SECTION 1: INTRODUCTION AND BACKGROUND

Radiation exposure through consumption of radium-bearing groundwater or exposure to radon from accumulated subsurface radium represents an ongoing threat to human health worldwide [REF]. Radium (Ra) is a naturally-occurring radionuclide commonly found in soils, aquifer solids, and natural waters, with four environmentally-relevant isotopes, 223Ra, 224Ra, 226Ra, and 228Ra that arise through spontaneous fission within several decay series (i.e. 235U, 238U, and 232Th). Chemical dissolution and alteration of Ra-bearing minerals may liberate Ra to porewater, but most is contributed from soilds to porewater through alpha recoil during transmutation of mineral-bound parent isotopes (Fesenko, Carvalho, Martin, Moore, & Yankovich, 2014).

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, however typical activities are around 1 mBq/L (Moore, 1996), posing little risk to human populations. Nevertheless, some subsurface formations possess hazardous levels of Ra, particularly in deep shales, where low groundwater flux yields significantly elevated concentrations (>1 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.). Anthropogenic activities including Uranium mining and recently, hydraulic fracturing, can redistribute these naturally occurring radioactive materials (NORM), raising the risk of releasing these radium bearing waters to the surface either through improper storage or handling. Legacy contamination also poses a risk to deeper drinking water aquifers, necessitating better quantification of key radium transport processes.

Ra 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). In this method, a simple conservative mixing model of local groundwater containing naturally occurring Ra isotopes is tuned to reach a target off shore end member (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). Ra isotopes are retarded by the presence of iron and manganese oxides in estuarine aquifers, which will result in non-conservative mixing, creating spatial and temporal variations in radium concentrations (Gonneea, Morris, Dulaiova, & Charette, 2008). These systems can experience rapid changes in solution salinity, pH, and redox state, potentially violating assumptions of conservative Ra transport. Indeed, variations of Ra release from estuarine groundwater have already been observed (Hughes, Wilson, & Moore, 2015). 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 local, oxic, low salinity groundwater.

Although radium can precipitate with sulfate (log Ksp = -10.38) and will co-precipitate with barium and strontium bearing minerals (barite, celestine log Ksp = -6.63, -9.99), their low solubility and rapid precipitation generally do not constrain radium long term behavior in most natural systems barring radioactive decay (T. Zhang, Gregory, Hammack, & Vidic, 2014)). Hence, Ra adsorption to solids, particularly mineral surfaces, imparts the greatest chemical control on soluble Ra transport in groundwater systems (Fesenko et al., 2014; Gonneea et al., 2008). 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 are high (greater than 1 M) (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 the most potent sorbents of Ra. Organic matter also plays an important role, but it is unclear how it compares to the aforementioned 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 significant variations in Kd for common estuarine minerals, even when only representative 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). There is very little data examining the sorption of radium to reduced minerals that form during natural cycling of certain groundwaters. This is of particular interest during hydraulic fracturing when considering releases of deep, anoxic, radium enriched waters to the surface, or injection of oxic water into deep, anoxic formations that have accumulated radium over long time periods. The gaps in the available data make it difficult to predict radium fate in groundwater where multiple mineral surfaces will compete to sorb dissolved radium in constantly shifting solution conditions.

Recently, a more sophisticated approach for modeling Ra adsorption to minerals was considered by Sajih et al, who used surface complexation modeling (SCM) to predict radium adsorption behavior to ferrihydrite and goethite. SCM accounts for variations in solution and solid phase chemistry that impart important controls on adsorption, including surface charge, surface area, solution speciation, surface site behavior with respect to ligands, and surface site availability. SCM’s are often informed by spectroscopic measurements or *ab intio* modeling of sorbate coordination with a mineral surface (Brown  Jr. et al., 1999; Sverjensky, 2006). As of current, there are not agreed upon formulations for these models, resulting in large variations in the specific factors considered. Particularly, the experimental systems, sets of surface complexation reactions and associated constants have not been subjected to a high-level standardization between labs, hindering attempts to make comparisons between different studies (Duster, 2016).

