SECTION 1: INTRODUCTION AND BACKGROUND

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 particularly prevalent in some parts of the US (PA, WY, TX) and abroad (Middle East, etc.) [7], [8]. Anthropogenic activities including uranium mining and recently, 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. A well-established example uses the mass balance of Ra isotopes in estuarine and near shore systems to provide estimates of subterranean groundwater discharge (SGD) [9]. This model of SGD fluxes matches well with other measurement methods, 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.

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]. 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. 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]. 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].

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 [29], [30]. 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 [31], sometimes with the aid of spectroscopic tools or *ab inito* modeling [32], [33]. 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 [34], [35]. 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.

Although a wealth of Kd values have been tabulated for Ra adsorption to natural and synthetic solids, only a few studies have used SCM to examine Ra adsorption to ferrihydrite and goethite [33], [36], and 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. 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, however, the formation of iron (hydr)oxide coatings after O2 exposure that possess high adsorption capacity toward Ra demonstrates that oxidation of Fe(II)-bearing minerals under altered or fluctuating redox conditions can impart overarching controls on Ra mobility.

SECTION 2: EXPERIMENTAL AND MODELING METHODS

Reagents used in the experiments were of reagent grade or better, and all solutions were made with 18 M Ohm water. 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 [37]. Briefly, ferrihydrite was precipitated by dissolving FeCl3\*6 H2O in water, and rapidly titrating the solution to pH 7, followed by repeated centrifugation and washing to remove background electrolytes. The iron content of the prepared ferrhydrite slurry was characterized using digestion with the ferrozine method [38]. 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, and then dried for 2 hours at 70 °C. Calcium montmorillonite STX-1b was ordered from the clay minerals society (clays.org), but was converted to sodium montmorillonite to allow for closer comparisons to previous studies of radium sorption to montmorillonites [28]. The clay was dispersed with 1 M NaCl, and the <0.2 um clay fraction siphoned off after successive washes with DI water. The siphoned clay particles were then treated with a 1 M Sodium Acetate solution (pH 5) to remove residual carbonate minerals [39]. The clay was then centrifuged and equilibrated with the experimental background solution, resulting in a sodium montmorillonite. The clay was 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 remove any 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; dessicant (Drierite) was placed in the glovebag to facilitate moisture removal. The composition of pyrite, ferrihydrite and goethite was confirmed using XRD, and surface area was measured for all minerals using BET (table 1).

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 [36]. 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.

2.1 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 [40]. 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 quantified to develop a limit of blank of 1.4 counts per second (cps), and activities 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-confirm the 226-Ra standard curve used in scintillation counting.

2.2 SURFACE COMPLEXATION MODELING

Radium binding to mineral surfaces was modeled through a double diffuse layer (DDL) surface complexation model implemented in PHREEQC [41]. Both simple reaction formulations and complex reaction formulations established by fitting data to spectroscopic measurements [31], [33], [36], [42]. 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 [31], [35], [42]. The more complex models, in contrast, are valuable to fit since their formulations are often based on spectroscopic evidence, and thus are more accurate depictions of the processes controlling ion adsorption to surfaces [43], [44]. Experimental sorption data was fit only by varying radium sorption reaction constants and site densities, preferring literature values for fitted parameters [36], [45]. 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.

SECTION 3: RESULTS

SECTION 3.1.1 SORPTION ISOTHERMS

All fitted isotherms were linear within the range of activities studied, thus a Kd was calculated to enable comparisons to other work using radium by fitting a line to the experimental data (Table 1).

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 the most sorption at pH 9. Differences in the surface area (table 1) help explain some of the variations in the sorption extent when comparing goethite and ferrihydrite sorption, with ferrihydrite having nearly twice the surface area of goethite. A Ksa, defined as the Kd normalized by the mineral surface area (m2/g), reveals the extent of sorption with per unit surface area (table 1), and enables further examination of radium surface behavior. At circumneutral pHs, 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. It is difficult to predict what drives these differences without further examination of surface interactions between radium and mineral surface sites available for sorption.

