**Supporting Information for**

**Fe(II) interactions with smectites: temporal changes in redox reactivity and the formation of green rust**

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Number of pages: 11

Number of figures: 6

Number of tables: 5

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Table S1. Reduction potential measurements recorded for each 0.5 g/L clay suspension at pH 7.8 prior to the addition of any Fe(II).

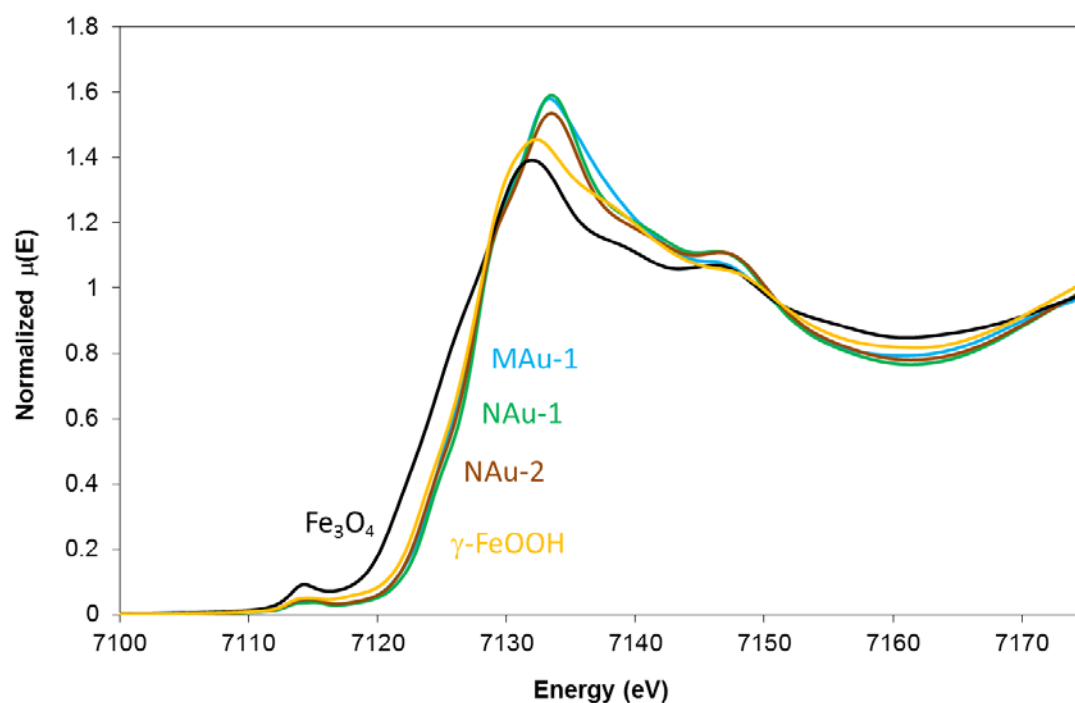| Clay | Reduction Potential (vs. SHE) |
|---|---|
| MAu-1 | + 288.7 ± 12.4 |
| NAu-1 | + 223.6 ± 4.0 |
| NAu-2 | + 283.6 ± 2.4 |



Figure S1: Fe-K edge XANES spectra of the native clay minerals and various Fe(II)/Fe(III) (oxyhydr)oxides showing that Fe is only detectable as Fe(III) in the clay minerals.

## Section S1. Further Materials and Method details

### Reference electrode care and calibration.

After each measurement the reference electrodes were immediately cleaned with DI water, gently dried with a kimwipe and then replaced in their 3 M NaCl storage solution which was replaced every week. The electrodes were also calibrated on a weekly basis using a saturated quinhydrone (97%, Sigma-Aldrich) suspension in pH 4.0, 7.0 and 7.8 buffers. The range of reduction potentials measured using these calibrations solutions are given in Table S-2 below. According to these measurements the maximum drift in the electrodes over time was no more than 10 mV. Any drift was accounted for in reported reduction potential values.

