Experimental and Surface Complexation Modeling of Radium Sorption to Iron Oxies, Iron Sulfides, and Montmorillonites

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**Introduction**

Chronic ingestion and inhalation of radioactive materials, including radium (Ra) and radon (Rd), is an ongoing threat to human health worldwide [1]. Of these, Ra is ubiquitous in soils, aquifers, and natural waters owing to the radioactive decay of primordial 235-U, 238-U, and 232-Th, and often accounts for the dominant fraction of total radiation found in groundwater. All isotopes of Ra are unstable, and four (223Ra, 224Ra, 226Ra, and 228Ra) possess half-lives sufficient to persist within environmental systems and present a risk for human exposure. Moreover, 226Ra (half-life of 1600 years) is the parent radionuclide of 222Rn; chronic inhalation of 222Rn is a major driver for increased risk of lung cancer [2]. Hence, geochemical controls on Ra mobility are directly tied to the mobility and accumulation of Rn within soil-sedimentary systems [3].

Several geochemical processes impart overarching controls on Ra within soils and aquifers. Alpha-recoil, the ejection of daughter radionuclides from soil and sedimentary minerals into adjacent porewater, is the primary process sourcing Ra to groundwater. Ongoing alpha recoil progressively elevates porewater Ra activities until hydrologic flushing removes the equilibrating solution, or Ra achieves secular equilibrium with its parent radionuclides. Most aquifer systems contain low but adequate (e.g. U, Th, <5 mg/kg) parent radionuclide and sufficiently favorable hydrological conditions to facilitate delivery of measurable Ra to solution [4]. In a recent USGS study [5], 3% of groundwater samples (n=1270) within 7 of 15 principal US aquifers exceeded the USEPA limit for total Ra of 0.185 Bq/L. Further, high levels of Ra are often present with deeper formations, particularly shales, where low groundwater flux yield potentially hazardous activities (0.102-343 Bq/L) [6]. These naturally elevated Ra bearing formations are prevalent in some parts of the US (PA, WY, TX) and abroad (Middle East, etc.) [7], [8]. Anthropogenic activities, including uranium mining and hydraulic fracturing, can redistribute Ra and other constituents of naturally occurring radioactive materials (NORM), posing potential hazard to soils, surface waters, and aquifers.

Radium isotopes have also been used as naturally occurring environmental tracers. Briefly, the mass balance of Ra isotopes in estuarine/near shore system have been used to provide estimates of subterranean groundwater discharge (SGD) [9]. This method matches well with other measurements ,but is unable to resolve groundwater behavior within the estuarine systems [10]; non-conservative mixing and retardation may occur in these zones owing to sorption (e.g. to iron and manganese oxides) and fluctuations in pH, salinity or redox state [11]. In addition to its use as a groundwater tracer, Ra has also been identified as a marker for historic spills associated with hydrocarbon extraction [8]. This is possible if the Ra isotopic signature of produced water significantly differs from that of local groundwater, which is typical in many hydrocarbon bearing formations [12]. Successful implementation of this method requires a comprehensive accounting of Ra behavior in groundwater, as transport may be significantly non-conservative due to mixing of the highly saline, often anoxic waste waters with shallow, oxic, low salinity groundwater.

While Ra transport is considered to be conservative in some groundwater systems, it nevertheless participates in geochemical reactions that may alter its subsurface distribution. Radium precipitates with sulfate (log Ksp = -10.38), and will co-precipitate with barium and strontium (Sr) bearing minerals (barite, celestine log Ksp = -6.63, -9.99) [1]. However their low solubility and rapid precipitation with any available sulfate generally do not constrain long term Ra behavior in most natural systems [13], [14]. Hence, Ra adsorption to solids, particularly mineral surfaces, imparts the greatest chemical control on soluble Ra transport in groundwater systems [11], [15]. Under environmental conditions, Ra is not redox active, and its solution speciation is dominated by free radium (Ra2+) across a wide range of chemical conditions (e.g. pH and salinity). Weak complexes with carbonate, sulfate, and chloride are observed, but these solution species dominate at extremely acidic or basic pH values and when ligand activities exceed environmentally relevant activities [16].