Previous work has covered a limited set of iron oxides and clays, however only iron oxides have had a more detailed examination through surface complexation modeling, while reduced minerals have only barely been addressed. Although numerous studies illuminate trends in Ra (ad)sorption to natural earth materials and specific minerals, there is a paucity of data evaluating Ra adsorption to common soil and aquifer minerals, particularly at low Ra concentrations observed within most groundwater systems. 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 and 2) use surface complexation modeling to test mechanistic descriptions of Ra adsorption to mineral surfaces, 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 with a low salinity background solution and then model radium sorption behavior through SCM. These minerals are representative of previously studied dominant sorbents (iron oxides, clays) and a relatively understudied sorbent (reduced iron minerals), allowing for comparison to previous work while also enabling comparison between the same experimental conditions to determine the minerals’ relative importance. 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 to dominate adsorption. This result is mirrored in the surface complexation modeling, suggesting that exchange reactions with inner layer cations drive the enhanced sorption of radium in montmorillonite compared to the other minerals. Lastly, pyrite shows little affinity for radium, however, the formation of iron oxide coatings after O2 exposure suggests the possibility that it will be a key sorbent in aquifers transitioning between anoxic and oxic states.

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.

2.1 MINERAL PREPARATION

Both ferrihydrite and goethite minerals 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 7-8, 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). Aliquots of the stirred slurry were added directly to the experiments to obtain the desired mineral mass. Goethite was prepared through slow oxidation of an 50 mM Fe2+ and 100 mM bicarbonate solution using air over the course of 2 days. The resulting goethite mineral was centrifuged and washed to remove background electrolyte, and then dried for 2 hours at 70 C. Both iron minerals were characterized using x-ray diffraction to confirm their composition, and had surface area measured using an N2 BET surface area analyzer (table 1). The ferrihydrite was air dried for these two analyses to prevent transformations to other iron minerals.

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, set to pH 5 using glacial acetic acid, which removed any carbonates (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 carefully ground using mortar and pestle. The surface area (table 1) of the montmorillonite was also measured using an N2 BET surface area analyzer to compare with the clay society measurements.

Pyrite was ordered from Ward’s Science (www.wardsci.com), ground using mortar and pestle, and passed through sieves to select for 45-250 um particles. The pyrite was then placed into an anaerobic glove bag with a 5% hydrogen and 95% nitrogen atmosphere. Once in the glove bag, the pyrite was washed in 6 N HCl overnight to remove any iron oxide coatings, and then rinsed with deoxygenated DI water multiple times to remove the remaining acid. Lastly, the pyrite was dried anaerobically in an open beaker; dessicant (Drierite) was placed in the glovebag to facilitate moisture removal. The pyrite composition was also confirmed through XRD, and surface area measured using an N2 BET surface area analyzer, reported in table 1.

2.2 SORPTION EXPERIMENTAL SETUP

Serum vials (200 mL) were filled with 100 mL of 10 mM NaCl stock solution, 30 mg of one 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 butyl stopper. Bottles were shaken for 24 hours, as previous work has established that this is sufficient time for sorption equilibrium to iron surfaces (Sajih et al., 2014a), while sorption to montmorillonite was evaluated using the same set up with different shaking times, finding 24 hours to be 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 polyethersulfone 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 a secular equilibrium with its daughter products. 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. Except for points involving ferrihydrite at pH 9, this was sufficient to determine the extent of sorption and develop isotherms. Background concentrations were also quantified to develop a limit of blank of 1.4 counts per second (cps). We only considered any samples having 1.5 times that limit in subsequent analyses.

Supernatent 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 in addition to the scintillation counted supernatant. A Canberra low energy germanium detector with a Canberra multichannel analyzer was calibrated using a multinuclide standard from Eckert and Ziegler (www.ezag.com). Counts were determined using the Canberra Genie software, which performed peak identification, peak area summation, background subtraction, and nuclide activity calculation. 226-Ra was primarily counted through 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. The physical arrangement closely matches that of the multinuclide standard, so no geometry corrections were used. This gamma counter was also used to quantify the 226-Ra standard curve used in the 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. 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, Grangeon, Leroy, & Giffaut, 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., 2014a). 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 AND DISCUSSION

SECTION 3.1.1 SORPTION ISOTHERM RESULTS: Iron Oxides

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 more overall sorption at a given pH compared to goethite, and the extent of sorption increasing with increasing pH for both iron oxides. Goethite shows limited, if any, sorption at acidic pHs, and ferrihydrite shows the most sorption at pH 9 compared to all of the other minerals. Both minerals clearly show pH dependent sorption behavior, though differences in sorption for the same mass, which are driven by the significant differences in mineral surface area. Kd values that have been normalized to experimental surface area reveal that goethite

There is an abundance of prior work examining sorption of radium to iron oxides such as ferrihydrite and goethite (Beck & Cochran, 2013; Beneš et al., 1984; Gonneea et al., 2008; Sajih et al., 2014b); 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). Table 1 compares selected experimental results from the literature, 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 style 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., 2014a). 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) , which matches with previous results suggesting that increased salinity will reduce radium sorption extent (Gonneea et al., 2008) and that increasing surface area will increase sorption extent. 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 that the sorption isotherm results found here represent an upper limit for radium sorption to iron oxides in these conditions.

