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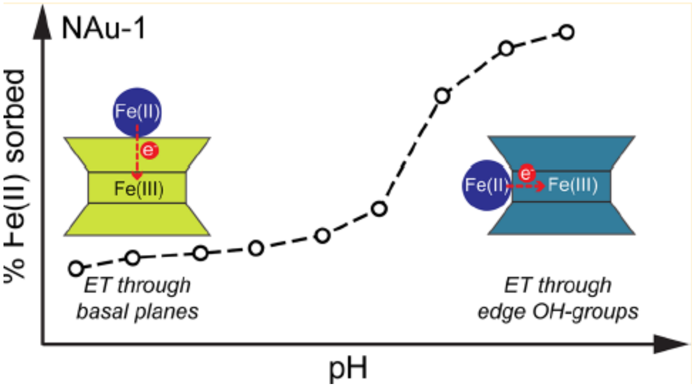
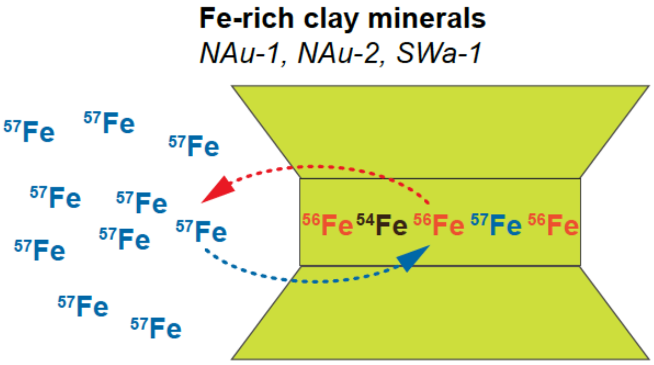
Co-PIs: Clark Johnson (University of Wisconsin), Kevin Rosso (Pacific Northwest National Laboratory), Ken Kemner, Maxim Boyanov, and Edward O'Loughlin and (Argonne National Laboratory)
Institution: University of Iowa
Title: Electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clays: Role in U and Hg(II) transformations
Program Manager: Roland Hirsch

Summary



During this project, we investigated Fe electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clay minerals. We used selective chemical extractions, enriched Fe isotope tracer experiments, computational molecular modeling, and Mössbauer spectroscopy. Our findings indicate that structural Fe(III) in clay minerals is reduced by aqueous Fe(II) and that electron transfer occurs when Fe(II) is sorbed to either basal planes and edge OH-groups of clay mineral. Findings from highly enriched isotope experiments suggest that up to 30 % of the Fe atoms in the structure of some clay minerals exhanges with aqueous Fe(II). First principles calculations using a small polaron hopping approach suggest surprisingly fast electron mobility at room temperature in a nontronite clay mineral and are consistent with temperature dependent Mössbauer data Fast electron mobility suggests that electrons may be able to conduct through the mineral fast enough to enable exchange of Fe between the aqueous phase and clay mineral structure. over the time periods we observed. Our findings suggest that Fe in clay minerals is not as stable as previously thought.



Project Background

The Fe(II)/Fe(III) redox couple plays a critical role in the biogeochemical cycling and bioavailability of Fe in air, water, and soils. Redox reactions at the mineral-water interface of Fe-bearing minerals strongly influence the mobility and cycling of trace elements, heavy metals and radionuclides in both soil and subsurface environments. Heterogeneous reactions between aqueous Fe(II) and Fe(III) oxides have been extensively studied, leading to a new conceptual framework which includes electron transfer between aqueous Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III) atom exchange. Reactions of aqueous Fe(II) with clay minerals, on the other hand, have received much less attention and are often described in terms of surface reactions including ion exchange, surface complexation, and/or surface precipitation. Currently, it is unclear whether similar processes as observed for the heterogeneous redox reaction in Fe(III) oxides are also occurring with Fe-bearing clay minerals.

In this research we will determine whether electron transfer and atom exchange occurs between aqueous Fe(II), a reductant abundant in natural anaerobic environments, and structural Fe(III) in clay minerals. Currently, we are investigating whether **electron transfer** between aqueous Fe(II) and structural Fe(III) in clay minerals occurs and are studying how clay mineral and solution properties influence this reaction. In collaboration with Kevin Rosso (PNNL), we are addressing this question by both laboratory experiments and computational molecular simulation. At the same time, we are investigating whether redox-driven **Fe atom exchange** occurs between aqueous Fe(II) and structural Fe(III) in clay minerals, and natural, clay-rich sediments. For this research question, our collaborators Clark Johnson and Brian Beard (University of Wisconsin, Madison) are providing extensive experience in Fe isotope tracer experiments and precise Fe isotope measurements. Future experiments will focus on the **impact** of electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clay minerals and natural, clay-rich sediments on the redox cycling of U in the subsurface. This research will be carried out in collaboration with Ken Kemner, Maxim Boyanov, and Edward O'Loughlin (ANL).