Numerous studies have examined Ra (ad)sorption to natural sediments and specific minerals by measuring and comparing distribution coefficients, Kd [13], [17]–[20]. In general, iron (hydr)oxides, manganese oxides, and some clay minerals are found to be potent sorbents of Ra [21]. Organic matter also plays an important role, but it is unclear how it compares to mineral phases [22], [23]. Sorption of other group II ions to montmorillonites and other clay minerals is also well studied [25]–[27], but there is only a limited data set for radium sorption [28]. Lastly, there is limited study of any group II cation sorption to reduced mineral phases (mackinawite, pyrite, pyrrhotite etc.) that are common in estuarine and other anoxic systems [29]. These phases may impart a direct control through sorption to their surfaces, or play a more complex role as shifting redox conditions spur the formation of oxic coatings that change Ra sorption properties of the aquifer over time. Moreover, while reported Kd values provide a useful indicator for the extent of radium retention in a given system, these coefficients are empirical and not easily adapted to chemically dynamic and mineralogically complex systems. In contrast, surface complexation modeling (SCM) employs mass action equations subject to thermodynamic and electrostatic constraints to describe solute-solid phase interactions. They are typically calibrated using adsorption isotherm/titration data collected across a range of geochemical conditions [32], sometimes with the aid of spectroscopic tools or *ab inito* modeling [33], [34]. In general, they are used to 1) describe and validate surface chemical reactions for specific minerals, with the goal of assessing and predicting their role in retaining or releasing important solutes and 2) define and estimate important surface reactions for complex mineral mixtures (e.g. soil and sediment samples) with the goal of refining a SCM that will facilitate predictions of solute mobility and fate in specific soil and aquifer systems. Challenges associated with using and comparing results of SCMs within the scientific literature include the variety of experimental systems and conditions used for model calibration, and non-standard methodology for choosing model parameters and SCM chemical reactions [35], [36].

Although a wealth of Kd values have been tabulated for Ra adsorption to natural and synthetic solids, limited studies have used SCM to examine Ra adsorption to ferrihydrite and goethite, and at levels far exceeding those found in most environmental systems [34], [37]; SCM’s have not yet been developed for Ra adsorption to reduced iron (sulfide) or clay minerals. Therefore, the objectives of this work are to 1) examine low-activity Ra adsorption to several ubiquitous minerals known or inferred to control Ra transport over a range of solution conditions found in soils and aquifers , 2) use SCM to test mechanistic descriptions of Ra adsorption to mineral surfaces, and 3) use SCM to provide quantitative comparisons of Ra adsorption to different minerals. We choose to compare sorption of radium to ferrihydrite, goethite, sodium montmorillonite, and pyrite within a low salinity background solution and model radium sorption behavior through SCM. These minerals are representative of widespread, dominant sorbents found in many soil-sediment systems (Na-montmorillonite) under oxic (iron oxides), and anoxic (iron sulfide—pyrite) conditions. As expected, we find that pH plays a crucial role in determining the extent of Ra sorption to most mineral surfaces; however, we also illustrate that Ra adsorption to montmorillonite is more extensive over a range of solution conditions compared to iron (hydr)oxides, which are often thought as dominant adsorbent minerals.

**Materials and Methods**

Dissolved 226-Ra stock in 3% HCl was provided by the MIT Environmental, Health, and Safety office and used for all experiments. Both ferrihydrite and goethite were prepared using standard methods [38]. Briefly, ferrihydrite was precipitated through rapid titration of xxx M ferric chloride with xxx M sodium hydroxide to an endpoint of pH 7.0. The resulting precipitate was then centrifuged and rinsed with 18 MOhm DI water remove background electrolytes. Rinsing and centrifugation was repeated 3 times. The iron content of the prepared ferrhydrite slurry was determined through colorimetry (ferrozine method [39]). Slurry aliquots were added directly to the experiments to acheive the desired mineral mass. Goethite was prepared through slow air-oxidation of a 50 mM Fe2+ and 100 mM bicarbonate solution over 2 days. The resulting goethite mineral was centrifuged and washed to remove background electrolyte, dried for 2 hours at 70 °C, and then gently ground to homogenize the mineral. Calcium montmorillonite STX-1b was ordered from the clay minerals society (clays.org), but was re-equilibrated with sodium chloride to allow for closer comparisons to previous studies of radium sorption to Na-montmorillonites [28]. 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 [40]. 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. Pyrite was ordered from Ward’s Science (www.wardsci.com), ground using mortar and pestle, passed through sieves to select for 45-250 um particles, and transferred to an anaerobic glove bag (5% H2: 95% N2: < 1 ppm O2). It was then was washed in 6 N HCl overnight to dissolve any thin iron oxide coatings, and rinsed with deoxygenated DI water three times to remove residual acid. Lastly, the pyrite was dried anaerobically at room temperature in an open beaker. The composition of pyrite, ferrihydrite and goethite was confirmed using XRD, and surface area was measured for all minerals using BET (table 1SI).