Goethite has a larger available pool of radium sorption data to draw from compared to ferrihydrite, however, there are also larger differences between the results in this study compared to others. The results are displayed in table 1, along with the other mineral specific results. Unlike with ferrihydrite, we observe a larger extent of sorption for solutions of similar pH compared to previous work (Beck & Cochran, 2013; Nirdosh et al., 1990; Sajih et al., 2014a). Two factors affecting this are the differences in solution ionic strength and surface area of the synthesized goethite. The Kd values when normalized by surface area are similar in some cases (Sajih et al., 2014b), though not in others (Beck & Cochran, 2013). Other possible deviations from previous studies could be derived from the crystallinity of the goethite used, which varies significantly depending on the synthesis method. We expect relatively low crystallinity 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 Kd style approaches, as they provide limited means to understand the driving factors that create the differences between different forms of the same mineral.

SECTION 3.1.2: SORPTION ISOTHERMS AND SORPTION KINETICS: MONTMORILLONITE

Sorption isotherm results for radium onto sodium montmorillonite are plotted in figure 2, the calculated Kd values listed in table 1, and the kinetic experiment results in figure 2b. The results for the isotherms are remarkably linear for the range of radium activities considered and that the 24 hour equilibration time was sufficient to achieve a steady state for sorption over relevant time scales for groundwater. The total extent of sorption to montmorillonite is significantly larger than iron oxides over the whole range of pH values. Only the isotherm for ferrihydrite at pH 9 shows a larger extent of sorption. However, a comparitively weaker pH dependence is observed for montmorillonite sorption. This result suggests that the dominant mechanism controlling montmorillonite sorption is not complexation with pH dependent surface groups, but rather exchange of radium with sodium in the inner layer of the clay. This concept is explored further in section 3.2 through the surface complexation modeling.

Comparison of the measured sorption Kd values here to earlier studies reveal significant differences. 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 in this study (300 mg/L) (L. L. Ames, 1983; Tamamura et al., 2013). The compared data span roughly an order of magnitude in difference for Kd value, in spite of distinct similarities in experimental methodology, particularly in dealing with clay treatment. 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 most likely impact the protonated surface sites, which would provide a modest adjustment to the Kd value calculated. Differences in the source region and geologic history for the clays, however may 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.

SECTION 3.1.3: SORPTION ISOTHERMS: PYRITE

Pyrite showed limited sorption of radium over most pH values, with almost no sorption at acidic pH values, and limited sorption at more basic pH values. Interestingly, there seems to be little difference in sorption at a circumneutral pH compared to basic pH (figure 3). As with the other minerals, Kd values were fit, showing very linear response in the range of radium activities considered (Table 1). 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 unoxidized 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 3.1.4: THE USE OF ANALOG COMPOUNDS

The availability and radiotoxicity of radium has limited its study, thus analog compounds possessing similar chemistry and lower health risks are often used (Sajih et al., 2014a). Barium is also a group 2 element, and possesses similar chemical characteristics to Ra; it is therefore commonly used as an experimental analog for radium (P. C. Zhang et al., 2001). Barium can remove radium from hydraulic fracturing produced waters by coprecipitation in the presence of sulfate, with barium sulfate and radium sulfate having similar solubility products (VALUES) (T. Zhang et al., 2014). This similarity in behavior suggests barium is a valid radium analog, and can be used when experiments require a high loading of sorbate. However, Sanjih et al (2014) found appreciable differences in Ra and Ba adsorption to goethite under the same experimental conditions, and Jones et al (2011) found distinct differences in Ra sorption to carbonate-bearing minerals (Jones et al., 2011). Comparison of barium and strontium, another possible group 2 radium analogue, also show significant differences in sorption to clay minerals (Grutter, HR, Rossler, & Keil, 1994). These differences underscore that using barium or strontium as chemical analogs to approximate radium adsorption may provide misleading results.

SECTION 3.2 SURFACE COMPLEXATION MODELING

Figure 4 compares the surface complexation modeling results for goethite and for ferrihydrite using a single site, monodentate reaction formulation, both showing a good fit to the corresponding experimental data. 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., 2014a; Sverjensky, 2006). Using a similar quantity of surface sites, we applied this model to our experimental data (Figure 5). 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) and 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.