Table S2. The range of reduction potential measurements recorded over time during periodic calibration of the reference electrodes using quinhydrone suspensions.

| pH | Expected mV reading Using a 3 M Ag/AgCl RE | Range of actual mV readings vs. 3 M Ag/AgCl | Max offset in mV |
|---|---|---|---|
| 4.0 | + 253 | +243.9 to 251.4 | 9.1 |
| 7.0 | +76 | + 67.1 to + 71.9 | 8.9 |
| 7.8 | + 29 | + 33.3 to + 35.9 | 6.9 |

### Details of the Fe(II) extraction procedure employed.

The initial step in the Fe(II) extraction procedure employed involved centrifuging a 1 mL aliquot of the clay mineral suspension at 10 000 rpm (BCMI 505 Biolab, Ontario, Canada) to isolate aqueous Fe(II) from the solid phase. Next 1 mL of 1 M $CaCl_2$, adjusted to pH 7, was mixed with the residual solid using a vortex mixer (VM1, Ratek Victoria, Australia) for 60 s and then centrifuged at 10 000 rpm again to isolate the extraction solution containing Fe(II). This extraction step has been postulated to displace Fe(II) sorbed to basal sites on the clay mineral or within the interlayer by the high concentration of $Ca^{2+}$.[1]

A 1 mL aliquot of 1 M $NaH_2PO_4$ at pH 5 was then vortex mixed with the residual solid for 60 s and centrifuged to isolate the extraction solution. Once again, this extraction solution has been postulated to displace Fe(II) from smectite edge sites.[2] The remaining solid was mixed with 1 mL of 1 M HCL for 30 s, and centrifuged, to determine the amount of "structural" Fe(II) within the clay minerals. Previous studies have demonstrated that reaction with 0.5 M HCl is sufficient to remove all possible structural Fe(II).[3]

Table S3. Electrochemical properties of the mediators employed to generate the redox profiles in this study and the amount of each mediator added to each electrochemical cell to achieve 100 µM of reduced or oxidized mediator upon equilibration with the applied potential.

| # | Set Potential (vs. SHE) | Mediator* | Mediator $E_h^o$ (mV) | % $med_{red}$ at set mV | % $med_{oxid}$ at set mV | µL of 10 mM stock soln req. to achieve… | |
|---|---|---|---|---|---|---|---|
| | | | | | | [$med_{red}$] = 100 µM | [$med_{oxid}$] = 100 µM |
| 1 | -470 mV | DQ | -350 | 99.1 | 0.9 | 50.45 | Not req. |
| 2 | -400 mV | DQ | -350 | 87.5 | 12.5 | 57.14 | 40** |
| 3 | -300 mV | DQ | -350 | 12.5 | 87.5 | 40** | 57.14 |
| 4a | -230 mV | DQ | -350 | 0.9 | 99.1 | Use CyV | 50.45 |
| 4b | -230 mV | CyV | -140 | 97.1 | 2.9 | 51.5 | Use DQ |
| 5 | -130 mV | CyV | -140 | 50 | 50 | 100 | 100 |
| 6a | -30 mV | CyV | -140 | 1.4 | 98.6 | Use Ru | 50.71 |
| 6b | -30 mV | Ru | +90 | 99.1 | 0.9 | 50.45 | Use CyV |
| 7 | +100 mV | Ru | +90 | 40.3 | 49.7 | 12.41** | 83.75 |
| 8 | +200 mV | Ru | +90 | 1.4 | 98.6 | Not req. | 50.71 |

