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 (T. Zhang, Gregory, Hammack, & Vidic, 2014). 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 (Subramanian & Govindan, 2007). Hence, geochemical controls on Ra mobility are directly tied to the mobility and accumulation of Rn within soil-sedimentary systems (Jones, 1999).

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 (Lu & Mason, 2001). In a recent USGS study (Szabo, dePaul, Fischer, Kraemer, & Jacobsen, 2012), 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) (Barbot, Vidic, Gregory, & Vidic, 2013). These naturally elevated Ra bearing formations are particularly prevalent in some parts of the US (PA, WY, TX) and abroad (Middle East, etc.) (Lauer & Vengosh, 2016; Vengosh et al., 2009). 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) (Moore, 2003). This model of SGD fluxes matches well with other measurement methods, but is unable to resolve groundwater behavior within the estuarine systems (Burnett et al., 2002); 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 (Gonneea, Morris, Dulaiova, & Charette, 2008). In addition to its use as a groundwater tracer, Ra has also been identified as a marker for historic spills associated with hydrocarbon extraction (Lauer & Vengosh, 2016). 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 (Warner, Christie, Jackson, & Vengosh, 2013). 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 bearing minerals (barite, celestine log Ksp = -6.63, -9.99) (T. Zhang et al., 2014). However their low solubility and rapid precipitation generally do not constrain long term Ra behavior in most natural systems (Fesenko, Carvalho, Martin, Moore, & Yankovich, 2014). Hence, Ra adsorption to solids, particularly mineral surfaces, imparts the greatest chemical control on soluble Ra transport in groundwater systems (Gonneea et al., 2008; Porcelli & Swarzenski, 2003). 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 (Grivé, Duro, Colàs, & Giffaut, 2015).

Numerous studies have examined Ra (ad)sorption to natural sediments and specific minerals by measuring and comparing distribution coefficients, Kd (L. Ames, McGarrah, & Walker, 1983; Bassot, Stammose, & Benitah, 2005; Beneš, Strejc, Lukavec, & Borovec, 1984; Fesenko et al., 2014; Nirdosh, Trembley, & Johnson, 1990). In general, iron (hydr)oxides, manganese oxides, and some clay minerals are found to be potent sorbents of Ra. Organic matter also plays an important role, but it is unclear how it compares to mineral phases (Greeman, Rose, Washington, Dobos, & Ciolkosz, 1999). 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 (Beck & Cochran, 2013). Sorption of other group II ions to montmorillonites and other clay minerals is also well studied (Bas, 2006; Michael H. Bradbury & Baeyens, 2005; Kraepiel, Keiler, & Morel, 1999), but there is only a limited data set for radium sorption (Tamamura et al., 2013).

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 (Fesenko et al., 2014). However, Kd-based geochemical models are prone to uncertainty when describing adsorption and transport within natural systems where geochemical variation is common (Bethke and Brady, 2000, Davis et al, 2004). 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 (Dzombak & Morel, 1990), sometimes with the aid of spectroscopic tools or *ab inito* modeling (Brown  Jr. et al., 1999; Sverjensky, 2006). 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 (Duster, 2016; Tournassat, Grangeon, Leroy, & Giffaut, 2013). 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 (Sajih et al., 2014; Sverjensky, 2006), 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 (Schwertmann & Cornell, 2000). 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 (Stookey, 1970). 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 (Tamamura et al., 2013). 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 (Klute, Kunze, & Dixon, 1986). 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). 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 (Sajih et al., 2014). 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.

2.3 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 (referencexxx). 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 . 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.