While the set of data that uses surface complex modeling to examine radium behavior is limited, there is a broader set of surface complexation studies examining iron oxide interactions with the analog compounds barium and strontium. Comparison of these results can elucidate how closely radium behavior compares with that of its analogs. A number of X-ray absorption spectroscopy studies focused on strontium behavior in contact with the surface of an iron oxide, generally finding 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). 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., 2014a), nor with the experimental data fit here. 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 on sodium montmorillonite was fit using two sites with one monodentate reaction per site and an exchange reaction with the inner layer cations, as seen in figure 6, and in the fitted reaction constants in table 2. Fitting the data required an exchange reaction where radium displaced sodium in the inner layer of the clay. 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). X-ray absorption spectroscopy studies of the analog compound, barium, with montmorillonite confirm this dualistic behavior, finding the formation of both inner sphere and outer sphere complexes (P. C. Zhang et al., 2001). Previous 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 site density 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 SCMs for montmorillonites. The presence of exchange in this simplified model accounts 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.

Unfortunately, there is a limited data set that uses surface complexation modeling to examine group II cation behavior with montmorillonites. There is, however, 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). Selectivity coefficients for other metals and sodium montmorillonite have been calculated previously, showing 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 reveal a different story, where 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 significantly different 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, pyrite experimental data was fit using the same method as described for the others, however, the surface reactions bear some difference due to the nature of the surface being modeled, as can be seen in table 2 using a sulfur site instead of an oxygen site. The data fit is acceptable for the experimental data, though it is not as good as for the montmorillonite or iron oxides, which indicates that a simple complexation model may not be sufficient to describe the observed behavior. Reactions with the protonated site were considered, but did not fit the data. 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 extenisive sorbent of all those considered here. This is reinforced by the observation of limited radium sorption over all pH ranges.

Obtaining data for surface complexation modeling of the pyrite surface is a particularly difficult problem, owing to the high reactivity of the pyrite surface with any available oxidant (Murphy & Strongin, 2009). Examination of sorption of strontium to a clean, unoxidized pyrite surface found that no sorption occurred, matching the relatively low amount of sorption observed for pyrite, only using surface complexation modeling to determine sorption to the oxidized pyrite surface (Naveau et al., 2006). An earlier 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 found in fitted surface complexation model, as a complex with the deprotonated site was necessary to fit the experimental data. As discussed previously, this is a likely indication that the pyrite surface behavior cannot be easily captured by a single surface site complexation model. Unraveling the intertwined behaviors at work here 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, and differences observed in fitted thermodynamic constants with previously reported values highlight that variability in mineralogical conditions can result in heterogeneous radium retention. Our results also indicate that it is crucial to consider the role of clay minerals on the retention of Ra, particularly those with an accessible interlayer such as the 2:1 montmorillonite studied here—here, Ra bound most extensively to montmorillonite compared to all other minerals besides ferrihydrite at pH 9.0. 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. All of the observed minerals displayed some sensitivity to solution pH. Previous research also suggets ionic strength will also control radium retention (Beck & Cochran, 2013; Tamamura et al., 2013). Based on these results, variations in the groundwater radium concentration are driven by local shifts in pH or salinity, common in estuarine aquifers or when high salinity produced waters leaked from hydraulic fracturing operations interact with low salinity local groundwater. These complex interactions have significant implications for the use of radium as tracers in the natural environment for groundwater. Assumptions of conservative, equilibrium behavior clearly can be violated when assemblages of minerals result in differential sorption, particularly when solution states (e.g. pH, ORP, ionic strength) are changing in time and space. Only a careful accounting of the relevant controlling mineral phases can allow for full use of radium isotopes as natural tracers. The composition of a given water’s salinity (Ca, Ba, other metals content, etc.) will also likely have an impact on the retention of radium on the mineral surfaces of the aquifers based on the different sorption properties of various metals ions and competition for surface sites between those ions.

The surface complexation constants fitted from the experimental data are largest for sodium montmorillonite surface sites, followed by ferrihydrite, goethite, and then pyrite. Montmorillonite also required an (interlayer) exchange reaction, which was the dominant retention mechanism. Comparison of these constants with other constants for barium or strontium, common analogs for radium, reveal similarities in overall behavior, but it is unclear on how to make estimations of radium behavior from solely the analog’s behavior. The constants provided here also can inform models of transport used to predict radium behavior, and are simple enough to be included in comprehensive multi-element models of transport.