Several studies examine sorption of radium to iron (hydr)oxides such as ferrihydrite and goethite, reporting either a K­d or data that can be used to calculate one [11], [17], [24], [36]. Selected experimental results from the literature are presented in Table 1, using calculated Kd values to compare relative sorption extent. In some cases where a different type of isotherm was fit (ie. Langmuir or Freundlich), it was necessary to calculate a Kd value from the reported data by fitting a line. The solid/solution ratios (solid mass divided by total solution), as well as the pH and background electrolyte are also reported for these studies. 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], [36]. 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.

A greater number studies were found that examined radium adsorption to goethite than to ferrihydrite [19], [24], [36] and reported values of Kd and experimental conditions vary widely (Table 1). Unlike results obtained for ferrihydrite, we observe a larger extent of Ra sorption at pH values similar to previous. Two factors affecting this are the differences in solution ionic strength and surface area of the synthesized goethite. When normalized by surface area, Kd values are similar in some cases [36], but are different in others where ionic strength was much higher [24]. Additionally, methods of goethite synthesis vary, and may yield product with disparate surface area; this may also impact the extent of Ra adsorption and account for discrepancies between reported values. The goethite synthesized here has relatively high surface area compared to other studies’ synthesized goethite. Additionally, the goethite synthesized here should more closely match those found in natural settings [37]. 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 1. 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 oxides over all pH values. However, 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 functional groups, but rather exchange of radium with ions in the inner layer of the clay.

Comparison of the measured sorption Kd values here to earlier studies reveal appreciable differences, with values spanning approximately one order of magnitude. Previous studies 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], [46]. The CEC of the montmorillonites are close (within 10 meq/100 g clay), while the surface areas are within a factor of 3 of each other, suggesting that the isomorphic substitutions and layer charge are also similar. The surface area of the clay here is higher, which can help account for some of the increased sorption we have observed. It is well established that both surface reactions and exchange reactions with the inner layer of the clay play a role in sorption [27], [35], [47], thus these variations in measured properties in the clays may explain the large discrepancy in sorption observed here compared to in previous works. However, a more detailed investigation into the sorption mechanisms at play in these clays 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, Kd values were fit, showing very linear response in the range of radium activities considered (Table 1). 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 [48]. The results here suggest that reduced iron solids will play a key role in aquifers where they exist, where dynamic variations in redox will alter the surface mineralogy of reduced iron, possible decreasing or increasing radium retention depending on specific solution conditions.

SECTION 3.2 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 2) show that surface complex reaction constants are higher for ferrihydrite as compared to goethite, which is mirrored in the 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 [31]. 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 [33], [36]. Using a similar quantity of surface sites, we applied this model to our experimental data (Figures 5a and 5b). 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 3). 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 3). 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]. X-ray standing wave measurements of Sr near a rutile surface showed that it coordinated with four surface sites [43]. 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 was also occurring during sorption to iron oxides [33]. 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 [35]. Similarly, there are large variations in the experimental methods that generate date used to fit these models [34]. 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 2). 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 [44]. Other models of metal sorption to clays have used a similar scheme for surface behavior as here, instead using multiple types of sites to represent surface sorption using the strong and weak site formulation described for ferrihydrite [31], [52]. We also fitted a model using two sites to our data using a similar formulation (Figure 6b) which had visually similar fits to the single site, two reaction model. The 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 modeled low levels of radium. 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], [45], [52]. 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]. Comparisons of the fitted surface complex reactions here, in contrast, illustrate that the extent of radium adsorption in our study is noticeably larger than that found for other potentially hazardous metals such as uranium, americium, manganese, and cadmium, though not as strong as that of tin [27], [53], [54]. 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.

Lastly, SCM of Ra adsorption to pyrite was performed using surficial S as the adsorption site [55] (table 2), based on a previous SCM that model Sr sorption to pyrite [48]. 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 [48], [55]–[60]. 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) [61]. 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 [55]. Only spectroscopic investigation of Ra sorption to pyrite surface 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.

SECTION 3.3: IMPLICATIONS FOR RADIUM AS TRACER

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 including 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], [62]. The models used thus far are relatively simple mixing models, where transport within porous media is not considered [63]. 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 [64]. 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, interactions with redox sensitive metal ions, resolving sources of discrepancy, and further quantification of transport would be instrumental in improving radium utility as a tracer.

