**Supporting information for “Radium Sorption to Iron (hydr)oxides, Pyrite, and Montmorillonite: Implications for Mobility”**

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**Experimental Methods:** Ferrihydrite naturally exists as a hydrated mineral,1 thus it was important to prepare and handle the mineral such that its hydration was preserved. Here, a ferrihydrite slurry was synthesized by adding 0.4 M NaOH to a 50 mM ferric chloride hexahydrate solution, and then centrifuging and washing the resulting precipitate three times with 18 MΩ water, resulting in a thick paste of ferrihydrite. A small volume (<100 mL) of DI water was added to create a slurry consistency. The iron content of the prepared ferrhydrite slurry was determined through colorimetry (ferrozine method)2 and stirred slurry aliquots were added directly to the experiments to achieve the desired mineral mass.

Goethite was prepared through slow air-oxidation of a 50 mM Fe2+ and 100 mM bicarbonate solution over two days, and then centrifuged and washed three times with 18 MΩ water. The resultant slurry was then oven dried at 70 °C for two hours, resulting in a mineral powder that was gently ground with a mortar and pestle to homogenize the sample. This dried sample was added directly to experimental bottles.

There are well established methods for preparing natural clay mineral samples for use in experimental work.3 The STx-1b montmorillonite ordered from the clays society was originally a calcium montmorillonite, but was converted to sodium montmorillonite for easier comparison to other studies. This was achieved by first dispersing the clay with 1 M NaCl, then siphoning the suspended <0.2 µm clay fraction by successively centrifuging and suspending the clay eight times in DI water. The suspension was flocculated with saturated NaCl, and excess solution removed via centrifugation. The clay suspension was then treated with a 1 M sodium acetate solution (pH 5) to remove residual carbonate minerals. The resulting Na-equilibrated montomorillonite was then centrifuged and equilibrated with the experimental background solution (10 mM NaCl), centrifuged again, dried at 70 °C overnight, and then gently powdered using mortar and pestle. This dried powder was added directly to the experiments. Results of the kinetic experiments involving sodium montmorillonite are shown in figure S1, showing that over a 24 hour period, the water Ra concentrations stabilize.

All prepared minerals’ surface area was measured using a BET surface area analyzer (table S1). Ferrihydrite was dried for this analysis, and pyrite was held anaerobically until analysis.

Displacement of H+ from mineral surfaces can cause sorption experiments to drift in pH over time, requiring some pH adjustment. Following the equilibration period (24 hours), pH was checked and re-titrated to the desired value if necessary; if the pH deviated more than 0.1 pH units, the bottle was allowed to re-equilibrate for 15 minutes after titration, and the re-titration process repeated. This process was sufficient to maintain the experimental pHs described.

**Analytical Methods:** Background concentrations Ra were measured through scintillation counting to develop a limit of blank of 1.4 counts per second (cps), and activities are reported in this work only for samples that exceeded this value by a factor of 1.5. A Canberra low energy germanium detector and multichannel analyzer was calibrated using a multinuclide standard from Eckert and Ziegler ([www.ezag.com)](http://www.ezag.com)), and 226Ra activities for scintillation counting standards were determined using Canberra Genie software using the 186 keV peak.

**Surface Complexation Modeling:** Experimental sorption data was fit only by varying radium sorption reaction constants.4,5 Surface area, while a fittable parameter in the models, was not varied, instead using the surface areas reported in table S1. Solution complexation behavior was accounted for using the SIT database, which includes radium carbonate, sulfate, chloride, and hydroxide complexes, albeit these solution complexes had little impact over the experimental conditions considered.

**Sorption Experiments:**

The literature contains a wealth of studies studying sorption through the collection of experimental isotherms. Comparison of the results in this work with those was easiest done by comparing the measured K­d, compiled in table S2. The wide variety of experimental conditions can obfuscate the mechanisms controlling Ra sorption, further highlighting the need for SCM descriptions of Ra sorption.

**Table S1. Mineral Surface Areas and Calculated Sorption Constants**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Mineral | Surface Area (m2/g) | pH | Kd (mL/g) | Ksa (mL/m2) |
| Ferrihydrite | 382.9 | 3 | 229.9 | 0.600 |
|  | 5 | 471.4 | 1.231 |
|  | 7 | 2487 | 6.495 |
|  | 9 | 115900 | 302.8 |
| Goethite | 146.46 | 3 | 0 | 0 |
|  | 5 | 302.7 | 2.067 |
|  | 7 | 573.6 | 3.917 |
|  | 9 | 11670 | 76.87 |
| Sodium Montmorillonite | 50.162 | 3 | 6740 | 134.4 |
|  | 5 | 17750 | 353.8 |
|  | 7 | 21470 | 428.1 |
|  | 9 | 22890 | 456.4 |
| Pyrite | 0.0685 | 3 | 0 | 0 |
|  | 5 | 0 | 0 |
|  | 7 | 536 | 7825 |
|  | 9 | 520 | 7591 |