The *central hypothesis* of the proposed research is that electron transfer and atom exchange occurs between aqueous Fe(II) and structural Fe(III) in clay minerals and natural, clay-rich sediments. Although it is becoming increasingly clear that Fe in clay minerals plays an important role in determining the reactivity of clay minerals, the molecular-scale reactions governing Fe redox dynamics in clay minerals are largely unknown. Currently the fate of Fe(II) produced from chemical or biological reduction of clay minerals has been interpreted in the framework of ion exchange and surface complexation without consideration of the potential for dynamic redox cycling between aqueous Fe(II) and structural Fe(III) in the clay (i.e., $\mathrm{Fe(II)_{aq}}$-$\mathrm{Fe(III)_{clay}}$ electron transfer and atom exchange). *The objective of the proposed research* is to evaluate whether $\mathrm{Fe(II)_{aq}}$-$\mathrm{Fe(III)_{clay}}$ electron transfer and atom exchange is an important redox process at the mineral-microbe water interface, and how this new, tightly coupled biogeochemical process influences the redox behavior of U in the subsurface. We plan to test our central hypothesis and accomplish the overall objective by investigating the following specific hypotheses:

1. Electron transfer occurs between aqueous Fe(II) and structural Fe(III) in clay minerals and results in structural Fe(II) in the clay mineral and formation of an Fe(III) oxide on the surface of the clay.
2. Redox-driven Fe atom exchange occurs between aqueous Fe(II) and structural Fe(III) in clay minerals, and natural, clay-rich sediments.
3. Electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clay minerals and natural, clay-rich sediments will impact the redox cycling of U in the subsurface.

Hypothesis I: Electron transfer between aqueous Fe(II) and structural Fe(III) in clay minerals

Using the isotope specificity of Mössbauer spectroscopy and two well-characterized clay minerals (NAu−1, NAu−2), we previously showed that electron transfer occurs between aqueous Fe(II) and octahedral Fe(III) in clay minerals. We also carried out experiments with different aqueous Fe(II) concentrations and found that adsorption of aqueous Fe(II) is a prerequisite for electron transfer to structural Fe(III) in clay minerals. Fe(II) uptake beyond 15-20% of structural Fe(III) did not yield more reduced structural Fe, suggesting a limit to the extent of clay reduction. We hypothesize that this limit might be due to a thermodynamic effect, which likely depends on the specific structure of the clay mineral.

To test whether electron transfer to structural Fe(III) depends on the location of Fe(II) sorption, i.e. clay mineral basal planes or clay mineral edge OH-groups, we carried out experiments at different pH values (pH 6.0 vs pH 7.5) to modulate sorption to these two sites. Fe(II) sorbed predominantly to basal planes at pH values below 6.0 and to edge OH-groups at pH value 7.5. In **Figure 1A**, Fe-bearing clay mineral NAu−1 is shown, which contains sufficient ^{57}Fe to yield a clear Mössbauer spectrum. After reaction with aqueous ^{56}Fe(II), which is transparent to Mössbauer spectroscopy, an Fe(II) doublet emerges (**Figure 1B, C**). This Fe(II) doublet is due to the reduction of structural ^{57}Fe(III) in clay mineral NAu-1 by aqueous ^{56}Fe(II). Comparing the relative areas of the Fe(II) doublets in **Figure 1B** (pH 7.5) and 1C (pH 6.0), indicates a lower ratio of structural Fe(II) at pH 6.0 compared to the reaction at pH 7.5 (3% compared to 15%). This finding indicates that electron transfer occurs from Fe(II) sorbed to both basal planes and edge OH-groups.

We used Fe-free clay mineral SYn−1as well as sequential extractions to selectively remove basal plane-sorbed Fe(II) and Fe(II) bound to edge OH-groups to characterize the identity of the structural Fe(II) doublets at pH 6.0 and 7.5. In **Figure 2A**, the Mössbauer spectrum of SYn−1 reacted with Mössbauer-visible ^{57}Fe(II) at pH 7.5 is shown, which yields two distinct Fe(II) doublets. As Syn−1 does not contain any structural Fe(III), these Fe(II) doublets are due to Fe(II) sorbed to different clay mineral binding sites. After extraction with $CaCl_2$, targeting basal plane-sorbed Fe(II), the outer (blue) Fe(II) doublet disappeared (**Figure 2B**), whereas the inner (red) Fe(II) doublet was removed only after subsequent extraction with NaH_2PO_4 (**Figure 2C**), which is selective for edge OH-group bound Fe(II). We therefore assigned the Mössbauer parameters to Fe(II) sorbed to basal planes (blue) and Fe(II) sorbed to edge OH-groups (red). For Fe(II)-reacted NAu−1 at pH 7.5 the Mössbauer hyperfine parameters and the extraction behavior of the observed Fe(II) doublet were consistent with structural Fe(II) or Fe(II) sorbed to edge OH-groups. Thus, these two structural Fe(II) environments in clay minerals cannot be distinguished based on Mössbauer spectral data alone. In contrast, Mössbauer hyperfine parameters and extraction behavior of Fe(II)-reacted NAu−1 at pH 6.0 were indicative of binding environments similar to basal plane-sorbed Fe(II). In collaboration with Kevin Rosso's group, we are currently exploring the mechanism and kinetics of electron transfer from Fe(II) sorbed to basal planes and from Fe(II) bound edge OH-groups in more detail by applying computational molecular modeling.