[1] T. Zhang, K. Gregory, R. W. Hammack, and R. D. Vidic, “Co-precipitation of radium with barium and strontium sulfate and its impact on the fate of radium during treatment of produced water from unconventional gas extraction,” *Environ. Sci. Technol.*, vol. 48, no. 8, pp. 4596–4603, 2014.

[2] J. Subramanian and R. Govindan, “Lung cancer in never smokers: a review.,” *J. Clin. Oncol.*, vol. 25, no. 5, pp. 561–70, 2007.

[3] A. P. Jones, “Indoor air quality and health,” *Atmos. Environ.*, vol. 33, no. 28, pp. 4535–4564, 1999.

[4] N. Lu and C. F. V Mason, “Sorption-desorption behavior of strontium-85 onto montmorillonite and silica colloids,” *Appl. Geochemistry*, vol. 16, no. 14, pp. 1653–1662, 2001.

[5] Z. Szabo, V. T. dePaul, J. M. Fischer, T. F. Kraemer, and E. Jacobsen, “Occurrence and geochemistry of radium in water from principal drinking-water aquifer systems of the United States,” *Appl. Geochemistry*, vol. 27, no. 3, pp. 729–752, 2012.

[6] E. Barbot, N. S. Vidic, K. B. Gregory, and R. D. Vidic, “Spatial and temporal correlation of water quality parameters of produced waters from devonian-age shale following hydraulic fracturing.,” *Environ. Sci. Technol.*, vol. 47, no. 6, pp. 2562–9, Mar. 2013.

[7] A. Vengosh, D. Hirschfeld, D. Vinson, G. Dwyer, H. Raanan, O. Rimawi, A. Al-zoubi, E. Akkawi, A. Marie, G. Haquin, S. Zaarur, and J. Ganor, “High Naturally Occurring Radioactivity in Fossil Groundwater from the Middle East High Naturally Occurring Radioactivity in Fossil Groundwater from the Middle East,” *Environ. Sci. Technol.*, vol. 43, pp. 1769–1775, 2009.

[8] N. Lauer and A. Vengosh, “Age Dating Oil and Gas Wastewater Spills Using Radium Isotopes and Their Decay Products in Impacted Soil and Sediment,” *Environ. Sci. Technol. Lett.*, p. acs.estlett.6b00118, 2016.

[9] W. S. Moore, “Sources and fluxes of submarine groundwater discharge delineated by radium isotopes,” *Biogeochemistry*, vol. 66, no. 1, pp. 75–93, 2003.

[10] B. Burnett, J. Chanton, J. Christoff, E. Kontar, S. Krupa, M. Lambert, W. Moore, D. O’Rourke, R. Paulsen, C. Smith, L. Smith, and M. Taniguchi, “Assessing methodologies for measuring groundwater discharge to the ocean,” *Eos, Trans. Am. Geophys. Union*, vol. 83, no. 11, p. 117, 2002.

[11] M. E. Gonneea, P. J. Morris, H. Dulaiova, and M. a. Charette, “New perspectives on radium behavior within a subterranean estuary,” *Mar. Chem.*, vol. 109, no. 3–4, pp. 250–267, 2008.

[12] N. R. Warner, C. a. Christie, R. B. Jackson, and A. Vengosh, “Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania,” *Environ. Sci. Technol.*, vol. 47, pp. 11849–11857, 2013.

[13] S. Fesenko, F. Carvalho, P. Martin, W. S. Moore, and T. Yankovich, “Radium in the Environment,” 2014.

[14] R. A. Zielinski and J. R. Budahn, “Mode of occurrence and environmental mobility of oil-field radioactive material at US Geological Survey research site B, Osage-Skiatook Project, northeastern Oklahoma,” *Appl. Geochemistry*, vol. 22, no. 10, pp. 2125–2137, 2007.

[15] D. Porcelli and P. W. Swarzenski, “The Behavior of U- and Th-series Nuclides in Groundwater,” *Rev. Mineral. Geochemistry*, vol. 52, no. 1, pp. 317–361, 2003.

