(II)-reacted, pH 6.0(1.29)			
octahedral Fe(III)	0.48	0.44(0.37)	97.5(0.2)
"basal" Fe(II)	1.33	3.32(0.41)	2.5(0.2)
CaCl₂-extracted(1.60)			
octahedral Fe(III) 1	0.49	0.43(0.36)	93.8(0.3)
octahedral Fe(III) 2	0.33	0.59(0.27)	6.2(0.3)
⁵⁶Fe(II)-reacted, pH 6.5(2.31)			
octahedral Fe(III)	0.48	0.45(0.34)	95.6(0.2)
"basal" Fe(II)	1.33	3.35(0.29)	1.8(0.5)
"edge" Fe(II)	1.20	2.84(0.22)	2.6(0.5)
CaCl₂-extracted(1.16)			
octahedral Fe(III) 1	0.49	0.44(0.33)	91.3(0.3)
octahedral Fe(III) 2	0.35	0.55(0.19)	5.8(0.3)
"edge" Fe(II)	1.18	2.92(0.27)	2.9(0.2)
CaCl₂-NaH₂PO₄-extracted(1.03)			
octahedral Fe(III) 1	0.48	0.41(0.35)	95.3(1.6)
octahedral Fe(III) 2	0.46	0.65(0.17)	4.7(1.6)
SYn-1			
⁵⁷Fe(II)-reacted, pH 7.5(6.99)			
basal Fe(II)	1.43	3.38(0.24)	36.1(0.3)
edge Fe(II)	1.33	2.71(0.38)	61.7(0.3)
Fe(III)	0.33	0.77(0.09)	2.2(0.1)
CaCl₂-extracted(6.41)			
edge Fe(II)	1.28	2.67(0.35)	76.8(0.3)
Fe(III)	0.33	0.75(0.40)	23.2(0.3)
⁵⁷Fe(II)-reacted, pH 4.0(0.77)			
basal Fe(II) 1	1.40	3.38(0.24)	75.7(9.0)
basal Fe(II) 2	1.40	2.87(0.44)	24.3(9.1)

^aCenter shift relative to α -Fe(0). ^bQuadrupole splitting. ^cStandard deviation.

333 CS: 1.33 mm/s, QS: 2.71 mm/s as Fe(II) complexed to OH-
334 groups. In addition to the Fe(II) doublets, a small Fe(III)

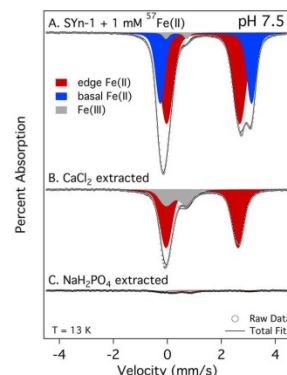


Figure 3. Mössbauer spectra of Fe-free clay mineral SYn-1: (A) After reaction with Mössbauer active ⁵⁷Fe(II) at pH 7.5 two Fe(II) doublets appear and a small contribution of Fe(III) was observed. (B) After extraction with CaCl₂, Fe(II) doublet 2 (blue) is absent. (C) In the subsequent extraction with NaH₂PO₄, Fe(II) doublet 1 (red) was also removed and only negligible Fe signals remained.

doublet (2% relative area) was also observed, indicating that some trace oxidation had occurred. We did not, however, find significant evidence for sorption-induced oxidation of Fe(II) as was suggested for a different Fe-free montmorillonite,⁶¹ where extensive Fe(II) oxidation of between 12% and 40% of sorbed Fe(II) was observed for pH 4.0 and 7.1, respectively. Note that the increased spectral area of Fe(III) in the spectrum of CaCl₂-extracted SYn-1 (Figure 3B) is mostly due to the removal of roughly one-third of the Mössbauer-active Fe mass in this extraction step and repeated cycles of glovebox transfers.