Also in collaboration with Kevin Rosso's group, we examined rates of Fe(II)-Fe(III) electron transfer in distinct local environments of the structure, both in bulk and on surfaces, in order to identify energetically preferable electron transfer pathways. We applied density functional theory with the Hubbard U correction to properly account for electron localization effects in conjunction with a small polaron hopping approach and Marcus electron transfer theory. Evaluation of the electron transfer rates for the Fe(II)/Fe(III) electron hopping in octahedral sheets, as well as across the sheets (tetrahedral to octahedral), showed that electron transfer within the octahedral sheets is the dominant process for bulk electronic conductivity in nontronite clay minerals at room temperature (**Figure 3**). However, the generally higher reorganization energy and weaker electronic coupling found in Fe-bearing clay minerals lead to lower electron transfer rates compared to iron oxides.

We also investigated electron transfer in a lower Fe containing clay mineral Wyoming montmorillonite SWy-2 (2.3 wt% Fe). Our results are fascinating and reveal extensive reduction of the Fe(III) in the clay despite the low concentration and large separation of Fe atoms in the structure. Up to 77% reduction of structural Fe(III) to Fe(II) in the clay mineral was observed (**Figure 4 and 5**). In comparison to high-iron nontronites (NAu-1), under similar conditions, the relative percent of Fe(III) in the SWy-2 structure reduced by aqueous Fe(II) is higher in SWy-2, despite macroscopically similar sorption. Furthermore, by investigating Fe(II) uptake at pH values of 4.0 and 6.0, we find that sorption of Fe(II) to the SWy-2 at these low pH values results in significant electron transfer (12 and 56%, respectively), despite conditions where sorption to basal planes is the favored Fe(II) uptake mechanism. Extensive electron transfer to SWy-2 occurs despite evidence for isolated Fe atoms within the SWy-2 structure (**Figure 4 and 5**). As expected, and in contrast to nontronites, electron delocalization between Fe(II) and Fe(III) in SWy-2 is not observed by Mössbauer spectroscopy (**Figure 6**). We suggest that electron transfer through the clay basal plane of SWy-2 is a major contributor to the observed reaction between aqueous Fe(II) and SWy-2 structural Fe(III). Furthermore, we show that electron transfer between Fe(II) and SWy-2 structural Fe(III) is relatively insensitive to the nature of the interlayer cation (Na+ vs. Cs+). Our work highlights the importance of abiotic clay mineral reduction by Fe(II), and suggests that structural Fe in clay minerals is more accessible then previously thought.

Hypothesis II: Fe atom exchange between aqueous Fe(II) and structural Fe(III) in clay minerals

Due to their stability towards reductive dissolution, Fe-bearing clay minerals are viewed as a renewable source of Fe redox activity in diverse environments. Recent findings of interfacial electron transfer between aqueous Fe(II) and structural Fe in clay minerals and electron conduction in octahedral sheets of nontronite, however, raise the fascinating question whether Fe interaction with clay minerals is more dynamic than previously thought. Here, we use an enriched isotope tracer approach to simultaneously and independently trace Fe atom movement from the aqueous phase to the solid (^{57}Fe) and from the solid into the aqueous phase (^{56}Fe). Over 6 months, we observed a significant decrease in aqueous ^{57}Fe isotope fraction, with after 3 days and stabilized after about 50 days (**Figure 7**). For the aqueous ^{56}Fe isotope fraction, we observed a similar but opposite trend, indicating that Fe atom movement had occurred in both directions: from the aqueous phase into the solid and from the solid intoaqueous phase. We calculated that 5–20% of structural Fe in clay minerals NAu–1, NAu–2, and SWa–1 exchanged with aqueous Fe(II), which significantly exceeds the Fe atom layer exposed directly to solution (**Figure 8**). Calculations based on electron-hopping rates in nontronite suggest that the bulk conduction mechanism previously demonstrated for hematite and suggested as an explanation for the significant Fe atom exchange observed in goethite may be a plausible mechanism for Fe atom exchange in Fe-bearing clay minerals. Our finding of 5–20% Fe atom exchange in clay minerals indicates that we need to rethink how Fe mobility affects the stability of Fe-bearing phyllosilicates and its role in Fe biogeochemical cycling, as well as its use in a variety of engineered applications, such as landfill liners and nuclear repositories.