* DQ = diquat; CyV = cyanomethyl viologen; Ru – hexaammineruthenium(II) chloride
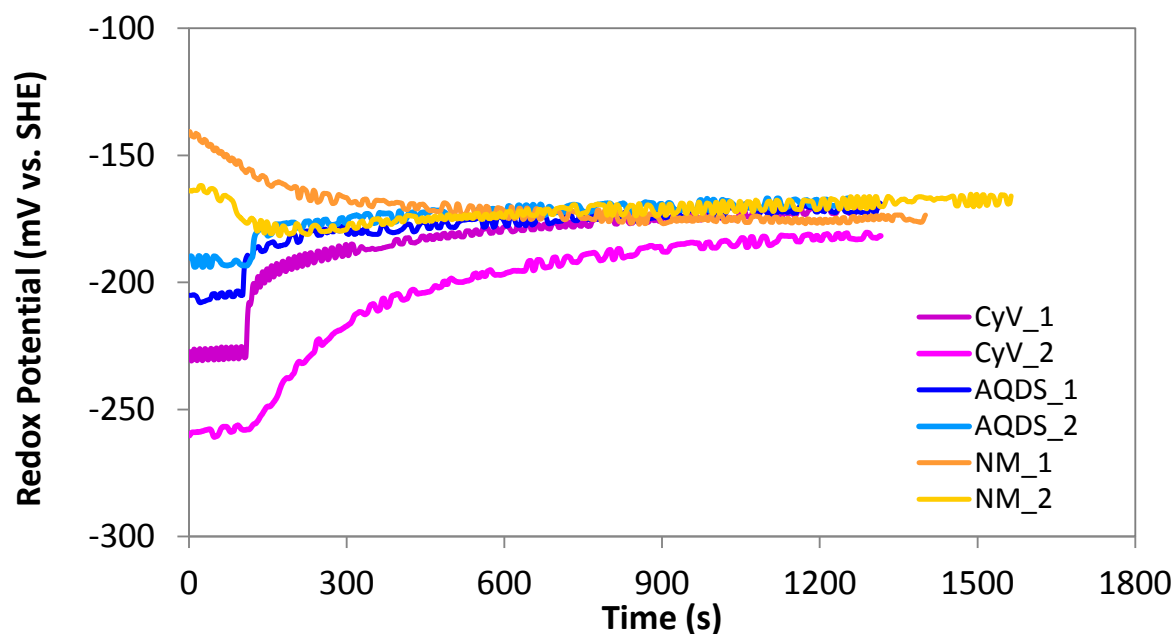
** 100 mM mediator stock solution required

Figure S2: Mediated and non-mediated measurements of a 1 mM Fe(II) and 5 mM Fe(III)-equivalent goethite suspension buffered at pH 7 using a 50 mM tetraethylethylene diamine buffer. Mediators employed were cyanomethylviologen (CyV) and anthraquinone-2,6-disulfonate ((AQDS). All measurements were conducted using high surface area glassy carbon crucibles which acted as the working electrode.

Table S4. Concentrations of Fe(III) reduced and Fe(II) oxidized (in µM) for the MAu-1, NAu-1 and NAu-2 suspensions aged from 1 hr to 18 days at pH 7.8 over an applied potential range of -470 to +100 mV vs SHE. Positive values represent the concentration of Fe(III) reduced and those values noted with a negative symbol are the concentrations of Fe(II) oxidized (as reduction resulted in positive current peak and oxidation a negative current peak). The adjacent cells highlighted indicate the applied potential range in which net Fe oxidation or reduction approaches zero, thus providing a range over which the reduction potential of the suspension at that particular time point can be estimated.

The suspensions contained 1 mM of Fe(II) and 0.205, 1.11 and 2.17 mM of Fe(III) in, respectively, the MAu-1, NAu-1 and NAu-2 suspensions. However, when the applied potential measurements were performed, the suspensions were diluted 10-fold. Thus, to compare the results tabulated with those in Figure 1, the following Fe concentrations should be used: 100 µM Fe(II) and 20.5, 111 and 217 µM of Fe(III) for, respectively, MAu-1, NAu-1 and NAu-2.