[16] M. Grivé, L. Duro, E. Colàs, and E. Giffaut, “Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB,” *Appl. Geochemistry*, vol. 55, pp. 85–94, Apr. 2015.

[17] P. Beneš, P. Strejc, Z. Lukavec, and Z. Borovec, “Interaction of radium with freshwater sediments and their mineral components. I.,” *J. Radioanal. Nucl. Chem. Artic.*, vol. 82, no. 2, pp. 275–285, May 1984.

[18] S. Bassot, D. Stammose, and S. Benitah, “Radium behaviour during ferric oxi-hydroxides ageing,” *Radioprotection*, vol. 40, pp. S277–S283, Jun. 2005.

[19] I. Nirdosh, W. Trembley, and C. Johnson, “Adsorption-desorption studies on the 226Ra-hydrated metal oxide systems,” *Hydrometallurgy*, vol. 24, no. 2, pp. 237–248, 1990.

[20] L. Ames, J. McGarrah, and B. Walker, “Sorption of trace constituents from aqueous solutions onto secondary minerals. II. Radium,” *Clays Clay Miner.*, vol. 31, no. 5, pp. 335–342, 1983.

[21] E. R. Landa and D. F. Reid, “Sorption of radium-226 from oil-production brine by sediments and soils,” *Environ. Geol.*, vol. 5, no. 1, pp. 1–8, 1983.

[22] D. J. Greeman, A. W. Rose, J. W. Washington, R. R. Dobos, and E. J. Ciolkosz, “Geochemistry of radium in soils of the Eastern United States,” *Appl. Geochemistry*, vol. 14, no. 3, pp. 365–385, 1999.

[23] J. S. Nathwani and C. R. Phillips, “Adsorption of 226Ra by soils (I),” *Chemosphere*, vol. 8, no. 5, pp. 285–291, Jan. 1979.

[24] A. J. Beck and M. a. Cochran, “Controls on solid-solution partitioning of radium in saturated marine sands,” *Mar. Chem.*, vol. 156, pp. 38–48, Oct. 2013.

[25] E. Bas, “Adsorption behavior of strontium on binary mineral mixtures of Montmorillonite and Kaolinite,” vol. 64, pp. 957–964, 2006.

[26] A. Kraepiel, K. C. Keiler, and F. M. M. Morel, “A Model for Metal Adsorption on Montmorillonite.,” *J. Colloid Interface Sci.*, vol. 210, no. 1, pp. 43–54, 1999.

[27] M. H. Bradbury and B. Baeyens, “Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinide,” *Geochim. Cosmochim. Acta*, vol. 69, no. 4, pp. 875–892, 2005.

[28] S. Tamamura, T. Takada, J. Tomita, S. Nagao, K. Fukushi, and M. Yamamoto, “Salinity dependence of 226Ra adsorption on montmorillonite and kaolinite,” *J. Radioanal. Nucl. Chem.*, vol. 299, no. 1, pp. 569–575, Sep. 2013.

[29] C. M. Bethke and P. V. Brady, “How the Kd Approach Undermines Ground Water Cleanup,” *Ground Water*, vol. 38, no. 3, pp. 435–443, May 2000.

[30] J. a. Davis, D. E. Meece, M. Kohler, and G. P. Curtis, “Approaches to surface complexation modeling of Uranium(VI) adsorption on aquifer sediments,” *Geochim. Cosmochim. Acta*, vol. 68, no. 18, pp. 3621–3641, 2004.

[31] D. Dzombak and F. Morel, *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York, NY: Wiley, 1990.

[32] G. E. Brown Jr., V. E. Henrich, W. H. Casey, D. L. Clark, C. Eggleston, A. Felmy, D. W. Goodman, M. Graetzel, G. Maciel, M. I. McCarthy, K. H. Nealson, D. a Sverjensky, M. F. Toney, J. M. Zachara, G. E. Brown, V. E. Henrich, W. H. Casey, D. L. Clark, C. Eggleston, A. Felmy, D. W. Goodman, M. Grätzel, G. Maciel, M. I. McCarthy, K. H. Nealson, D. a Sverjensky, M. F. Toney, and J. M. Zachara, “Metal Oxide Surfaces and Their Interactions with Aqueous Solutions and Microbial Organisms,” *Chem. Rev.*, vol. 99, no. 1, pp. 77–174, 1999.