2.4 SURFACE COMPLEXATION MODELING

Radium binding to mineral surfaces was modeled through a double diffuse layer (DDL) surface complexation model implemented in PHREEQC (Parkhurst & Appela, 2013). Simple single site models were used to fit the data alongside models previously established in the literature (xxx). These simplified models allow for easy comparison of the relative importance of the different minerals for radium retention, as well as comparison with currently existing surface complexation modeling results, while not making explicit statements about molecular level radium surface behavior (Dixit & Hering, 2003; Dzombak & Morel, 1990; Tournassat et al., 2013). The literature models, in contrast, are valuable to fit since their formulations are often based on spectroscopic evidence (Fenter et al., 2000; P. C. Zhang et al., 2001). Experimental sorption data was fit only by varying radium sorption reaction constants and site densities, though surface area measurements or literature values were preferred (Mike H. Bradbury, Baeyens, Geckeis, & Rabung, 2005; Sajih et al., 2014). 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

The sorption isotherm results for ferrihydrite and goethite are plotted in figures 1a and 1b, respectively. The data points for each mineral and pH combination show linear behavior in the range considered, and the associated Kd values presented in table 1. This Kd is calculated from the slope of the line fitted to the experimental points. 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. Both minerals clearly show pH dependent sorption behavior, though differences in sorption for the same mass, which are likely driven by the significant differences in mineral surface area.

Several studies examine sorption of radium to iron (hydr) oxides such as ferrihydrite and goethite (Beck & Cochran, 2013; Beneš et al., 1984; Gonneea et al., 2008; Sajih et al., 2014); however direct comparison is problematic, owing to differences in solution composition and solid-solution ratio, which are known to impact fitting parameters (Tournassat et al., 2013). Selected experimental results from the literature are presented in Table 1, using calculated Kd values to compare relative sorption extent. In some cases, it was necessary to calculate a Kd value from the reported data, since none was calculated or was calculated using a different formulation, such as a Langmuir or Freundlich isotherm. The solid/solution ratios (solid mass divided by total solution), as well as the pH and background electrolyte are also reported. 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 (Beck & Cochran, 2013; Sajih et al., 2014). 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 (Gonneea et al., 2008) and that sorption increases with increasing surface area. In our study, Ra adsorbed more extensively to ferrihiydrite than goethite across all solution conditions, except at pH 5 where goethite sorbed slightly more radium compared to ferrihydrite. One study compared radium sorption to hematite, ferrihydrite, goethite, and lepidocrocite, finding that ferrihydrite sorbs radium most extensively (Beck & Cochran, 2013). 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 (references xxxx), 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 studies (Beck & Cochran, 2013; Nirdosh et al., 1990; Sajih et al., 2014). 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 (Sajih et al., 2014), but appdifferent in others where ionic strength was much higher (Beck & Cochran, 2013). 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 . We expect relatively low surface-area goethite based on the previously described experimental method, which should more closely match goethites found in natural settings (Schwertmann & Cornell, 2000). These differences 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 2a, the calculated Kd values listed in table 1, and the kinetic experiment results in figure 2b. 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 sodium 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 sorption with the lower solid solution ratio used here (300 mg/L) (L. L. Ames, 1983; Tamamura et al., 2013). It is possible that differences in the source clay itself may drive some of this variation, as the CEC and measured surface areas are close (Tamamura et al., 2013). The differences in surface area, however, will most likely impact the protonated surface sites, which would provide only a modest adjustment to the Kd value calculated. Differences in the source region and geologic history for the clays could result in major variations in isomorphic substitutions, layer charge, and metal ion loading, which in turn would alter the radium sorption affinity of a given clay. These differences would more likely affect exchange with the inner layer of the clay, and could explain the results found here.

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). While the quantity of sorbed Ra at pH 5 and 7 per unit mass was lower than ferrihydrite, goethite and Na-montmorillonite, the Kd at these pH values was highest for all minerals when normalized to surface area. Radium sorption to goethite is comparable to that of pyrite at circumneutral pH values, though the extent of sorption to goethite is much larger at increasingly basic solution conditions . 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, which suggests radium sorption would also be limited as found here (Naveau, Monteil-Rivera, Dumonceau, Catalette, & Simoni, 2006). ~~These results suggest that reduced iron sulfide minerals may play a limited role in controlling radium sorption in anoxic environments~~, however, the iron oxides result suggests the formation of oxic coatings on the pyrite surface may lead to enhanced sorption following oxidation.