| Sample | Applied Potential (mV vs. SHE) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | - 470 | - 400 | - 300 | - 230 | - 130 | -30 | + 100 | + 200 |
| MAu-1 1 hr | 2.17±0.60 | 0.21±0.02 | -0.33±0.03 | -3.08±0.30 | -5.66±0.52 | -9.41±0.83 | -16.02±4.51 | -31.22±3.06 |
| MAu-1 1 d | 2.31±0.21 | 0.09±0.02 | 0.04±0.05 | -0.01±0.01 | -0.36±0.28 | -16.80±1.30 | -29.50±2.87 | -30.84±2.97 |
| MAu-1 4 d | 3.47±0.89 | 2.60±0.55 | 1.11±0.10 | 0.58±0.42 | -1.29±0.11 | -1.32±0.12 | -8.68±3.81 | -13.24±2.28 |
| MAu-1 8 d | 2.66±0.25 | 1.90±0.94 | 1.14±0.11 | 0.49±0.23 | -1.26±0.12 | -1.57±0.14 | -7.11±0.70 | -10.44±1.03 |
| MAu-1 18 d | 3.26±0.73 | 1.85±0.13 | 1.99±0.18 | 0.52±0.05 | 0.20±0.03 | -0.74±0.07 | -4.42±0.41 | -8.24±0.81 |
| NAu-1 1hr | 9.47±1.59 | 6.58±0.01 | -3.11±2.70 | -3.43±0.21 | -11.23±0.71 | -39.87±6.86 | -65.86±1.02 | -73.50±0.29 |
| NAu-1 1 d | 6.41±2.90 | 13.91±4.79 | 1.57±0.54 | -0.05±0.14 | -3.88±2.10 | -20.29±7.64 | -36.31±10.24 | -46.26±12.80 |
| NAu-1 4 d | 12.19±4.59 | 5.50±1.53 | 3.59±1.05 | 0.63±0.58 | -4.37±1.15 | -7.79±5.51 | -25.86±9.51 | -43.72±4.87 |
| NAu-1 8 d | 18.39±0.08 | 17.53±0.75 | 5.98±3.70 | 0.25±0.03 | -1.45±0.96 | -1.63±1.72 | -12.27±11.55 | -67.90±13.71 |