Isotherms were conducted using serum vials (200 mL) filled with 100 mL of 10 mM NaCl stock solution, 30 mg of a single mineral (except for the case of pyrite, where 40 mg was used), and 5-270 Bq of 226-Ra stock. Experiments using pyrite were performed in an anaerobic glove bag, and all solutions were purged with N2 prior to placement in the anaerobic chamber. The pH was titrated to 3,5,7 or 9 +/- 0.05 through use of an autotitrator, and the bottle was sealed with a thick butyl stopper. Bottles were shaken for 24 hours to allow sufficient time for sorption equilibrium [37]. A kinetic study of Ra adsorption to montmorillonite confirmed 24 hours is sufficient to achieve equilibrium. 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. Acid (HCl) and base (NaOH) volume additions did not exceed 5% of the original volume. Once re-titration and re-equilibration were complete, samples were filtered using 0.22 um PES filters, which did not sorb significant quantities of Ra. Experimental error was quantified by measuring the standard deviation of triplicates for each data point.

**Analytical Techniques.** Solutions of Ra were quantified using scintillation counting. Up to 10 mL of sample were mixed with 10 mL of Ultima Gold XR (Perkin Elmer) and sealed for 30 days to allow 226-Ra to reach secular equilibrium with its daughter products [41]. The equilibrated samples were then counted using a Beckman Coulter LS 6500 scintillation counter, and the resulting counts were compared to a calibration curve of similarly prepared 226-Ra standards to determine solution activities. This was sufficient to determine the extent of sorption and develop isotherms, with the single exception of experiments using ferrihydrite at pH 9, where gamma spectroscopy was used to quantify Ra (see below). 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.

Supernatant samples collected from the ferrihydrite isotherm, pH 9, were below the defined detection limit, so solid associated radium 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.** Radium binding to mineral surfaces was modeled through a double diffuse layer (DDL) surface complexation model implemented in PHREEQC [42]. Simple and complex reaction formulations developed from spectroscopic measurements were used to fit the experimental data [32], [34], [37], [43]. 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 [32], [36], [43]. 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 [44], [45]. Further details of the SCM are provided in the supplementary information.

RESULTS AND DISCUSSION

**Sorption isotherms.** All fitted isotherms were linear within the range of activities studied, thus a Kd value was calculated by fitting a line to the experimental data (Table 2. The sorption isotherm results for ferrihydrite and goethite are plotted in figures 1a and 1b, respectively. Sorption to both iron oxides show a strong dependence on pH, with ferrihydrite showing greater sorption across all pH values compared to goethite, and the extent of sorption increasing with increasing pH for both iron oxides. Goethite shows limited, if any, sorption at acidic pH values, and ferrihydrite shows maximal sorption at pH 9. Differences in the surface area (table 1SI) explain some of the variation when comparing the extent of Ra sorption for goethite and ferrihydrite sorption, with ferrihydrite having nearly twice the surface area of goethite. Accordingly, A Ksa, defined as the Kd normalized by the mineral surface area (m2 g-1) (Table 2), is used to compare the extent of Ra adsorption between treatments. At circumneutral pH, goethite and ferrihydrite have relatively close Ksa values, however at more extreme values (pH = 3 and pH = 9), ferrihydrite demonstrates an appreciably larger extent of sorption compared to goethite. Several studies examine sorption of radium to iron (hydr)oxides, including ferrihydrite and goethite, reporting either a K­d or data that can be used to calculate one [11], [17], [24], [37] (Table 3). Two studies report isotherm data for Ra sorption to ferrihydrite, and the experimental results presented here match both reported values to within an order of magnitude of the Kd values [24], [37]. The K­d found in our study is the largest of the collected data sets, but was also performed at lower background ionic strength (here, 10 mM, others, 100-500 mM) and higher mineral surface area (here, 382.9 m2/g, others, ~250 m2/g) , consistent with previous results suggesting increased salinity reduces the extent of radium sorption [11]. In our study, Ra adsorbed more extensively to ferrihiydrite than goethite across all solution conditions when examining Kd. One study compared radium sorption to hematite, ferrihydrite, goethite, and lepidocrocite, finding that ferrihydrite sorbs radium most extensively [24]. This suggests the sorption isotherm results presented here represent an upper limit for radium sorption to iron oxides in these conditions.