[33] D. A. Sverjensky, “Prediction of the speciation of alkaline earths adsorbed on mineral surfaces in salt solutions,” *Geochim. Cosmochim. Acta*, vol. 70, no. 10, pp. 2427–2453, 2006.

[34] T. A. Duster, “An Integrated Approach to Standard Methods, Materials, and Databases for the Measurements Used To Develop Surface Complexation Models,” *Environ. Sci. Technol.*, vol. 50, no. 14, pp. 7274–7275, 2016.

[35] C. Tournassat, S. Grangeon, P. Leroy, and E. Giffaut, “Modeling specific ph dependent sorption of divalent metals on montmorillonite surfaces. a review of pitfalls, recent achievements and current challenges,” *Am. J. Sci.*, vol. 313, no. 5, pp. 395–451, 2013.

[36] M. Sajih, N. D. D. Bryan, F. R. R. Livens, D. J. J. Vaughan, M. Descostes, V. Phrommavanh, J. Nos, and K. Morris, “Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study,” *Geochim. Cosmochim. Acta*, vol. 146, pp. 150–163, Dec. 2014.

[37] U. Schwertmann and R. Cornell, *Iron Oxides in the Laboratary*. Weinheim, Germany: Wiley-VCH Verlag GmbH, 2000.

[38] L. L. Stookey, “Ferrozine---a new spectrophotometric reagent for iron,” *Anal. Chem.*, vol. 42, no. 7, pp. 779–781, 1970.

[39] A. Klute, G. W. Kunze, and J. B. Dixon, “Pretreatment for Mineralogical Analysis,” in *Methods of Soil Analysis Part 1 - Physical and Mineralogical Methods*, Soil Science Society of America, American Society of Agronomy, 1986.

[40] G. Jia and J. Jia, “Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology,” *J. Environ. Radioact.*, vol. 106, pp. 98–119, Apr. 2012.

[41] D. L. Parkhurst and C. A. J. Appela, “Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation , Batch-Reaction , One-Dimensional Transport , and Inverse Geochemical Calculations Chapter 43 of,” 2013.

[42] S. Dixit and J. G. Hering, “Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility.,” *Environ. Sci. Technol.*, vol. 37, no. 18, pp. 4182–9, Sep. 2003.

[43] P. Fenter, L. Cheng, S. Rihs, M. L. Machesky, M. J. Bedzyk, and N. C. Sturchio, “Electrical Double-Layer Structure at the Rutile-Water Interface as Observed in Situ with Small-Period X-Ray Standing Waves.,” *J. Colloid Interface Sci.*, vol. 225, pp. 154–165, 2000.

[44] P. C. Zhang, P. V. Brady, S. E. Arthur, W. Q. Zhou, D. Sawyer, and D. A. Hesterberg, “Adsorption of barium(II) on montmorillonite: An EXAFS study,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 190, no. 3, pp. 239–249, 2001.

[45] M. H. Bradbury, B. Baeyens, H. Geckeis, and T. Rabung, “Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part 2: Surface complexation modelling,” *Geochim. Cosmochim. Acta*, vol. 69, no. 23, pp. 5403–5412, 2005.

[46] L. L. Ames, “Sorption of Trace Constituents from Aqueous Solutions onto Secondary Minerals. I. Uranium,” *Clays Clay Miner.*, vol. 31, no. 5, pp. 321–334, 1983.

[47] K. Emmerich, F. Wolters, G. Kahr, and G. Lagaly, “Clay profiling: The classification of montmorillonites,” *Clays Clay Miner.*, vol. 57, no. 1, pp. 104–114, 2009.

[48] A. Naveau, F. Monteil-Rivera, J. Dumonceau, H. Catalette, and E. Simoni, “Sorption of Sr(II) and Eu(III) onto pyrite under different redox potential conditions,” *J. Colloid Interface Sci.*, vol. 293, no. 1, pp. 27–35, 2006.