Please briefly (7000 chars or less) describe papers and other products delivered:

Publications

1. Bingjie Shi, Kai Liu, Lingling Wu, Weiqiang Li, Christina M. Smeaton, Brian L. Beard, Clark M. Johnson, Eric E. Roden, and Philippe Van Cappellen. Iron Isotope Fractionations Reveal a Finite Bioavailable Fe Pool for Structural Fe(III) Reduction in Nontronite. *Environ. Sci. Technol.*, **2016**, 50 (16), pp 8661–8669. DOI: 10.1021/acs.est.6b02019.
2. Anke Neumann, A., Lingling Wu, Weiqiang Li, Brian Beard, Clark M. Johnson, Kevin M. Rosso, Andrew Frierdich, and Michelle M. Scherer. Atom Exchange between Aqueous Fe(II) and Structural Fe in Clay Minerals. *Environ Sci Technol* **2015**, 49(5), p. 2786-2795. DOI. 10.1021/es504984q
3. Anke Neumann, Tyler L. Olson, and Michelle M. Scherer. Spectroscopic Evidence for Fe(II)–Fe(III) Electron Transfer at Clay Mineral Edge and Basal Sites. *Environ. Sci. Technol.*, **2013**, *47* (13), pp 6969–6977. DOI: 10.1021/es304744v. *Tribute Issue for Rene Scharzenbach.*
4. Vitaly Alexandrov, Anke Neumann, Michelle M. Scherer, and Kevin M. Rosso. Electron Exchange and Conduction in Nontronite from First-Principles *J. Phys. Chem. C*, **2013**, *117* (5), pp 2032–2040 DOI: 10.1021/jp3110776.

Publications In Preparation

5. Drew E. Latta, Anke Neumann, W.A.P.J. Premaratne, Michelle M. Scherer. Extensive Fe(II) - Fe(III) electron transfer in a low Fe clay mineral: A Mossbauer spectroscopy investigation. *Invited paper* for Chemical Geology: Adsorption of Metals on Geomedia III special issue.
6. A. Neumann and M. M. Scherer. Fe(II)-driven remobilization of Fe in clay minerals. In preparation for *Environ. Sci. Technol.*
7. D. Latta, M. Boyanov, K. Kemner. Uranium reduction by reduced clay minerals.

Conference Presentations

2012

1. A. Neumann, M. M. Scherer. Electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clay minerals. Monte Verità Conference: Iron Biogeochemistry - From molecular processes to global cycles, Ascona, Switzerland, March 3–8, 2013.
2. A. Neumann, M. M. Scherer. Fe(II)-driven Fe clay mineral reorganization. *Invited talk* Telluride Workshop: Biogeochemistry and Redox Transformations of Iron, Telluride, CO, USA, August 7–10, 2012.
3. M. M. Scherer. Fe(II)-catalyzed Fe oxide recrystallization: An update. *Invited talk* Telluride Workshop: Biogeochemistry and Redox Transformations of Iron, Telluride, CO, USA, August 7-10, 2012
4. M. Scherer, D. Latta, T. Pasakarnis, A. Neumann, M. Barger, K. Rosso, C. Johnson. Fe electron transfer and atom exchange at mineral/water interfaces. *Invited talk* 22nd Goldschmidt Conference, Montreal, Canada, June 24-29. Abstract published by Geochimica et Cosmochimica Acta.
5. A. Neumann, M. Scherer. Interfacial Fe(II)-Fe(III) electron transfer and atom exchange in smectites: effect of smectite properties. 22nd Goldschmidt Conference, Montreal, Canada, June 24-29. Abstract published by Geochimica et Cosmochimica Acta.

6. L. Wu, B. L. Beard, E. E. Roden, and C. M. Johnson. Stable iron isotope fractionation between aquoeus Fe(II) and smectite SWa-1. 22nd Goldschmidt Conference, Montreal, Canada, June 24-29. Abstract published by Geochimica et Cosmochimica Acta.
7. A. Neumann, M. M. Scherer, M. Barger, C. Johnson, L. Wu, K. Rosso, K. Kemner, M. Boyanov, E. O'Loughlin. Electron transfer and atom exchange between aqueous Fe(II) and structural Fe(III) in clays: Role in U and Hg(II) transformations. SBR/DOE Annual Meeting, April/May 2012, Washington DC.

2013

8. Anke Neumann, Tyler L. Olson, Weiqiang Li, Brian L. Beard, Clark M. Johnson, Kevin Rosso, VitalyAlexandrov, and Michelle M. Scherer*: Redox reactions between aqueous Fe(II) and structural Fe(III) in clay minerals: A new conceptual framework. 50th Anniversary of Clay Minerals Society. Oct 6 - 8, 2013. University of Illinois at Urbana-Champaign (**Invited Talk*).
9. A. Neumann, M. Scherer, D. Latta, C. Gorski, B. Huhmann. Behavior of Contaminants at Environmental Interfaces. 246th American Chemical Society National Meeting. Indianapolis, IN. March 2013. (*Invited Talk*).
10. A. Neumann, M. Scherer, D. Latta, C. Gorski, B. Huhmann. Influence of Fe(II)-catalyzed Fe oxide recrystallization on metal cycling. 50th Anniversary conference of the Association of Environmental Engineering and Science Professors (AEESP). Golden, California. July 14-16. 2013.

2014

11. A. Neumann and M. Scherer. Fe(II)-driven mineral reorganization in Fe-containing clay minerals. Telluride Workshop on Fe Biogeochemistry. August 2014. Telluride, Colorado. (*Invited Talk*).
12. M. Scherer. Redox chemistry at the Fe mineral-water interface: New insightes from isotope games. *Keynote lecture* at ACS National Meeting "Women Leaders in Environmental Chemistry". 248th American Chemical Society National Meeting, San Francisco, CA, 2014.