SECTION 3.2 SURFACE COMPLEXATION MODELING

A single site, monodentate reaction was used to describe Ra adsorption to goethite and ferrihydrite; constrained fitting of xxx-xxx closely simulated experimental data. (Figures 4a and 4b). The fitted reactions and constants, which can be found in table 2, show that radium adsorption to ferrihydrite is more extensive than to goethite, matching the relative extents of sorption observed in the sorption isotherms. 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 (Dzombak & Morel, 1990). 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 to note 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 simpler two site model, and obtained a complexation constant that was roughly 1-2 log units larger than found here. Other recent work examining radium sorption to ferrihydrite used a single site model, with two tetradentate reactions to fit experimental data (Sajih et al., 2014; Sverjensky, 2006). Using a similar quantity of surface sites, we applied this model to our experimental data (Figures 5a and 5b). Fits to ferrihydrite data were not noticeably better, but the fits to the goethite data were improved using the tetradentate model. Moreover, the fitted constants for ferrihydrite were significantly different (nearly 20 log units smaller) while the goethite constants were only 1-2 log units different. 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 (Michel et al., 2007). It is unclear though, why there would be similarities in the sorption Kd values, but such larger differences in log K for surface complexation.

Concentrations of Ra used here are far below the analytical detection limits for techniques used to describe and constrain the bonding environment of Ra to solids. Hence, the SCM developed here for Ra adsorption is compared with similar studies that combine SCM with spectroscopic techniques used to constrain surface reactions of other group 2 elements, which may react with solids in a similar way as Ra. X-ray absorption spectroscopy was used to examine strontium behavior in contact with the surface of an iron oxide, and illustrated that strontium forms weaker bound outer sphere complexes with the surface of iron oxides (Axe, Bunker, Anderson, & Tyson, 1998; Sahai, Carroll, Roberts, & O’Day, 2000). (in separate study?- )Modeling results of strontium behavior with goethite reinforce these spectroscopic results (Rahnemaie, Hiemstra, & van Riemsdijk, 2006), suggesting that barium and radium would then also form outer sphere complexes. Other modeling efforts used a tetradentate model based on x-ray spectroscopy results, and predicted that radium and barium would form slightly weaker complexes compared to strontium (Fenter et al., 2000; Sverjensky, 2006). This prediction matches with some modeling of experimental data comparing radium and barium, though the pattern does not match as well when considering strontium data (Carroll, Roberts, Criscenti, & O’Day, 2008; Sajih et al., 2014), nor with the experimental data fit here (Table 3). These comparisons have their limitations since many different reaction formulations are used, even though they all fall under a “single site tetradentate” model. These uncertainties underscore the need to study specific radium behavior, comparing with model predicted behavior based on analogs even on the relatively well studied iron oxides.