Radium isotopes have played a crucial role in tracing the flux of groundwater into the ocean, and also has 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 et al., 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.

Ames, L. L. (1983). Sorption of Trace Constituents from Aqueous Solutions onto Secondary Minerals. I. Uranium. *Clays and Clay Minerals*, *31*(5), 321–334. http://doi.org/10.1346/CCMN.1983.0310501

Ames, L., McGarrah, J., & Walker, B. (1983). Sorption of trace constituents from aqueous solutions onto secondary minerals. II. Radium. *Clays and Clay Minerals*, *31*(5), 335–342. Retrieved from http://www.clays.org/journal/archive/volume 31/31-5-335.pdf

Axe, L., Bunker, G. B., Anderson, P. R., & Tyson, T. a. (1998). An XAFS analysis of strontium at the hydrous ferric oxide surface. *Journal of Colloid and Interface Science*, *199*(1), 44–52. http://doi.org/10.1006/jcis.1997.5347

Barbot, E., Vidic, N. S., Gregory, K. B., & Vidic, R. D. (2013). Spatial and temporal correlation of water quality parameters of produced waters from devonian-age shale following hydraulic fracturing. *Environmental Science & Technology*, *47*(6), 2562–9. http://doi.org/10.1021/es304638h

Bas, E. (2006). Adsorption behavior of strontium on binary mineral mixtures of Montmorillonite and Kaolinite, *64*, 957–964. http://doi.org/10.1016/j.apradiso.2006.03.008

Bassot, S., Stammose, D., & Benitah, S. (2005). Radium behaviour during ferric oxi-hydroxides ageing. *Radioprotection*, *40*, S277–S283. http://doi.org/10.1051/radiopro:2005s1-042

Beck, A. J., & Cochran, M. a. (2013). Controls on solid-solution partitioning of radium in saturated marine sands. *Marine Chemistry*, *156*, 38–48. http://doi.org/10.1016/j.marchem.2013.01.008

Beneš, P., Strejc, P., Lukavec, Z., & Borovec, Z. (1984). Interaction of radium with freshwater sediments and their mineral components. I. *Journal of Radioanalytical and Nuclear Chemistry Articles*, *82*(2), 275–285. http://doi.org/10.1007/BF02037050

Bradbury, M. H., & Baeyens, B. (2002). Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation. *Geochimica et Cosmochimica Acta*, *66*(13), 2325–2334. http://doi.org/10.1016/S0016-7037(02)00841-4

Bradbury, M. H., & Baeyens, B. (2005). 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. *Geochimica et Cosmochimica Acta*, *69*(4), 875–892. http://doi.org/10.1016/j.gca.2004.07.020

Bradbury, M. H., Baeyens, B., Geckeis, H., & Rabung, T. (2005). Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part 2: Surface complexation modelling. *Geochimica et Cosmochimica Acta*, *69*(23), 5403–5412. http://doi.org/10.1016/j.gca.2005.06.031

Brown Jr., G. E., Henrich, V. E., Casey, W. H., Clark, D. L., Eggleston, C., Felmy, A., … Zachara, J. M. (1999). Metal Oxide Surfaces and Their Interactions with Aqueous Solutions and Microbial Organisms. *Chemical Reviews*, *99*(1), 77–174. http://doi.org/10.1021/cr980011z

Burnett, B., Chanton, J., Christoff, J., Kontar, E., Krupa, S., Lambert, M., … Taniguchi, M. (2002). Assessing methodologies for measuring groundwater discharge to the ocean. *Eos, Transactions American Geophysical Union*, *83*(11), 117. http://doi.org/10.1029/2002EO000069

Carroll, S. a, Roberts, S. K., Criscenti, L. J., & O’Day, P. a. (2008). Surface complexation model for strontium sorption to amorphous silica and goethite. *Geochemical Transactions*, *9*, 2. http://doi.org/10.1186/1467-4866-9-2

Dixit, S., & Hering, J. G. (2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environmental Science & Technology*, *37*(18), 4182–9. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/14524451

Duster, T. A. (2016). An Integrated Approach to Standard Methods, Materials, and Databases for the Measurements Used To Develop Surface Complexation Models. *Environmental Science & Technology*, *50*(14), 7274–7275. http://doi.org/10.1021/acs.est.6b02669

Dzombak, D., & Morel, F. (1990). *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York, NY: Wiley.