Reported Kd values for Ra adsorption to goethite [19], [24], [37] (and experimental conditions) vary widely (Table 3). Unlike results obtained for ferrihydrite, we observe a larger extent of Ra sorption at specific pH values , which may be attributed to differences in solution ionic strength and surface area of the synthesized goethite. When normalized by surface area, Kd values are similar in some cases [37], but are different in others where ionic strength was much higher [24]. Althoug the goethite synthesized here should more closely match those found in natural settings [38], other studies used different synthesis methods that often result in lower SA. The differences between the results here and in other studies underscore the limitations of using Kd to describe and report solute-solid interactions.

Sorption isotherm results for radium onto sodium montmorillonite are plotted in figure 2, the calculated Kd values listed in table 2. The Ra-Na montomorillonite isotherms are remarkably linear for the range of radium activities considered. With the exception of ferrihydrite at pH 9, the total extent of sorption to montmorillonite is larger than iron (hydr)oxides over all pH values. Also, a comparatively weaker pH dependence is observed for montmorillonite sorption; above pH 3, quantities of Ra adsorbed by Na-montomorillointe is similar in all pH treatments. This result suggests that the dominant mechanism controlling montmorillonite sorption is not complexation with pH dependent surface (edge)functional groups, but rather exchange of radium with ions in clay interlayer. Comparison of the measured sorption Kd values here to earlier studies reveal appreciable differences, with values spanning approximately one order of magnitude. Those using a high solid-solution ratio (3000-50000 mg/L) resulted in less sorption compared to the sorption found here, which used only a 300 mg/L solid-solution ratio [28], [47]. The CEC of the montmorillonites are similar to that used in this experiment (within 10 meq/100 g clay), and albeit higher here, surface areas are within a factor of 3 of each other, suggesting interlayer charge is also similar. It is well established that both surface reactions and exchange reactions with the inner layer of the clay play a role in sorption [27], [36], [48], thus these variations in measured properties in the clays may explain the some of the discrepancy in sorption observed here compared to in previous works. However, a more detailed investigation into the sorption mechanisms at play in these clays, and the underlying clay features controlling will be necessary to understand the key factors controlling radium sorption.

Pyrite showed limited sorption of radium at low pH (3 and 5), but appreciable sorption at higher values, with little difference observed between isotherms performed at pH 7 and 9 (figure 3). As with other minerals, fitted Kd show very linear response in the range of radium activities considered (Table 2). The circumneutral and basic Kd values for pyrite are comparable to that of goethite at a circumneutral pH. Unexpectedly, calculated Ksa values show that pyrite has the largest sorption of all of the minerals considered here. There is very little, if any existing data examining the sorption of radium to any reduced iron solid. A previous study examining sorption of strontium to pyrite found no discernable sorption, contradicting the K­sa and Kd results found here [29]. It is unclear why this should be the case, as pyrite treatment was similar in both this study and the study of strontium. The results here suggest that reduced iron solids will play a key role in anoxic aquifers, where dynamic variations in redox will alter the surface mineralogy of reduced iron. This could decrease or increase radium retention depending on specific solution conditions. For example, a weakly acidic (pH 5) aquifer with reduced iron sulfides may see enhanced Ra sorption after exposure to oxic solutions, since iron oxic coatings will generally sorb more than pyrite at pH 5. In constrast, a more basic aquifer might see the release of Ra from the surface, since Ksa is so large for pyrite at circumneutral and basic pHs. Further investigation of surface complexation reactions may elucidate the source of this discrepancy with previous work with Sr, as well as enable predictions of Ra surface complexation with pyrite under shifting environmental conditions.