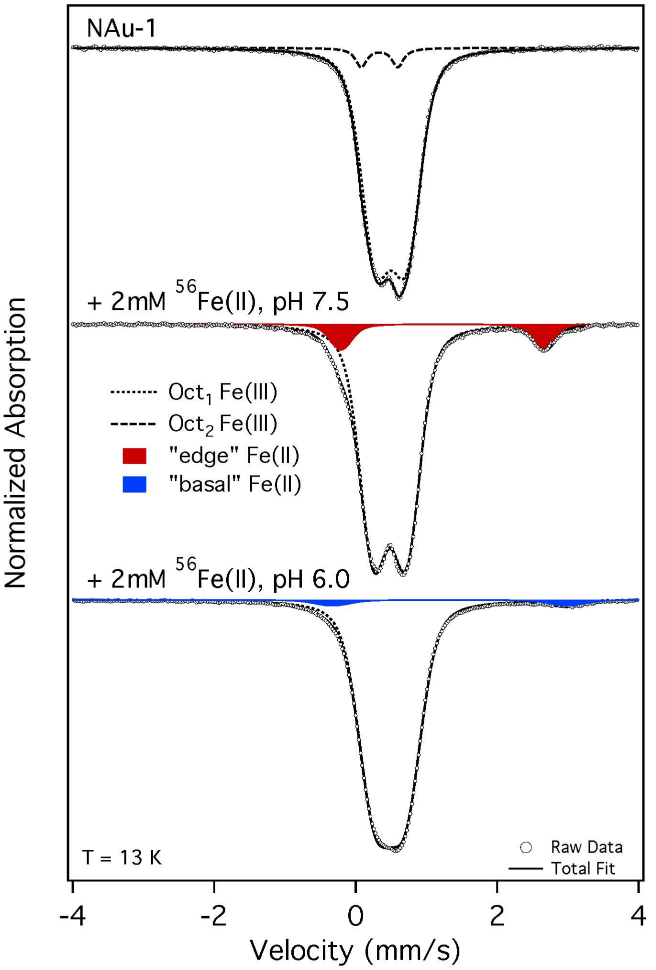


Figure 1. Mössbauer spectra showing reduction of structural Fe in clay mineral NAu-2 after reaction with Mössbauer-invisible aqueous ^{56}Fe(II) at pH 7.5 (B) and pH 6.0 (C).

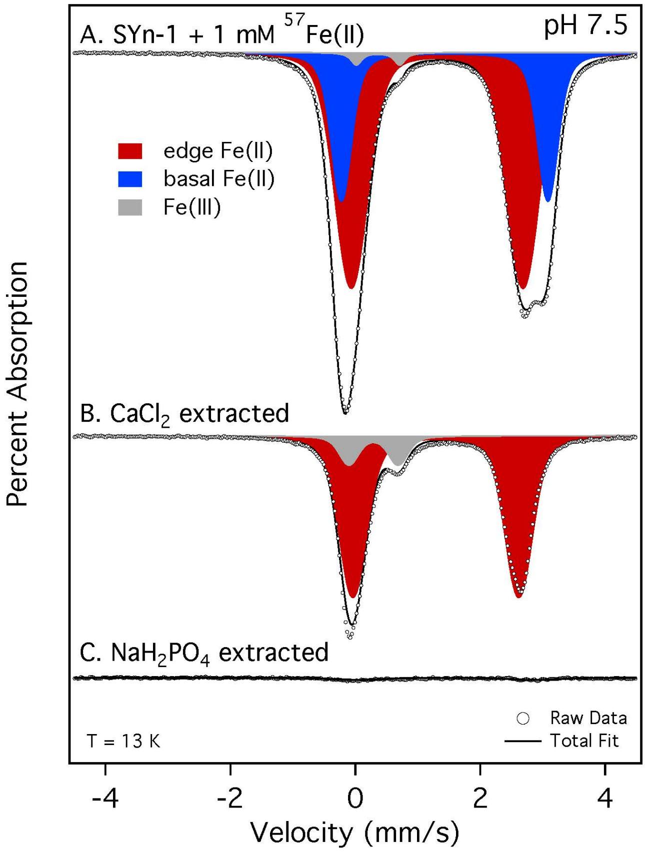


Figure 2. After adsorption of Mössbauer-visible ^{57}Fe(II) to Fe-free montmorillonite SYn-1 (Mössbauer-invisble) two distinct Fe(II) doublets appear (A). Extraction with CaCl$_2$ removes the outer (blue) Fe(II) doublet (B), whereas the inner (red) Fe(II) doublet was removed only once NaH$_2$PO$_4$ was used (C).

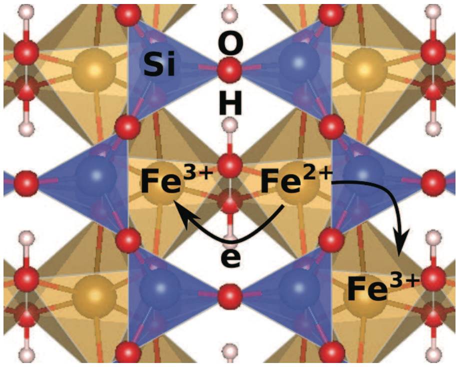


Figure 3. Schematic representation of the predominant electron transfer pathways occurring within the octahedral sheet of nontronite clay minerals as determined by applying computational molecular modeling.