| NAu-1 18 d | 20.39±0.43 | 14.47±0.12 | 9.35±1.26 | 2.05±0.11 | -0.71±0.53 | -2.37±0.08 | -20.87±0.09 | -34.14±0.83 |
| NAu-2 1hr | 40.26±5.82 | 34.42±1.92 | 16.43±4.08 | 2.57±0.53 | 1.12±2.78 | -12.81±5.19 | -34.34±7.16 | -36.20±4.05 |
| NAu-2 1 d | 33.65±5.23 | 47.03±2.08 | 6.51±2.03 | 0.64±0.01 | 0.33±0.20 | -5.49±6.22 | -10.09±0.94 | -16.40±0.24 |
| NAu-2 4 d | 44.36±19.12 | 50.88±2.87 | 9.98±6.56 | 1.16±1.11 | 0.12±0.28 | -1.93±1.03 | -7.00±4.15 | -6.40±5.86 |
| NAu-2 8 d | 54.21±2.24 | 60.96±6.27 | 10.72±0.78 | 2.32±2.32 | 1.82±0.34 | -2.08±0.30 | -4.31±0.26 | -8.45±0.51 |
| NAu-2 18 d | 51.72±1.12 | 57.09±5.99 | 13.88±0.95 | 2.31±0.53 | 4.38±0.37 | -2.27±1.38 | -2.57±1.38 | -7.40±1.27 |
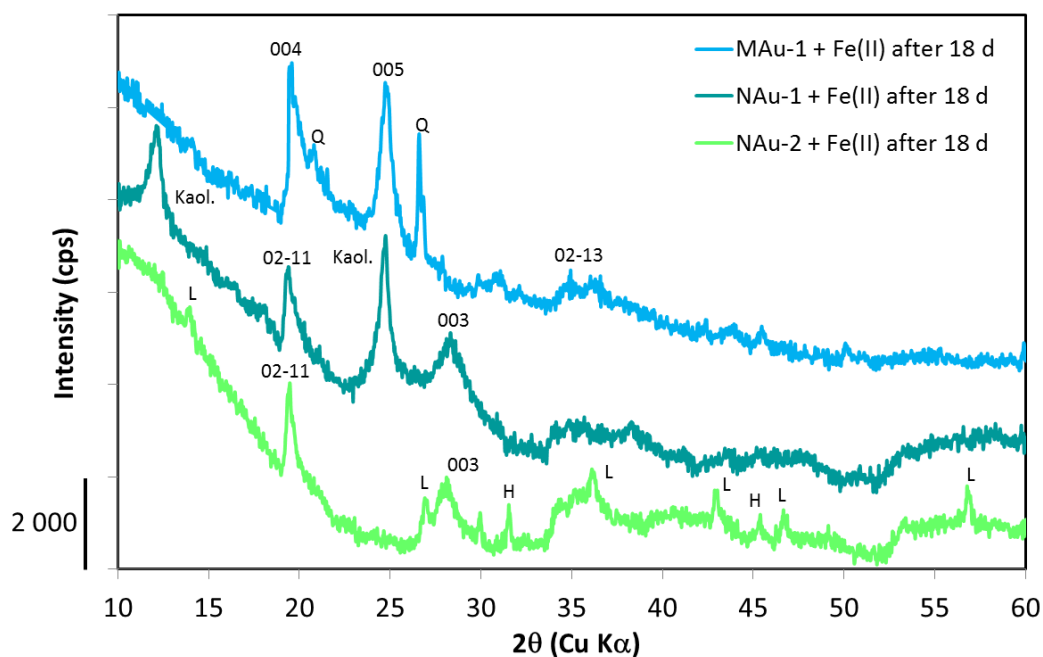
Figure S3: Random-orientated X-ray diffractograms of the smectite clay minerals after 18 days of reaction with 1 mM Fe(II) at pH 7.8. The samples were measured in glycerol mulls to protect air-sensitive mineral phases (e.g. Cl-green rust) from oxidation. H = halite, Kaol. = kaolinite, L = lepidocrocite, Q = quartz and numbers represent smectite clay mineral reflections.
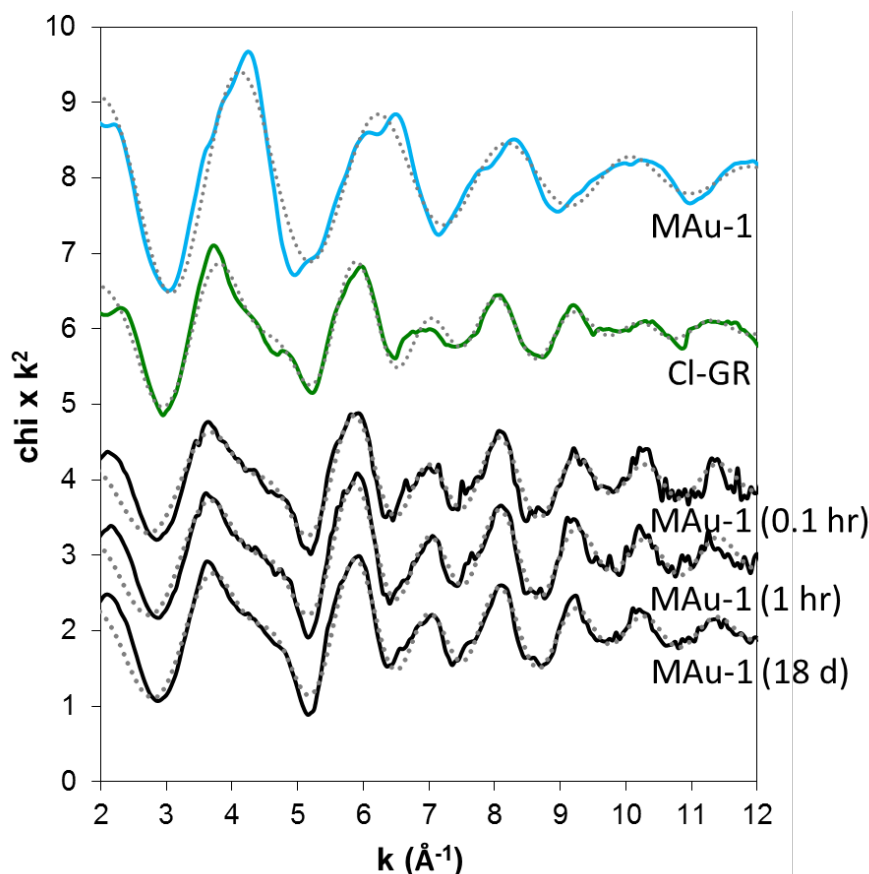
Figure S4: EXAFS spectra of MAu-1, Cl-GR and Fe(II)-reacted MAu-1 samples and their non-linear least-squares fits (dotted grey lines).