**Surface Complexation Modeling**. A single site, monodentate reaction was used to describe Ra adsorption to goethite and ferrihydrite; constrained fitting of radium sorption reaction constants and total number of surface sites closely simulated experimental data. (Figures 4a and 4b). The fitted reactions and constants (table 4) show that surface complex reaction constants are higher for ferrihydrite as compared to goethite, which is mirrored in the generally larger extent of sorption as normalized by surface area. Models of solute adsorption to ferrihydrite often use a two site model consisting of strong and weak sites; strong sites control sorption at low levels of sorbate, and weak sites at high levels of sorbate [32]. This type of model was first considered when fitting our experimental data, but we observed low sensitivity with respect to the weak site parameter; hence, only a single (strong) parameter was needed. It is not surprising that no weak site behavior was observed, since such low levels of radium were used. Sajih (2014) and Sverjensky (2006) also fitted their experimental data using a strong and weak site, obtaining a strong site complexation constant that was roughly 1-2 log units larger than found here. These two studies also fitted two tetradentate reactions with a single site to fit radium and barium sorption to ferrihydrite and goethite [34], [37]. Using a similar quantity of surface sites, we applied this model to our experimental data (Figures 5a and 5b, table 5). Fits to ferrihydrite data were similar to the single strong site fit here, but the fits to the goethite data were visually improved using the tetradentate model. Moreover, the fitted constants for ferrihydrite were nearly 20 log units smaller in this model compared to theirs while the goethite constants were only 1-2 log units larger (Table 6). Although the disparity between these studies and the constant reported here is quite high, it is known that the structural properties (crystallinity, crystal unit size, water content) of ferrihydrite may vary substantially according to the method used for synthesis, which may account for some of the variance [49]. It is unclear though, why there would be similarities in the sorption Kd values, but such larger differences in fitted log K for surface complexation.

Concentrations of Ra used here are far below the analytical detection limits of techniques used to describe and constrain the bonding environment of Ra to solids. Hence, SCM developed here for Ra adsorption is compared with other studies that combine SCM with spectroscopic measurements, which were used to constrain surface reactions of other group 2 elements (Table 6). Surface site reactions involving these other elements may have similar coordination environment and complexation reactions with solid surfaces. X-ray absorption spectroscopy was used to examine Sr binding with the surface of iron oxides, and illustrated that it forms outer sphere complexes with those surfaces [50], [51]. Additionally, X-ray standing wave measurements of Sr near a rutile surface showed that it coordinated with four surface sites [44]. A separate study used those x-ray standing wave measurements to constrain SCM of group II elements with iron oxides, suggesting that the observed rutile coordination with was also occurring during Ra sorption to iron oxides [34]. The tetradentate binding model posed by some [37], [52] to describe group II cation sorption to iron oxides is based on these measurements. Experimental fitting of SCM here, and for Sr surface complexation, however, have not matched the predictions of that modeling. A problem that arises when comparing SCM results is that multiple reaction formulations can satisfy the constraints developed by spectroscopic observations, without a clear indication as to which is a more accurate description of sorption or if those constraints are applicable to other elements with similar chemistry [36]. Similarly, there are large variations in the experimental methods that generate date used to fit these models [35]. These complications underscore the need to make measurements of Ra sorption to mineral surfaces using the same spectroscopic techniques used for other group II elements.

Surface complexation modeling of radium adsorption to sodium montmorillonite was initially fit using a surface site with two reactions, and a single exchange reaction (Figure 6a). Fitting the data required an exchange reaction where radium displaced sodium in the inner layer of the clay (table 4). This method is commonly used to predict metal sorption behavior with clays, and explains the large extent of sorption over the whole pH range [26], [27]. A similar suite of reactions was used to describe Ba adsorption to Na-montmorillonite, and X-ray absorption spectroscopy confirmed the formation of both inner sphere and outer sphere complexes on the montmorillonite surface corresponding with the need for both an exchange reaction and surface site reactions in the SCM [45]. Other models of metal sorption to clays have used a similar scheme for sorption as here, instead using multiple types of sites to represent surface sorption using the strong and weak site formulation described for ferrihydrite in addition to an exchange reaction [32], [53]. We also fitted a model using two sites to our data using a similar formulation (Figure 6b, Table 5) which had visually similar fits to the single site, two reaction model. The standard designation of “strong” and “weak” sites, however, does not apply to the sites used in the two site model fitted here since both were needed to describe sorption at the low levels of Ra modeled. The number of fitted sites in this two site model was also significantly lower than reported in the literature, with literature values producing poor fits. The presence of exchange in these models account for the significant extent of sorption at acidic pHs, however, the fitted surface complexation constants in either model also suggest that radium binds more strongly with the clay surface than either of the iron oxides.