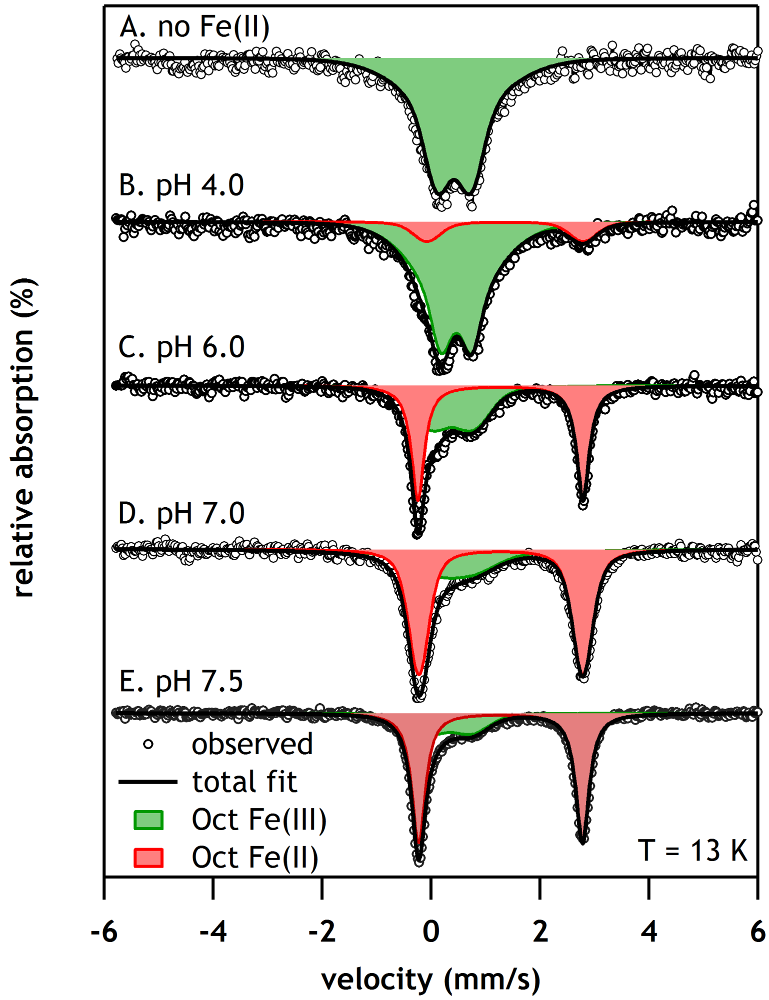


Figure 4. Mössbauer spectra of SWy-2 collected before reactions (A) and after reaction with 2.2 mM aqueous ^{56}Fe(II) (B-E) as a function of pH with for pH 4.0 (B), pH 6.0 (C),pH 7.0 (D) and pH 7.5 (E). Spectra are modeled with Fe^{2+} (green) and Fe^{3+} (red) doublets, with the sum from fitting shown as the solid black line. Mössbauer spectral fitting parameters are reported in **Table 2**.