**Figure S1:** Results of Montmorillonite Kinetic Experiment

**Table S2: Major Salt Concentrations in the different background treatments**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Experiment** | **Na (mM)** | **K (mM)** | **Mg (mM)** | **Ca (mM)** | **Sr (mM)** | **Cl (mM)** |
| NaCl | 10 |  |  |  |  | 10 |
| KCl |  | 10 |  |  |  | 10 |
| MgCl2 |  |  | 10 |  |  | 20 |
| CaCl2 |  |  |  | 10 |  | 20 |
| SrCl2 |  |  |  |  | 10 | 20 |
| AGW | 5 | 2 | 0.5 | 0.5 | 0.0001 | 9 |
| ABW | 50 | 20 | 5 | 5 | 0.001 | 90 |
| ASW | 400 | 160 | 40 | 40 | 0.008 | 720 |

**Table S3. Comparison of Literature Ra Sorption Experiments and Fitted Kd Values**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Mineral | Solid/Solution Ratio (mg/L) | Background Solution | pH | Kd (mL/g) | Source |
| Ferrihydrite | 300 | 10 mM NaCl | 7 | 2487 | Experimental |
| 300 | 10 mM NaCl | 9 | 115900 | Experimental |
| 25000 | Seawater | 8.25 | 1535 | 11 |
| 10000 | 100 mM NaClO4 | 7 | 1440 | 5 |
| Goethite | 300 | 10 mM NaCl | 3 | 0 | Experimental |
| 300 | 10 mM NaCl | 5 | 302.7 | Experimental |
| 300 | 10 mM NaCl | 7 | 573.6 | Experimental |
| 300 | 10 mM NaCl | 9 | 11670 | Experimental |
| 25000 | Seawater | 8.25 | 20 | 11 |
| 10000 | 100 mM NaClO4 | 7 | 50.6 | 5 |
| 500000 | “pH 1 solution” | 1 | 0.752 | 12 |
| 500000 | “pH 10 solution” | 10.1 | 544 | 12 |
| Lepidocrocite | 25000 | Seawater | 8.25 | 174 | 11 |
| Hematite | 25000 | Seawater | 8.25 | 75 | 11 |
| Sodium Montmorillonite | 300 | 10 mM NaCl | 5 | 17750 | Experimental |
| 300 | 10 mM NaCl | 7 | 21470 | Experimental |
| 3333 | 10 mM NaCl | 5.25 | 9700 | 13 |
| 50000 | 10 mM NaCl | 6.5 | 3724 | 14 |

**Table S3. Altnernate Simplified Reactions considered in Surface Complexation Modelinga**

|  |  |  |  |
| --- | --- | --- | --- |
| Reactions | Sites (mol/g) | log K | Source |
| Ferrihydrite  ≡FhyOH + H+ ⇄ ≡FhyOH2+  ≡FhyOH ⇄ ≡FhyO- + H+  ≡FhyOH + Ra2+ ⇄ ≡FhyOHRa2+ | 1.87E-3 | 7.92  -8.93  5.7 | 5  8  8  Fitting |
| Goethite  ≡GoeOH + H+ ⇄ ≡GoeOH2+  ≡GoeOH ⇄ ≡GoeO- + H+  ≡GoeOH + Ra2+ ⇄ ≡GoeOHRa2+ | 3.99E-3 | 4.8  -10.4  3.5 | 15  15  15  Fitting |
| Sodium Montmorillonite  2 ≡Clay-Na + Ra2+ ⇄ ≡Clay2-Ra + 2 Na+  ≡ClayOH + H+ ⇄ ≡ClayOH2+  ≡ClayOH ⇄ ≡Clay- + H+  ≡ClayOH + Ra2+ ⇄ ≡ClayOHRa2+  ≡ClayO- + Ra2+ ⇄ ≡ClayORa+ | Surf: 3.33E-9  Exch: 8.43E-4 | 0.15  4.5  -7.9  9.8  10.1 | Fitting, clays.org CEC  Fitting  4  4  Fitting  Fitting |
| Pyrite  ≡PyrSH ⇄ ≡PyrS- + H+  ≡PyrS- + Ra2+ ⇄ ≡PyrSRa+ | 2.23E-5 | 6.45  -10.5 | 16  16  Fitting |

**a Does not consider tetradentate coordination for Ra adsorption to Fe (hydr)oxides**

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