Although SCM has not been extensively used to examine group II cation adsorption with montmorillonites, there is a broad base of literature examining the strength of exchange and surface reactions with other metals [27], [46], [53]. Previously calculated metal exchange reactions with sodium montmorillonite cations show a range of values from 0.7 to 398. Here, the exchange constant for radium is 1.41, which suggests that radium could easily be displaced by other metals in solution. Since a large fraction of the observed Ra adsorption is associated with the exchange reaction (ie sorption observed at low pH), this competition from other metals will likely play a large role in controlling Ra sorption to montmorillonites. This matches with observations that increases in ionic strength result in radium displacement [13], [24]. In consrast, Radium had the largest surface complex reaction constants compared to those found for other potentially hazardous metals such as uranium, americium, manganese, and cadmium, though not as large as that of tin [27], [54], [55]. This suggests that less competition for the protonated surface sites will occur in the presence of other metals, though it is unclear how competition between the protonated surface sites and ion exchange will control the ultimate fate of Ra in a multi species system, such as those found in estuaries or in deep, briny formations. Given the large amount of sorption associated with ion exchange, we would expect radium would be displaced by other metals in solution.

Lastly, SCM of Ra adsorption to pyrite was performed using surficial S as the adsorption site [56] (table 4), based on a previous SCM that model Sr sorption to pyrite [29]. The experimental results of that work did not observe Sr sorption on an unoxidized pyrite surface, so only the surface site and protonation constant were applied to the model here. Model fits of Ra sorption capture the observed data points, though not as well as for Ra adsorption to montmorillonite or iron oxides (figure 7). The fitted reaction constant is also the lowest of all of the fitted reaction constants found here by multiple log K units, suggesting that pyrite is the least extensive sorbent of all those considered here. This confirms the results when comparing K­d values in between minerals, yet is contradicted by the earlier K­sa results which showed that pyrite had the largest amount of sorption per unit surface area. Increases in the total number of surface sites in the SCM were not able to fit the experimental data accurately, suggesting therefore that the formulation of the SCM is likely inaccurate with respect to the actual surface complexes Ra forms with the pyrite surface.

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 [29], [56]–[61]. 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) [62]. 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 [56]. 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.

Implications for radium as a tracer in hydrogeologic settings

The experimental results here confirm that iron oxides play a key role in retaining radium in natural environments, but also illustrate that Ra bound most extensively to Na-montmorillionte, a 2:1 layer clay with a solute-accessible interlayer and that pyrite demonstrates sorption at circumneutral or basic pH values. Pyrite sorption was most extensive of all minerals when normalized by surface area, followed by Na-montmorillonite, ferrihydrite, and then goethite. Sensitivity to pH was observed for Ra adsorption to all minerals, and previous research shows that ionic strength will also control radium retention [13], [24], [28]. SCM reaction constants for Ra adsorption to goethite and ferrihydrite found here differed from previous studies using the same suite of reactions; this was likely a result of mineralogical or differences in experimental design (e.g. solid-solution ratios, etc.). We also present SCM results for Ra sorption to Na-montmorillonite and pyrite, noting that further investigation is necessary to constrain Ra sorption to these minerals, especially when considering competition with other metal ions. These results highlight the dynamic adsorption equilibria of Ra when (bio) geochemical conditions are altered, including changes in pH, salinity, and mineralogy. This may complicate the use of Ra as a tracer of contamination or for use in other applications, including making estimates of groundwater flux, particularly when total Ra activity (any isotope) is used as an important model parameter. Results here suggest that groundwater model predictions and estimations may improve by measuring total Ra (and in some scenarios, Ra isotopes) associated with dominant subsurface minerals, and incorporating adsorption processes into simplistic mixing models.

