Leftovers (no home)

. As an example, a compilation of radium isotope Kd values saw appreciable variations in Kd for common estuarine minerals, even when only synthetic iron oxides were considered [1].

Nevertheless, SCM provides a quantitative and (chemically) descriptive framework for comparing and estimating solute-solid interactions, which is particularly valuable when important reactions governing the fate of a particular solute such as Ra are poorly constrained.

Radium adsorption is most often described using the distribution coefficient (Kd), a useful parameter when making general comparisons of solute-solid partitioning under specific geochemical conditions [4]. However, Kd-based geochemical models are prone to uncertainty when describing adsorption and transport within natural systems where geochemical variation is common [5], [6].

This result is mirrored in the surface complexation modeling; exchange reactions with clay inner layer cations drive the enhanced sorption of radium in montmorillonite compared to the other minerals. Lastly, pyrite shows some affinity for Ra, potentially controlling Ra adsorption in anoxic conditions. The formation of iron (hydr)oxide coatings after O2 exposure that possess high adsorption capacity toward Ra, however, demonstrates that oxidation of Fe(II)-bearing minerals under altered or fluctuating redox conditions can impart overarching controls on Ra mobility.

Simplified models pose only the existence of the reaction, making no assumptions about the specific surface complexes that form, but allow for easy comparison of the relative importance of the different minerals for radium retention [7]–[9] (SI). Complex adsorption reactions, in contrast, are based on *ab initio* or spectroscopic evidence and thereby may represent more accurate depictions of the processes controlling Ra adsorption to surfaces [10], [11].

Table 3: 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  300  25000  10000 | 10 mM NaCl  10 mM NaCl  Seawater  100 mM NaClO4 | 7  9  8.25  7 | 2487  115900  1535  1440 | Experimental  Experimental  [32]  [28] |
| Goethite | 300  300  300  300  25000  10000  500000  500000 | 10 mM NaCl  10 mM NaCl  10 mM NaCl  10 mM NaCl  Seawater  100 mM NaClO4  “pH 1 solution”  “pH 10 solution” | 3  5  7  9  8.25  7  1  10.1 | 0  302.7  573.6  11670  20  50.6  0.752  544 | Experimental  Experimental  Experimental  Experimental  [32]  [28]  [16]  [16] |
| Lepidocrocite | 25000 | Seawater | 8.25 | 174 | [32] |
| Hematite | 25000 | Seawater | 8.25 | 75 | [32] |
| Sodium Montmorillonite | 300  300  3333  50000 | 10 mM NaCl  10 mM NaCl  10 mM NaCl  10 mM NaCl | 5  7  5.25  6.5 | 17750  21470  9700  3724 | Experimental  Experimental  [22]  [17] |

**Supporting information**

**Table 1: Mineral Surface Areas**

|  |  |
| --- | --- |
| **Mineral** | **Surface Area (m2/g)** |
| Ferrihydrite | 382.9 |
| Goethite | 146.46 |
| Sodium Montmorillonite | 50.162 |
| Pyrite | 0.0685 |

**Table 2: 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  300  25000  10000 | 10 mM NaCl  10 mM NaCl  Seawater  100 mM NaClO4 | 7  9  8.25  7 | 2487  115900  1535  1440 | Experimental  Experimental  [24]  [37] |
| Goethite | 300  300  300  300  25000  10000  500000  500000 | 10 mM NaCl  10 mM NaCl  10 mM NaCl  10 mM NaCl  Seawater  100 mM NaClO4  “pH 1 solution”  “pH 10 solution” | 3  5  7  9  8.25  7  1  10.1 | 0  302.7  573.6  11670  20  50.6  0.752  544 | Experimental  Experimental  Experimental  Experimental  [24]  [37]  [19]  [19] |
| Lepidocrocite | 25000 | Seawater | 8.25 | 174 | [24] |
| Hematite | 25000 | Seawater | 8.25 | 75 | [24] |
| Sodium Montmorillonite | 300  300  3333  50000 | 10 mM NaCl  10 mM NaCl  10 mM NaCl  10 mM NaCl | 5  7  5.25  6.5 | 17750  21470  9700  3724 | Experimental  Experimental  [28]  [20] |

**Additional Methods Information**

A ferrihydrite slurry was prepared by adding 0.4 M NaOH to a 50 mM ferric chloride hexahydrate solution, and then centrifuging and washing the resulting precipitate 3 times with 18 MΩ water. The iron content of the prepared ferrhydrite slurry was determined through colorimetry (ferrozine method [2]) and 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 2 days, and then centrifuged and washed 3 times.