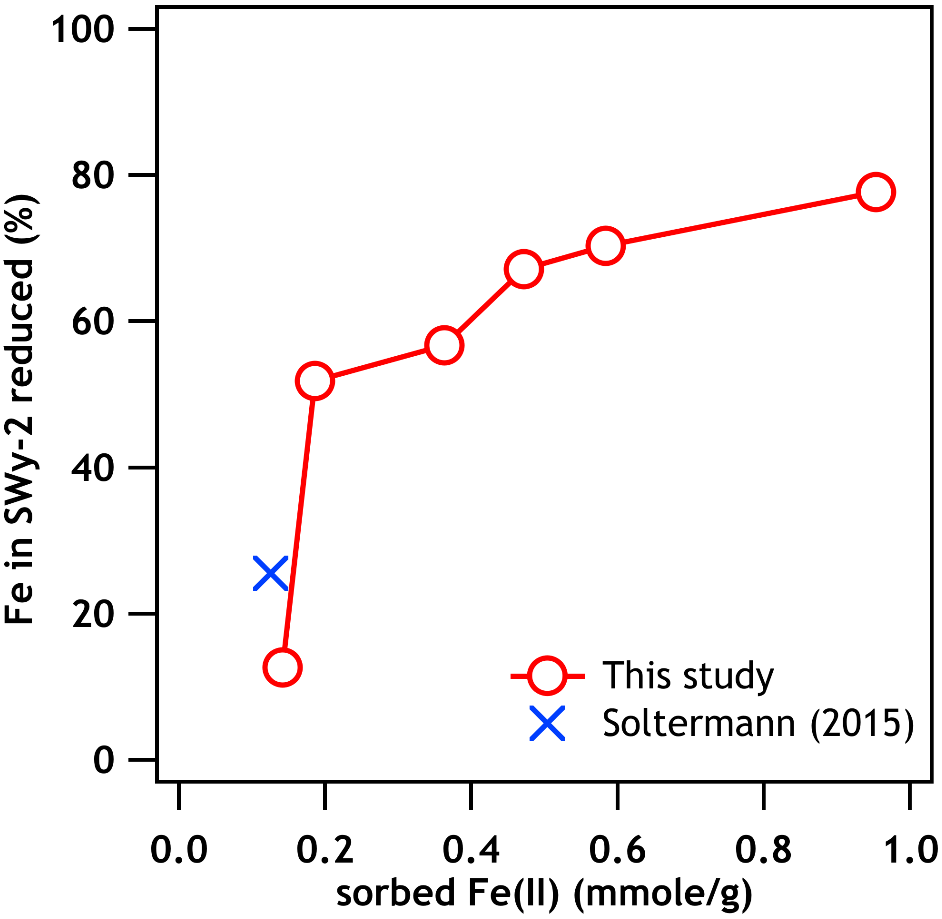


Figure 5. Plot of Mössbauer spectra derived Fe(II):Fe_{total} content of Na^+-SWy-2 as a function of Fe(II) sorption. Data from both varying pH and Fe(II) concentration experiments are plotted as one curve. The blue filled circle represents data from Soltermann et al. with SWy-2.

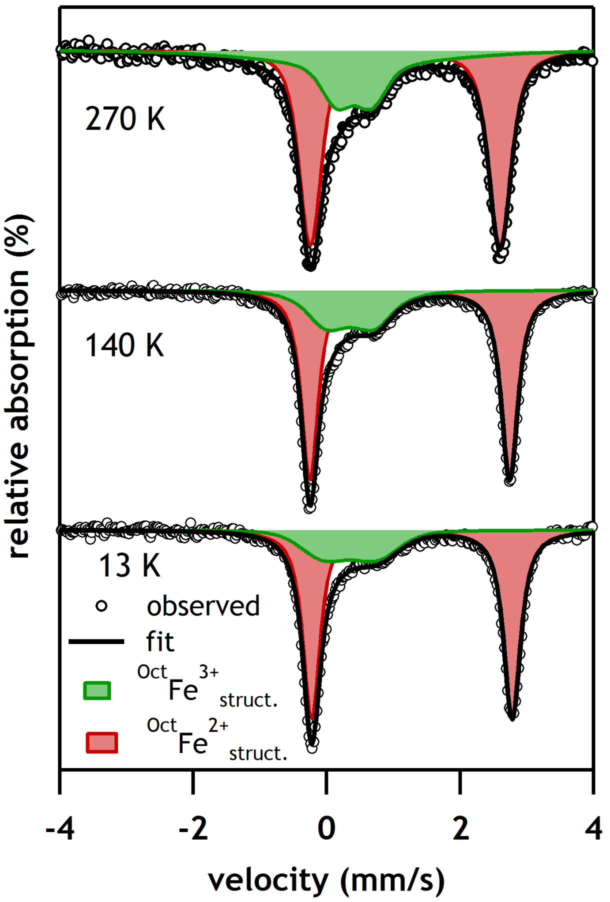


Figure 6. Mössbauer spectroscopy temperature profiles for SWy-2 reacted with 2.2 mM ^{56}Fe(II). Conditions are 2 g/L SWy-2 clay mineral in pH 7.5 buffer of 25 mM MOPS/50 mM NaCl.