[49] F. M. Michel, L. Ehm, S. M. Antao, P. L. Lee, P. J. Chupas, G. Liu, D. R. Strongin, M. a a Schoonen, B. L. Phillips, and J. B. Parise, “The structure of ferrihydrite, a nanocrystalline material.,” *Science*, vol. 316, no. 5832, pp. 1726–9, Jun. 2007.

[50] L. Axe, G. B. Bunker, P. R. Anderson, and T. a Tyson, “An XAFS analysis of strontium at the hydrous ferric oxide surface,” *J. Colloid Interface Sci.*, vol. 199, no. 1, pp. 44–52, 1998.

[51] N. Sahai, S. A. Carroll, S. Roberts, and P. A. O’Day, “X-Ray Absorption Spectroscopy of Strontium(II) Coordination,” *J. Colloid Interface Sci.*, vol. 222, no. 2, pp. 198–212, 2000.

[52] M. H. Bradbury and B. Baeyens, “Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation,” *Geochim. Cosmochim. Acta*, vol. 66, no. 13, pp. 2325–2334, 2002.

[53] L. Gorgeon, “Contribution à la Modélisation Physico-Chimique de la Retention de Radioéléments à Vie Longue par des Matériaux Argileux,” Universite Paris, 1994.

[54] J. M. Zachara, S. C. Smith, J. P. McKinley, and C. T. Resch, “Cadmium Sorption on Specimen and Soil Smectites in Sodium and Calcium Electrolytes,” *Soil Sci. Soc. Am. J.*, vol. 57, no. 6, p. 1491, 1993.

[55] R. Murphy and D. Strongin, “Surface reactivity of pyrite and related sulfides,” *Surf. Sci. Rep.*, vol. 64, no. 1, pp. 1–45, Jan. 2009.

[56] W. A. Kornicker and J. W. Morse, “Interactions of divalent cations with the surface of pyrite,” *Geochim. Cosmochim. Acta*, vol. 55, no. 8, pp. 2159–2171, 1991.

[57] P. Wersin, M. F. Hochella, P. Persson, G. Redden, J. O. Leckie, and D. W. Harris, “Interaction between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence for sorption and reduction,” *Geochim. Cosmochim. Acta*, vol. 58, no. 13, pp. 2829–2843, 1994.

[58] A. Naveau, F. Monteil-Rivera, E. Guillon, and J. Dumonceau, “Interactions of aqueous selenium (-II) and (IV) with metallic sulfide surfaces,” *Environ. Sci. Technol.*, vol. 41, no. 15, pp. 5376–5382, 2007.

[59] D. K. Das, P. N. Pathak, S. Kumar, and V. K. Manchanda, “Sorption behavior of Am3+ on suspended pyrite,” *J. Radioanal. Nucl. Chem.*, vol. 281, no. 3, pp. 449–455, 2009.

[60] A. Naveau, F. Monteil-Rivera, E. Guillon, and J. Dumonceau, “XPS and XAS studies of copper(II) sorbed onto a synthetic pyrite surface,” *J. Colloid Interface Sci.*, vol. 303, no. 1, pp. 25–31, 2006.

[61] F. Sun, B. A. Dempsey, and K. A. Osseo-Asare, “As(V) and As(III) reactions on pristine pyrite and on surface-oxidized pyrite,” *J. Colloid Interface Sci.*, vol. 388, no. 1, pp. 170–175, 2012.

[62] M. J. Lambert and W. C. Burnett, “Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements,” *Biogeochemistry*, vol. 66, no. 1–2, pp. 55–73, 2003.

[63] Rama and W. S. Moore, “Using the radium quartet for evaluating groundwater input and water exchange in salt marshes,” *Geochim. Cosmochim. Acta*, vol. 60, no. 23, pp. 4645–4652, Dec. 1996.

[64] A. L. H. Hughes, A. M. Wilson, and W. S. Moore, “Groundwater transport and radium variability in coastal porewaters,” *Estuar. Coast. Shelf Sci.*, vol. 164, pp. 94–104, Oct. 2015.