This was achieved by first dispersing the clay with 1 M NaCl, siphoning the suspended, <0.2 um clay fraction, and successively centrifuging and resuspending xxx times in DI water. The clay suspension was then treated with a 1 M Sodium Acetate solution (pH 5) to remove residual carbonate minerals [3]. The resulting Na-equilibrated montomorillonite was then centrifuged and equilibrated with the experimental background solution, centrifuged again, dried at 70 C overnight, and then gently powdered using mortar and pestle.

Background concentrations were also measured on the scintillation counter to develop a limit of blank of 1.4 counts per second (cps), and activities are reported only for samples that exceeded this value by a factor of 1.5.

Following equilibration, 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 pH

Supernatant samples collected from the ferrihydrite isotherm, pH 9, did not have scintillation counter detectable Ra, so solid associated Ra on the filtered ferrihydrite itself was counted using gamma spectroscopy. 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 Ra-226 activities were determined using Canberra Genie software using the 186 keV peak. The solid samples on PES filters were placed in scintillation vials, and counted directly on the counter, with the resulting counts being adjusted for ferrihydrite loss during filtration. Gamma spectroscopy was also used to quantify and confirm the 226-Ra standard curve used in scintillation counting.

**Surface Complexation Modeling: SI**

Experimental sorption data was fit only by varying radium sorption reaction constants and site densities, preferring literature values for fitted parameters [12], [13]. Surface area, while a fittable parameter in the models, was not varied, instead using the surface areas reported in Table 1-SI. 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. The fitted site densities and reaction constants are then compared to other work that has examined either radium or various analog compounds.

Table 4: SCM reaction formulas and fitted constants

|  |  |  |  |
| --- | --- | --- | --- |
| 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 | [28]  [24]  [24]  Fitting |
| Goethite  ≡GoeOH + H+ = ≡GoeOH2+  ≡GoeOH = ≡GoeO- + H+  ≡GoeOH + Ra2+ = ≡GoeOHRa2+ | 3.99E-3 | 4.8  -10.4  3.5 | [25]  [25]  [25]  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  [40]  [40]  Fitting  Fitting |
| Pyrite  ≡PyrSH = ≡PyrS- + H+  ≡PyrS- + Ra2+ = ≡PyrSRa+ | 2.23E-5 | 6.45  -10.5 | [23]  [23]  Fitting |

**The impact of Pyrite surface treatment on results**

It is difficult to explain why previous studies have not observed adsorption of Sr to a cleaned and unoxidized pyrite surface, yet we have observed appreciable sorption of Ra to pyrite. Aside from the previously referenced Sr sorption modeling work, we could not find any other study that specifically examined Ra or other group II cation sorption to unoxidized pyrite surfaces. However, many have used a variety of experimental and spectroscopic techniques to study redox active metal ions sorption to the pyrite surface, which often includes redox reactions between the metal ion and pyrite surface groups [14]–[20]. The results of these studies imply that redox active metal ions in solutions with Ra may alter the pyrite surface, consequentially blocking or enhancing Ra sorption. A notable study of an oxidized synthetic pyrite under an extremely O2 free atmosphere (O2 < 0.01 ppm) found that As(III) sorption was similar to other studies of As(III) sorption to unoxidized pyrite in less rigorously anaerobic systems (O2 < 1 ppm) [21]. This suggests that pyrite typically considered “unoxidized” (including the pyrite surface used here) have some differences in surface chemistry compared to a “pristine” synthetic pyrite surface. It is possible that differences in pyrite treatment and cleaning during experiments can drive differences in surface sites that result in this unexpected Ra sorption. Two different natural pyrites were used in the experiment here and for studying Sr sorption, thus it is also possible there are structural differences relating to impurity lattice substitutions or other inclusions into the pyrite [15]. Only spectroscopic investigation of Ra sorption to pyrite surface, however, can elucidate the large differences between Sr and Ra sorption as well as enable the development of an SCM that accurately predicts Ra speciation in the presence of an unoxidized pyrite surface.

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