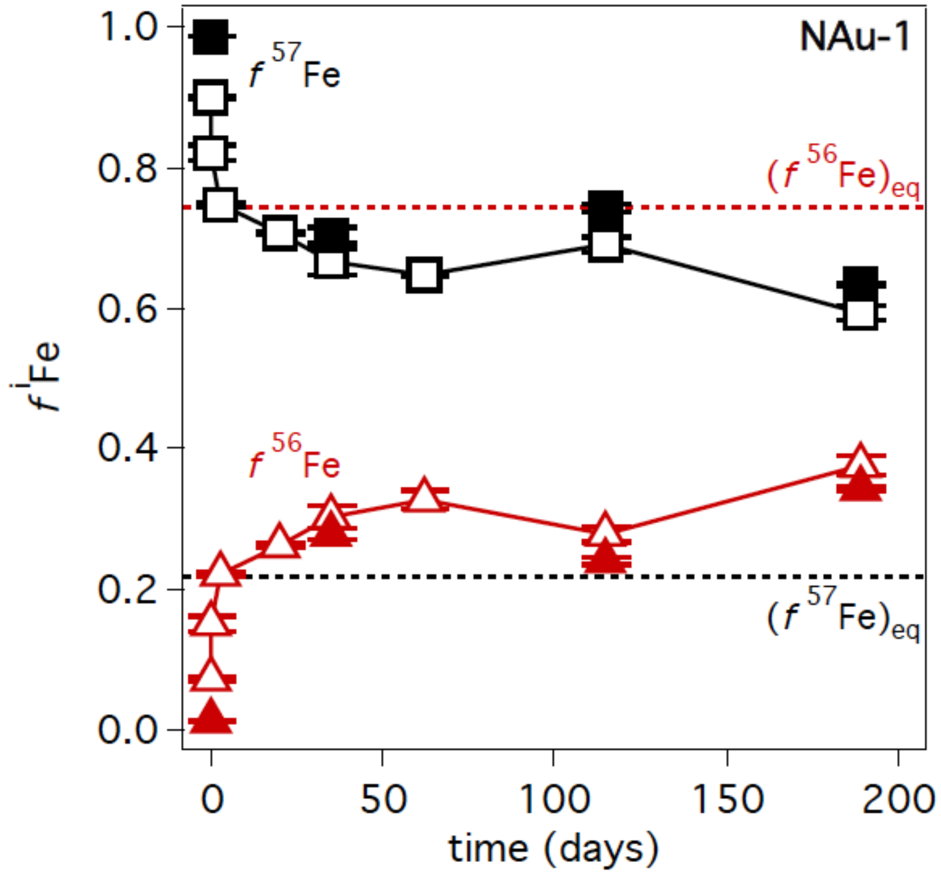


Figure 7. Fractions of ^{57}Fe (black) and ^{56}Fe (red) in the aqueous phase at pH 7.5 during the reaction of aqueous Fe(II) enriched in ^{57}Fe and depleted in ^{56}Fe with clay mineral NAu–1 containing ^{57}Fe and ^{56}Fe in their natural abundance. Good agreement of isotope measure- ments with a quadrupole inductively coupled mass spectrometer (Q–ICP–MS, open markers) and with a multi-collector ICP–MS (MC–ICP–MS, fi markers) were achieved. Dashed lines indicate the calculated isotope equilibrium fraction for ^{57}Fe (black) and ^{56}Fe (red).

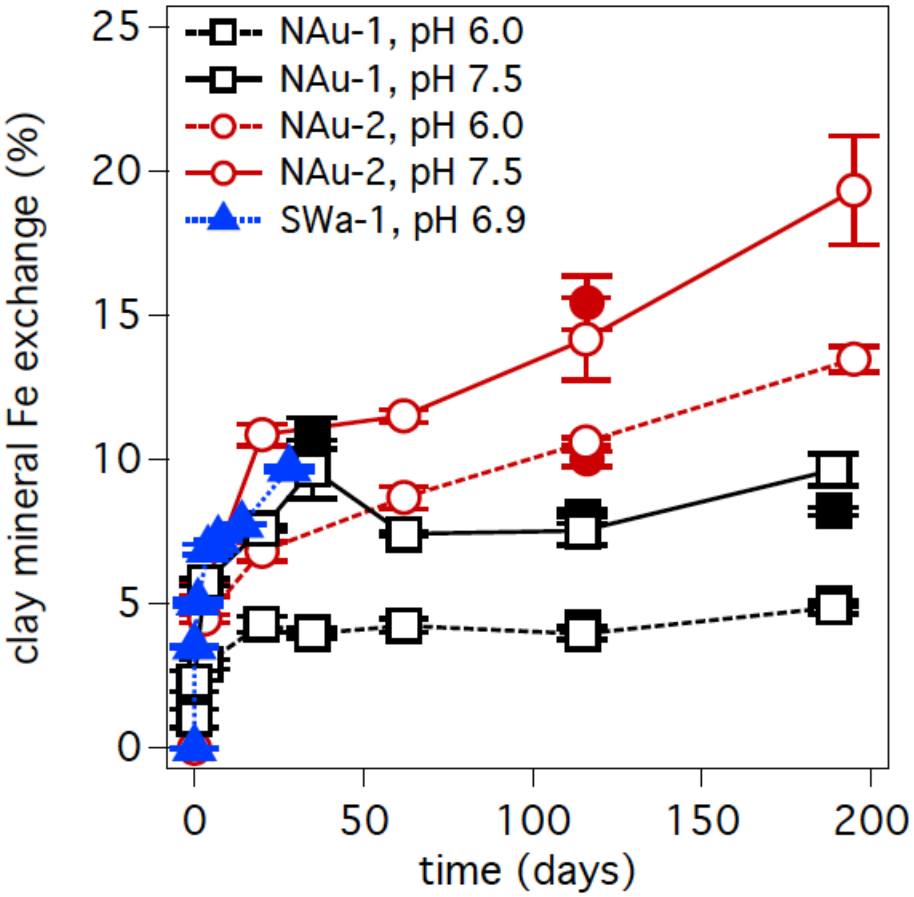


Figure 8. Extent of Fe isotope exchange between aqueous Fe(II) and structural Fe in clay minerals NAu–1 (black squares) and NAu–2 (red circles) at pH 6.0 (dashed line) and pH 7.5 (solid line), and in clay mineral SWa–1 at pH 6.9 (blue triangles), calculated from aqueous phase ^{57}Fe according to equation 2. Fe atom exchange was calculated from isotope fractions measured with a quadrupole inductively coupled mass spectrometer (Q–ICP–MS, open markers) and with a multi-collector ICP–MS (MC–ICP–MS). Exper- iments were carried out with aqueous Fe(II) highly enriched in ^{57}Fe (NAu–1, NAu–2) and with low ^{57}Fe-enriched aqueous Fe(II) (SWa–1).