To confirm the assignment of the unusual Fe(II) doublet with CS: 1.43 mm/s and QS: 3.38 mm/s (outer doublet at pH 7.5) to basal plane-bound Fe(II), we reacted SYn-1 with aqueous ⁵⁷Fe(II) at pH 4.0 where sorption to edge OH-groups should be negligible (Figure 1). In the Mössbauer spectrum, we observed one broad doublet that required two Fe(II) doublets to achieve a reasonable fit (Figure S1B). Consistent with the assignment of basal plane bound Fe(II) dominating at pH 4.0, the doublet was completely removed with CaCl₂ extraction (Figure S1C) and all of the sorbed Fe(II) was recovered (Table 1). The hyperfine parameters of the dominant doublet (76% of the relative area) were consistent with the CS: 1.43 mm/s and QS: 3.38 mm/s found for the outer, unusual doublet for ⁵⁷Fe(II) sorbed to SYn-1 (Table 2). The minor doublet had a similar center shift and a slightly narrower quadrupole splitting (CS: 1.40 mm/s, QS: 2.87 mm/s). In a previous study of Fe(II) sorption to a synthetic Fe-free montmorillonite, the resulting Mössbauer spectra were also fitted using two Fe(II) doublet contributions, which were assigned to exchangeable Fe(II) (CS: 1.40 mm/s, QS: 3.10 mm/s) and FeCl⁻ entities (CS: 1.38 mm/s, QS: 3.43 mm/s).⁶¹ Detailed studies of Fe(II) in frozen solutions showed that the hyperfine parameters do indeed depend on the anion present in solution. Dilute Fe(ClO₄)₂ frozen solutions contain Fe(II) in largely unperturbed octahedral coordination environment in the form of hexa-aquo complex ([Fe(H₂O)₆]²⁺) with hyperfine parameters similar to the ones observed for the larger doublet of Fe(II) reacted with SYn-1 at pH 4.0 (CS: 1.40

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372 mm/s, QS: 3.38 mm/s⁶²). In contrast, frozen solutions of FeCl₂
 373 exhibit lower values for CS (1.37 mm/s) and QS (3.18 mm/s)
 374 and are thought to be the opposite limiting case of perturbed
 375 octahedral binding environment.⁶² We therefore suggest that
 376 the Fe(II) doublet with the larger QS (3.38 mm/s) is due to
 377 Fe(II) cation sorption, whereas the second doublet (QS: 2.87 mm/s)
 378 may be representing FeCl⁻ pairs sorbed to the basal planes.

379 **pH-Dependence of Fe(II)–Fe(III) Electron Transfer at**
 380 **Clay Mineral NAu–1.** To assess whether electron transfer to
 381 structural Fe in NAu–1 will also occur from Fe(II) sorbed to
 382 basal planes, we conducted additional experiments with NAu–1
 383 at pH 4.0. Based on our isotherm data (Figure 1) and sorption
 384 experiments with SYn–1 (pH 4.0, Figure S1), Fe(II) sorption
 385 should predominantly occur to basal planes at this low pH
 386 value. In order to confirm this hypothesis, we reacted NAu–1
 387 with ⁵⁷Fe(II) at pH 4.0. We observed a prominent Fe(II) doublet
 388 (Figure 4A), which was absent after extraction with CaCl₂ (data

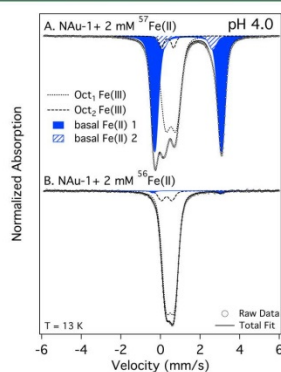


Figure 4. Mössbauer spectra of clay mineral NAu–1 at pH 4.0 (A) after reaction with Mössbauer visible ⁵⁷Fe(II) and (B) after reaction with Mössbauer invisible ⁵⁶Fe(II). The Fe(II) doublet (blue) in (B) is indicative for structural Fe reduction and the appearance of the same Fe(II) doublet in (A) suggests similar binding environment for basal plane-sorbed Fe(II) and structural Fe(II) formed in the electron transfer reaction.

389 not shown) and thus indicative of basal plane-sorbed Fe(II).
 390 Similar to what we found for Fe(II) sorbed to SYn–1 at pH 4.0,
 391 a reasonable fit of the Mössbauer spectrum of NAu–1 reacted
 392 with ⁵⁷Fe(II) at pH 4.0 was achieved only by including two
 393 Fe(II) contributions. The hyperfine parameters of the two Fe(II)
 394 doublets agree with the values found for basal plane-bound Fe(II)
 395 at SYn–1 at pH 4.0 (CS: 1.40 mm/s, QS: 3.37 mm/s, Table 2)
 396 and for sorbed FeCl⁻ pairs at SYn–1 at pH 4.0 (CS: 1.38 mm/s,
 397 QS: 2.52 mm/s, Table 2).