Table S5. Non-linear least-squares fitting parameters of the EXAFS spectra shown in Figure S4.

| Sample/ Reference | Path | $\Delta E$ (eV) | CN[a] | Interatomic distance (Å)[c] | $\sigma^2$ (Å$^2$) | R-factor |
|---|---|---|---|---|---|---|
| MAu-1 | Fe-O | 0.2 | $5.7 \pm 0.6$ | $2.010 \pm 0.010$ | $0.0053 \pm 0.0014$ | 0.011 |
| | Fe-Al | | $1.7 \pm 1.7$[b] | $3.085 \pm 0.042$ | $0.0085 \pm 0.0012$ | |
| Green Rust | Fe-O | -5.8 | $4.5 \pm 0.7$ | $2.102 \pm 0.016$ | $0.0101 \pm 0.0028$ | 0.035 |
| | Fe-Fe | | $4.5 \pm 0.7$ | $3.227 \pm 0.016$ | $0.0108 \pm 0.0020$ | |
| MAu-1 (0.1 hr) | Fe-O | -5.8 | $3.5 \pm 0.4$ | $2.081 \pm 0.011$ | $0.0079 \pm 0.0019$ | 0.019 |
| | Fe-Fe | | $3.5 \pm 0.4$ | $3.209 \pm 0.009$ | $0.0057 \pm 0.0010$ | |
| MAu-1 (1 hr) | Fe-O | -5.2 | $4.0 \pm 0.5$ | $2.090 \pm 0.011$ | $0.0081 \pm 0.0019$ | 0.020 |
| | Fe-Fe | | $4.0 \pm 0.5$ | $3.211 \pm 0.009$ | $0.0058 \pm 0.0011$ | |
| MAu-1 (18 d) | Fe-O | -4.3 | $4.4 \pm 0.5$ | $2.085 \pm 0.011$ | $0.0098 \pm 0.0019$ | 0.015 |
| | Fe-Fe | | $4.4 \pm 0.5$ | $3.218 \pm 0.011$ | $0.0073 \pm 0.0011$ | |

[a] CN was fixed to be equal as the crystal structure of fougerite (green rust) has 6 O atoms in the first coordination shell and 6 Fe atoms in the second coordination shell. [b] CNs were not fixed to be equal. [c] Crystallographic interatomic distances (Å) for fougerite are 2.09 and 3.190.[49]
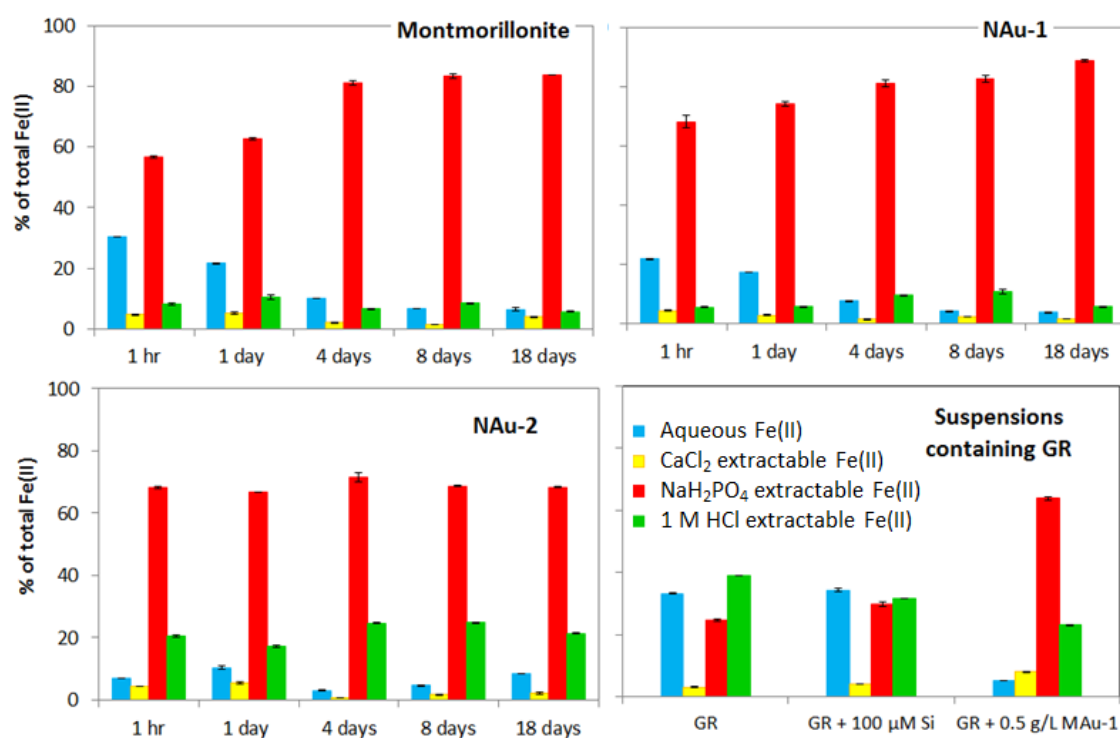
Figure S5: Fe(II) fractions extracted from 1 mM Fe(II) and 0.5 g/L MAu-1, NAu-1 or NAu-2 suspensions aged from 1 hr to 18 days. Results are also shown for the extraction of Fe(II) from suspensions containing 1 mM green rust (GR), 1 mM GR + 100 μM Si or 1 mM GR + 0.5 g/L MAu-1 aged for 1 hr. Error bars represent the standard deviation of triplicate measurements.
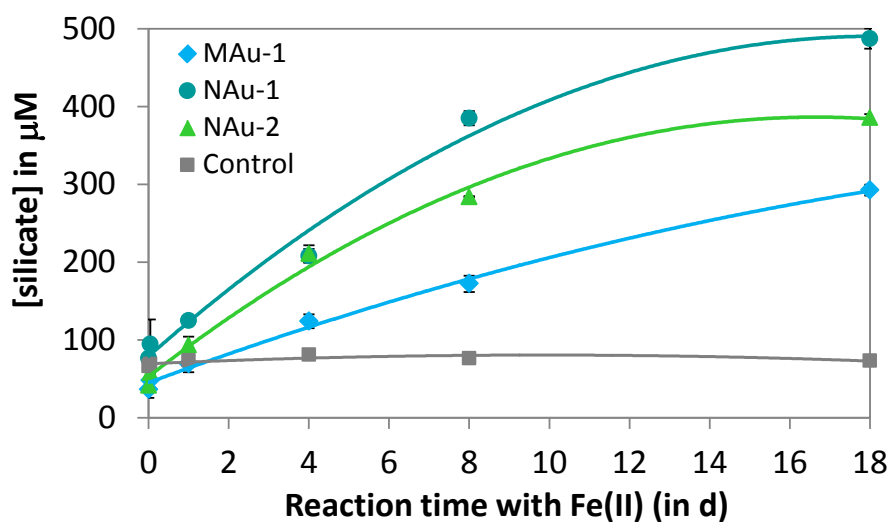
Figure S6: Concentrations of Si produced over 18 days following the addition of 1 mM Fe(II) to suspensions containing 0.5 g/L of MAu-1, NAu-1 or NAu-2. The control contains no clay suspension. Second order polynomial lines are added as a visual aid.