Radium isotopes have played a crucial role in tracing the flux of groundwater into the ocean, and have been highlighted as a potential marker for investigating ground contamination resulting from hydraulic fracturing operations [8], [63]. The models used thus far are relatively simple mixing models, where transport within porous media is not considered [64]. Study of natural radium variations showed transport plays a critical role in controlling radium isotope concentrations, particularly the short lived isotopes radium 223 and radium 224, and needs more detailed models of transport to resolve these isotopes’ behavior [65]. Previous studies of radium sorption in batch systems has provided a first basis with which to develop these models of transport, and this work contributes to these models by highlighting and comparing critical minerals that control transport, as well as providing constants and reactions to constrain radium sorption. It also highlights areas in need of additional work to better quantify these transport processes. Further study, particularly probing radium complexation at these surfaces, competition with redox sensitive metal ions, resolving sources of discrepancy, and further quantification of transport would be instrumental in improving radium utility as a tracer.

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TABLES

Table 1: Mineral Properties

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

Table 2: Calculated Sorption Constants

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

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  [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] |

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 | [37]  [32]  [32]  Fitting |
| Goethite  ≡GoeOH + H+ = ≡GoeOH2+  ≡GoeOH = ≡GoeO- + H+  ≡GoeOH + Ra2+ = ≡GoeOHRa2+ | 3.99E-3 | 4.8  -10.4  3.5 | [34]  [34]  [34]  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  [46]  [46]  Fitting  Fitting |
| Pyrite  ≡PyrSH = ≡PyrS- + H+  ≡PyrS- + Ra2+ = ≡PyrSRa+ | 2.23E-5 | 6.45  -10.5 | [29]  [29]  Fitting |

Table 5: Fitting of literature SCM reactions to experimental data

|  |  |  |  |
| --- | --- | --- | --- |
| Reactions | Sites (mol/g) | log K | Source |
| Ferrihydrite  ≡FhyOH + H+ = ≡FhyOH2+  ≡FhyOH = ≡FhyO- + H+  4≡FhyOH + Ra2+ = ≡(FhyOH)3­FhyORa+ + H+  4≡FhyOH + Ra2+ + 2H+= ≡(FhyOH2)2­(FhyOH)2Ra4+ | 1.75E-3 | 7.92  -8.93  -1.4  0 | [37]  [32]  [32]  Fitting  Fitting |
| Goethite  ≡GoeOH + H+ = ≡GoeOH2+  ≡GoeOH = ≡GoeO- + H+  4≡GoeOH +Ra2+ = ≡(GoeOH)3GoeORa+  4≡GoeOH + Ra2+ = ≡(GoeOH)4Ra2+ | 6.4E-5 | 4.8  -10.4  -2.9  4.6 | [34]  [34]  [34]  Fitting  Fitting |
| Sodium Montmorillonite  2 ≡Clay-Na + Ra2+ = ≡Clay2-Ra + 2 Na+  ≡ClayAOH + H+ = ClayAOH2+  ≡ClayAOH = ≡ClayA- + H+  ≡ClayBOH + H+ = ClayBOH2+  ≡ClayBOH = ≡ClayB- + H+  ≡ClayAOH + Ra2+ = ≡ClayAORa+ + H+  ≡ClayBOH + Ra2+ = ≡ClayBOHRa2+ | Exch: 8.43E-4  Site A: 2E-7  Site B: 6.33E-7 | 0.15  4.5  -7.9  4.5  -7.9  0  7.5 | Clays.org CEC, fitting for surface sites  [46]  [46]  [46]  [46]  Fitting  Fitting |