398 The combined evidence from our sequential extraction and
 399 Mössbauer results confirms predominant basal plane-sorbed
 400 Fe(II) in NAu–1 at pH 4.0, and thus we reacted NAu–1 with
 401 aqueous ⁵⁶Fe(II) at pH 4.0 to assess electron transfer from
 402 Fe(II) sorbed to basal planes. We found that little interfacial elec-
 403 tron transfer occurred to structural Fe in NAu–1 based on the
 404 resulting Mössbauer spectrum (1%, Figure 4B, Table 2) despite
 405 a significant portion of aqueous Fe(II) sorbing (21%, Table 1).
 406 To test whether greater stabilization of aqueous Fe(II) at the

low pH value of 4.0 made electron transfer to structural Fe in
 NAu–1 thermodynamically unfavorable, we also subjected NAu–1
 to aqueous ⁵⁶Fe(II) at pH 6.0 and found slightly increased electron
 transfer to structural Fe in NAu–1 (3%, Table 2). The extent of
 interfacial electron transfer at both pH 4.0 and 6.0 was still
 significantly lower compared to Fe(II)-reacted NAu–1 at pH
 7.5. The Fe(II) doublet in ⁵⁶Fe(II)-reacted NAu–1 (pH 4.0,
 6.0) disappeared after extraction with CaCl₂ (Figures S2, S3)
 and further treatment with NaH₂PO₄ did not yield significant
 changes in the Mössbauer spectra (data not shown), indicating
 that all structural Fe(II) in NAu–1 was removed or reoxidized
 during CaCl₂ extraction. This conclusion is corroborated by 95–
 119% recovery of initially sorbed Fe(II) in the CaCl₂ extraction
 and only up to 34% in the NaH₂PO₄ extraction (Table 1). Our
 findings indicate that electron transfer from basal plane-sorbed
 Fe(II) to structural Fe(III) in clay mineral NAu–1 does indeed
 occur but to a much lesser extent than what we observed for
 electron transfer from edge OH-group bound Fe(II).

Fascinatingly, the hyperfine parameters of the Fe(II) doublet
 formed at pH 4.0 and pH 6.0 (CS: 1.33 mm/s, QS: 3.43 mm/s
 and CS: 1.32 mm/s, QS: 3.30 mm/s, Table 2) are quite dif-
 ferent from those found at pH 7.5 but very similar to the values
 obtained for basal plane-sorbed Fe(II) at NAu–1 and SYn–1.
 We therefore suggest that the Fe(II) doublet we observed for
 Fe(II)-reacted NAu–1 (pH 4.0, 6.0) is due to reduced struc-
 tural Fe in a binding environment similar to basal plane sorbed
 Fe(II), which resulted from electron transfer from Fe(II) sorbed
 to the basal planes to structural Fe(III) in clay mineral NAu–1.
 From our results we can only conclude that structural Fe, which is
 the only source of Mössbauer active ⁵⁷Fe, was reduced to Fe(II) in
 our experiments. We cannot, however, determine the binding
 location of the formed structural Fe(II), i.e., whether the reduced
 structural Fe still resides in the clay mineral structure or whether it
 was released into solution and resorbed.

The finding of electron transfer from basal plane-sorbed
 Fe(II) at low pH values (<6.0) and from Fe(II) bound to edge
 OH-groups at pH 7.5 leads to the interesting question whether
 Fe(II) sorbed to basal planes and edge OH-groups can
 contribute simultaneously to Fe(II)–Fe(III) electron transfer
 at clay mineral NAu–1. To address this question, we reacted
 NAu–1 with aqueous ⁵⁶Fe(II) at pH 6.5, where we expect that
 both Fe(II) species are present (Figure 1). Interestingly, we
 observed a broad peak at 2.3 mm/s in the Mössbauer spectrum,
 which was indeed composed of two overlapping Fe(II) doublets
 (Figure S4B). What is more, the hyperfine parameters of the two
 observed Fe(II) doublets are similar to the values for structural Fe
 reduced at pH 4.0 and 6.0 (CS: 1.33 mm/s, QS: 3.35 mm/s) and
 at pH 7.5 (CS: 1.20 mm/s, QS: 2.84 mm/s, Table 2), con-
 sistent with electron transfer occurring from both Fe(II) sorbed
 to basal planes and Fe(II) bound to edge OH-groups. In
 agreement with an overall Fe(II) sorption extent between those
 encountered at pH 6.0 and pH 7.5, the extent of structural Fe
 reduction (5%) was between those observed at pH 6.0 and pH
 7.5 (Table 2).