Section S2

The maximum amount of silicate released was 219.2, 414.2 and 312.5 µM for MAu-1, NAu-1 and NAu-2 respectively.  This is equal to 6.16, 11.64 and 8.78 mg/L of silica. According to the % of Si in each clay as measured by X-ray fluorescence (which was 24.4, 21.2 and 24.2 % for MAu-1, NAu-1 and NAu-2 respectively), for a 0.5 g/L suspension, the amount of Si in each suspension would be 122, 105.5 and 121 mg/L respectively.  As such, the amount of clay dissolution required to account for the increase in Si concentrations measured over time would be 5.05, 11.03 and 7.26 % for MAu-1, NAu-1 and NAu-2 respectively.

**References**
1. Bergaya, F.; Lagaly, G.; Vayer, M., Cation and anion exchange. In *Developments in Clay Science Vol. 1.*, Bergaya, F.; Theng, B. K. G.; Lagaly, G., Eds. Elsevier: 2006; pp 979-1001.
2. Schoonheydt, R. A.; Johnon, C. T., Surface and interface chemistry of clay minerals. In *Developments in Clay Science Vol. 1.*, Bergaya, F.; Theng, B. K. G.; Lagaly, G., Eds. Elsevier: 2006; pp 87-113.
3. Shi, B.; Liu, K.; Wu, L.; Li, W.; Smeaton, C. M.; Beard, B. L.; Johnson, C. M.; Roden, E. E.; Van Capellen, P., Iron isotope fractionations reveal a finite bioavailable Fe pool for structural Fe(III) reduction in nontronite. *Environ. Sci. Technol.* **2016,** *50*, 8661-8669.