Surface complexation modeling of radium ~~behavior~~adsorption to sodium montmorillonite was fit using two sites. One monodentate reaction was used to describe adsorption to xxx, and an exchange reaction was used to describe adsorption to inner layer sites, ( figure 6), ). 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 (Michael H. Bradbury & Baeyens, 2005; Kraepiel et al., 1999). 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 (P. C. Zhang et al., 2001). Other models of metal sorption to clays have used a similar scheme for surface behavior as here, however used multiple types of sites to represent surface sorption using the strong and weak site formulation described for ferrihydrite (M. H. Bradbury & Baeyens, 2002). The designation of “strong” and “weak” sites does not apply to the sites used in this model since both contribute to sorption at the modeled low levels of radium. The number of fitted sites was also significantly lower than reported in the literature, with literature values producing poor fits. A single site, two reaction model was also considered but did not fit the experimental data as well the two site model, nor did it match previous SCM formulations for montmorillonites. The presence of exchange in these models account for the significant extent of sorption at acidic pHs, however, the fitted surface complexation constants 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 ~~behavior~~ adsorption with montmorillonites, there is a broad base of literature examining the strength of exchange and surface reactions with other metals (M. H. Bradbury & Baeyens, 2002; Michael H. Bradbury & Baeyens, 2005; Mike H. Bradbury et al., 2005). Previously calculated metal exchange reactions with sodium montmorillonite cations show a range of values from 0.7 to 398. Here, the calculated selectivity coefficient for radium is 1.41, which suggests that radium could easily be displaced by other metals in solution. This matches with observations that increases in ionic strength result in radium displacement (Beck & Cochran, 2013; Fesenko et al., 2014). Comparisons of typical surface site reactions, in contrast, illustrate that the extent of radium adsorption in our study is significantly more extensive than that found for other potentially hazardous metals such as uranium, americium, manganese, and cadmium, though not as strong as that of tin (Michael H. Bradbury & Baeyens, 2005; Gorgeon, 1994; Zachara, Smith, McKinley, & Resch, 1993). This suggests that interactions between multiple metals with a clay surface will be intricate, resulting in differential competition for the various available sites. The differences between metal reactions with respect to the surface are likely less important than those in exchange, but the sum of their effects is difficult to predict a priori.

Lastly, SCM of Ra adsorption to pyrite was performed using a similar method as to iron (hdyr)oxides, using surficial S as the adsorption site (reference?xxx) (table 2). Model fits capture the observed data points , though not as well as for Ra adsorption to montmorillonite or iron oxides, which indicates that a simple complexation model may not be sufficient to describe the observed behavior. 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 is reinforced by the observation of limited radium sorption over all pH ranges. Similar to our results, a previous study found no adsorption of strontium to non-oxidized pyrite (Naveau et al., 2006), and another study of pyrite ~~behavior~~ with other non-redox active metals made no assumption of chemical reactions at the mineral surface, other than the existence of a protonated site (Kornicker & Morse, 1991). This differs from ~~suggested behavior~~ results found in fitted surface complexation model, as a complex with the deprotonated site was necessary to fit the experimental data.

nraveling adsorption processes occurring on the surfaces of pyrite requires observation and measurement of surface behavior through techniques such as x-ray spectroscopy and *ab initio* modeling. Indeed, signs of these intricate surface behaviors appear when studying redox-active metals such as selenium and uranium, which oxidize the pyrite surface, dramatically changing the surface properties (Naveau, Monteil-Rivera, Guillon, & Dumonceau, 2007; Wersin et al., 1994). Further characterization of the pyrite surface properties is necessary to better constrain radium behavior at the 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-montmorilliont, a 2:1 layer clay with a solute-accessible interlayer. Pyrite showed minimal sorption at best, however, it may play a limited role in controlling sorption in anoxic environments, and may impart important controls on Ra mobility when oxidation produces iron oxide coatings on pyrite surfaces. Sensitivity to pH was observed for Ra adsorption to all minerals, and previous research shows that ionic strength will also control radium retention (Beck & Cochran, 2013; Fesenko et al., 2014; Tamamura et al., 2013). Equilibrium constants for Ra adsorption to goethite and ferrihydrite found here differed from previous studies using the same suite of SCM reactions; this was likely a result of mineralogical or differences in experimental design (e.g. solid-solution ratios, etc.). 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 (Lambert & Burnett, 2003; Lauer & Vengosh, 2016). The models used thus far are relatively simple mixing models, where transport within porous media is not considered (Rama & Moore, 1996). 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 (Hughes, Wilson, & Moore, 2015). Previous studies of radium behavior 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 ~~behavior~~. Further study, particularly probing radium ~~behavior~~ at these surfaces, resolving sources of discrepancy, and further quantification of transport would be instrumental in improving radium utility as a tracer.

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