Analysis of Mössbauer spectra and aqueous Fe(II) concen-
 trations resulting after sequential extraction with CaCl₂ and
 NaH₂PO₄ yielded additional evidence consistent with Fe(II)
 sorption to both basal planes and edge OH-groups and contri-
 butions of both Fe(II) pools to electron transfer to structural
 Fe in NAu–1. Specifically, CaCl₂ extraction removed the Fe(II)
 doublet assigned to a binding environment similar to basal
 plane bound Fe(II) (Figure S4C), and only the Fe(II) doublet
 with hyperfine parameters similar to what we observed for

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470 NAu-1 reacted at pH 7.5 (CS: 1.18 mm/s, QS: 2.92 mm/s,
471 Table 2) remained. Subsequent extraction with NaH_2PO_4 also
472 removed the remaining Fe(II) doublet (Figure S4D), which is
473 consistent with our finding for the reaction at pH 7.5. The
474 observed loss of 40–50% of Fe(II) spectral area after CaCl_2
475 extraction compares well with the removal of 71% of the
476 initially sorbed Fe(II) (Table 1) and suggests that basal plane-
477 bound Fe(II) contributed to electron transfer to structural
478 Fe(III) in NAu-1 at pH 6.5. The removal of 3% total spectral
479 area after NaH_2PO_4 extraction is also consistent with recovery
480 of 41% of initially sorbed Fe(II) or an equivalent of 3% of
481 structural Fe in the extract (Table 1), indicating additional
482 contribution of edge OH-group bound Fe(II) to electron transfer
483 to structural Fe(III) in NAu-1 at pH 6.5.

484 **Significance and Implications.** Our results clearly show
485 that electron transfer to structural Fe in clay minerals can occur
486 from Fe(II) sorbed to both basal planes and edge OH-groups.
487 This finding has significant implications for the proposed me-
488 chanisms of structural Fe reduction in clay minerals, which were
489 developed based on spectroscopic evidence from dithionite and
490 microbially reduced clay minerals.^{27–29} From analysis of the
491 Fe(II)–O–Fe(III) intervalence transfer band at 730 nm it was
492 suggested that chemical structural Fe reduction with dithionite
493 followed a sequential reduction of Fe(III)–O–Fe(III) to
494 Fe(II)–O–Fe(III) and then Fe(II)–O–Fe(II) pairs.^{27,28} Later
495 the hypothesis was formed that this observed pattern was
496 indicative of pseudorandom electron transfer, which can occur
497 only via clay mineral basal plane surfaces.²⁶ Our finding of
498 electron transfer from basal plane-sorbed Fe(II) thus supports
499 the conclusions of this earlier work and suggests that electrons
500 can be transferred over distances of 3.2–3.3 Å, i.e., from basal
501 plane oxygens to octahedrally bound Fe in the structure.⁶³ This
502 is somewhat surprising as cations bound by ion exchange are
503 thought to be present in outer sphere complexes with small
504 covalent binding contribution,^{64,65} which would inhibit electron
505 transfer. Small cations, for example $\text{Li}^{+66,67}$ and $\text{Cu}^{2+68,69}$ are,
506 however, known to migrate into the structure of smectites upon
507 heating, possibly hinting at an alternative pathway for electron
508 transfer from basal plane-bound Fe(II) to structural Fe in clay
509 minerals.

510 Structural Fe reduction from clay mineral edges, in contrast,
511 was hypothesized to result in a maximum amount of Fe(II)–
512 O–Fe(III) pairs in the beginning of the reaction, which would
513 progress through the octahedral sheet like a moving front that
514 forms a boundary between Fe(II)–O–Fe(II) and Fe(III)–
515 O–Fe(III) domains.²⁶ In a recent study this idea was expanded
516 on, and Mössbauer spectra of microbially reduced nontronite
517 showing magnetic ordering of both Fe(II) and Fe(III) components,
518 which was absent in abiotically reduced nontronite samples,
519 were consistent with a moving front model and thus with reduc-
520 tion proceeding from the edges.²⁹ Another study challenged this
521 conclusion as the Mössbauer spectra of a different nontronite
522 microbially reduced with different *Shewanella* strain showed
523 ordering of only the nontronite Fe(III),⁷⁰ consistent with what
524 was observed for dithionite reduced nontronite.²⁹ Our findings
525 of electron transfer from edge OH-group bound Fe(II) support
526 that structural Fe can be reduced from clay mineral edges, a
527 mechanism which might be feasible for only specific types of
528 microorganism. It might be possible that microbes do not
529 reduce structural Fe in clay minerals directly but rather facilitate
530 Fe reduction by a more complex sequence. This process might
531 include structural Fe(III) mobilization by complex formation
532 with exuded organic ligands and acids, reduction of this complexed