Table 6: Comparison of Tetradentate SCM Reactions and Constants for Iron Oxides

|  |  |  |  |
| --- | --- | --- | --- |
| Reactions | Sites (mol/g) | Log K | Source |
| **Ferrihydrite**  4≡FhyOH + Ra2+ = ≡(FhyOH)3­FhyORa+ + H+  4≡FhyOH + Ra2+ + 2H+= ≡(FhyOH2)2­(FhyOH)2Ra4+  4≡FhyOH + Ra2+ = ≡(FhyOH)3­FhyORa+ + H+  4≡FhyOH + Ra2+ + 2H+= ≡(FhyOH2)2­(FhyOH)2Ra4+  4≡FhyOH + Ba2+ = ≡(FhyOH)3­FhyOBa+ + H+  4≡FhyOH + Ba2+ + 2H+= ≡(FhyOH2)2­(FhyOH)2Ba4+ | 1.75E-3  1.75E-3  1.75E-3 | -1.4  0  -4.45  22.2  -4.45  21.5 | Fitting  [37]  [37] |
| **Goethite**  4≡GoeOH +Ra2+ = ≡(GoeOH)3GoeORa+  4≡GoeOH + Ra2+ = ≡(GoeOH)4Ra2+  4≡GoeOH +Ra2+ = ≡(GoeOH)3GoeORa+  4≡GoeOH + Ra2+ = ≡(GoeOH)4Ra2+  4≡GoeOH +Ba2+ = ≡(GoeOH)3GoeOBa+  4≡GoeOH + Ba2+ = ≡(GoeOH)4Ba2+  4≡GoeOH +Ba2+ + H2O = ≡(≡GoeOH)2(≡GoeO)2BaOH+ + 3H+  4≡GoeOH + Ba2+ + H2O = ≡(≡GoeOH)4BaOH+ + H+  ≡GoeOH + Sr2+ + H2O = ≡GoeO-\_SrOH+ + 2H+  4≡GoeOH + Sr+2 + H2O = (≡GoeOH)2(≡GoeO-)2\_SrOH+ + 3H+  4≡GoeOH + 2Sr2+ = (≡GoeOH)2(≡GoeO-)2\_Sr24+ + 2H+ | 3.67E-4  6.4E-5  6.4E-5  1.42E-3  1.03E-3 | -2.9  4.6  -2.5  3.85  -4.9  3.8  -19.3  -1.8  -16.6  -20.7  -10.0 | Fitting  [37]  [37]  [34]  [52] |

FIGURE 1a and 1b: Radium isotherms for Iron (Hydr)Oxides

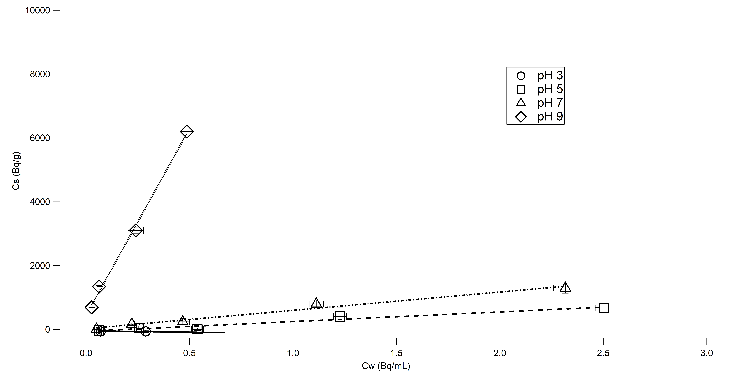
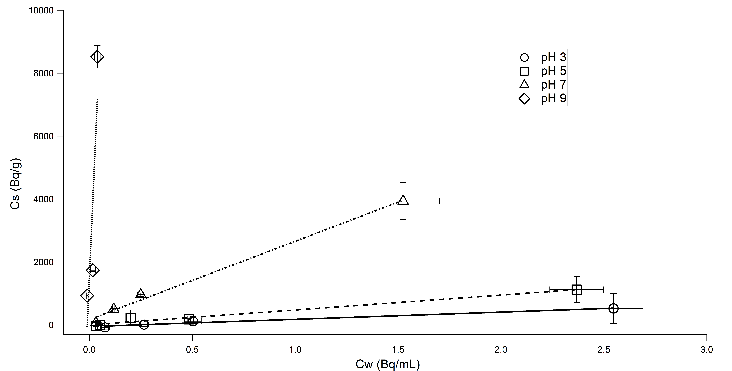


Figure 1a and 1b: Radium sorption isotherms to Goethite. Fitted lines’ slope indicates the Kd value for the given isotherm.

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 [24].

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 [13]. However, Kd-based geochemical models are prone to uncertainty when describing adsorption and transport within natural systems where geochemical variation is common [30], [31].

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.

Supporting information

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 [37], [46]. Surface area, while a fittable parameter in the models, was not varied, instead using the surface areas reported in Table 1. 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.