Fe by microbes, and resorption of Fe(II) to clay minerals, which
533 in turn could reduce structural Fe in clay minerals, similar to
534 the suggested mechanism of structural Fe(II) oxida-
535 tion in biotite.⁷¹ Furthermore, our finding of electron transfer
536 through edge OH-groups might also be viable electron transfer
537 pathway for other clay mineral types, for example for the group
538 of mainly uncharged 1:1 clay minerals, which exhibit only very
539 limited basal plane sorption.

540 Although our findings provide compelling evidence for dif-
541 ferent binding environments of structural Fe(II) resulting from
542 electron transfer from Fe(II) sorbed to basal planes and to edge
543 OH-groups, the consequences of these differences for Fe mobility
544 and reactivity remain unclear. Based on our experimental data
545 we cannot unambiguously determine whether removal of indi-
546 cative Fe(II) doublets in the Mössbauer spectra after extraction
547 was due to re-reduction and removal of initially sorbed ⁵⁶Fe(II)
548 or whether we extracted the Mössbauer-active structural ⁵⁷Fe-
549 (II). Nevertheless, the loss of Mössbauer Fe(II) doublets in our
550 sequential extraction procedure indicates that electrons trans-
551 ferred to structural Fe in clay mineral can be further transferred
552 when solution parameters such as cation or anion concen-
553 trations change. This suggests that Fe-bearing clay minerals can
554 act as intermediate storage or buffer of electrons in subsurface
555 environments. Indeed, it has been shown that contaminant
556 transformation is feasible with Fe(II)-reacted smectites at or
557 above pH 7.5,^{19,38} where we found electron transfer to struc-
558 tural Fe via edge OH-group bound Fe(II). At these pH values,
559 reduction of the used contaminants was slow in the absence of
560 smectite, indicating a contribution of structurally stored redox
561 equivalents. However, only low reactivity of the same smectites
562 was observed when reacted at pH values below 7.5,³⁸ and we
563 hypothesize that the different binding environment of structural
564 Fe(II) formed in the electron transfer reaction with basal plane-
565 bound Fe(II) and/or the smaller extent of structural Fe reduc-
566 tion might be responsible for the observed lower reactivity.

567 The finding of interfacial electron transfer between Fe(II)
568 sorbed to edge OH-groups of NAu-1 and structural Fe in this
569 clay minerals prompts a comparison with electron transfer pro-
570 cesses between sorbed Fe(II) on Fe(III) oxides, as the interacting
571 entities, i.e., OH groups and Fe(II), are the same. Recently, a new
572 conceptual framework for the heterogeneous reaction between
573 aqueous Fe(II) and Fe(III) oxides has been proposed, which
574 includes electron transfer between aqueous Fe(II) and structural
575 Fe(III),^{49,72,73} bulk electron conduction,⁷⁴ and Fe(II)–Fe(III)
576 atom exchange.⁷⁵ In this framework, interfacial electron transfer
577 is the first, crucial step that can eventually lead to complete Fe
578 atom mixing between aqueous and solid Fe pools.⁷⁵ Our finding of
579 electron transfer in the Fe(II)-clay mineral system thus leads to the
580 fascinating question whether Fe atom exchange might also occur
581 during the heterogeneous reaction between aqueous Fe(II) and
582 Fe-bearing clay minerals, in analogy to what was observed for
583 Fe oxides.

■ ASSOCIATED CONTENT

● Supporting Information

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587 Details on the clay minerals and their preparation, Mössbauer
588 instrumentation and fitting as well as additional figures of
589 Mössbauer spectra of Fe(II) adsorbed to SYN-1, and of the
590 reaction of NAu-1 at pH 4.0, 6.0, and 6.5. This material is
591 available free of charge via the Internet at <http://pubs.acs.org>.

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595 Notes

596 The authors declare no competing financial interest.

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