Fenter, P., Cheng, L., Rihs, S., Machesky, M. L., Bedzyk, M. J., & Sturchio, N. C. (2000). Electrical Double-Layer Structure at the Rutile-Water Interface as Observed in Situ with Small-Period X-Ray Standing Waves. *Journal of Colloid and Interface Science*, *225*, 154–165. http://doi.org/10.1006/jcis.2000.6756

Fesenko, S., Carvalho, F., Martin, P., Moore, W. S., & Yankovich, T. (2014). *Radium in the Environment*. *The Environmental Behavior of Radium*.

Gonneea, M. E., Morris, P. J., Dulaiova, H., & Charette, M. a. (2008). New perspectives on radium behavior within a subterranean estuary. *Marine Chemistry*, *109*(3–4), 250–267. http://doi.org/10.1016/j.marchem.2007.12.002

Gorgeon, L. (1994). *Contribution à la Modélisation Physico-Chimique de la Retention de Radioéléments à Vie Longue par des Matériaux Argileux*. Universite Paris.

Greeman, D. J., Rose, A. W., Washington, J. W., Dobos, R. R., & Ciolkosz, E. J. (1999). Geochemistry of radium in soils of the Eastern United States. *Applied Geochemistry*, *14*(3), 365–385. http://doi.org/10.1016/S0883-2927(98)00059-6

Grivé, M., Duro, L., Colàs, E., & Giffaut, E. (2015). Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB. *Applied Geochemistry*, *55*, 85–94. http://doi.org/10.1016/j.apgeochem.2014.12.017

Grutter, A., HR, V., Rossler, E., & Keil, R. (1994). Sorption of Strontium on Unconsolidated Glaciofluvial Deposits and Clay Minerals - Mutual Interference of Cesium, Strontium and Barium. *Radiochimica Acta*, *252*(3–4), 247–252. http://doi.org/10.1524/ract.1994.64.34.247

Hughes, A. L. H., Wilson, A. M., & Moore, W. S. (2015). Groundwater transport and radium variability in coastal porewaters. *Estuarine, Coastal and Shelf Science*, *164*, 94–104. http://doi.org/10.1016/j.ecss.2015.06.005

Jones, M. J., Butchins, L. J., Charnock, J. M., Pattrick, R. a D., Small, J. S., Vaughan, D. J., … Livens, F. R. (2011). Reactions of radium and barium with the surfaces of carbonate minerals. *Applied Geochemistry*, *26*(7), 1231–1238. http://doi.org/10.1016/j.apgeochem.2011.04.012

Klute, A., Kunze, G. W., & Dixon, J. B. (1986). Pretreatment for Mineralogical Analysis. In *Methods of Soil Analysis Part 1 - Physical and Mineralogical Methods*. Soil Science Society of America, American Society of Agronomy. http://doi.org/10.2136/sssabookser5.1.2ed.c5

Kornicker, W. A., & Morse, J. W. (1991). Interactions of divalent cations with the surface of pyrite. *Geochimica et Cosmochimica Acta*, *55*(8), 2159–2171. http://doi.org/10.1016/0016-7037(91)90094-L

Kraepiel, A., Keiler, K. C., & Morel, F. M. M. (1999). A Model for Metal Adsorption on Montmorillonite. *Journal of Colloid and Interface Science*, *210*(1), 43–54. http://doi.org/10.1006/jcis.1998.5947

Lambert, M. J., & Burnett, W. C. (2003). Submarine groundwater discharge estimates at a Florida coastal site based on continuous radon measurements. *Biogeochemistry*, *66*(1–2), 55–73. http://doi.org/10.1023/B:BIOG.0000006057.63478.fa

Lauer, N., & Vengosh, A. (2016). Age Dating Oil and Gas Wastewater Spills Using Radium Isotopes and Their Decay Products in Impacted Soil and Sediment. *Environmental Science & Technology Letters*, acs.estlett.6b00118. http://doi.org/10.1021/acs.estlett.6b00118

Michel, F. M., Ehm, L., Antao, S. M., Lee, P. L., Chupas, P. J., Liu, G., … Parise, J. B. (2007). The structure of ferrihydrite, a nanocrystalline material. *Science (New York, N.Y.)*, *316*(5832), 1726–9. http://doi.org/10.1126/science.1142525

Moore, W. S. (1996). Large groundwater inputs to coastal waters revealed by 226Ra enrichments. *Nature*, *380*(6575), 612–614. http://doi.org/10.1038/380612a0

Moore, W. S. (2003). Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. *Biogeochemistry*, *66*(1), 75–93. http://doi.org/10.1023/B:BIOG.0000006065.77764.a0

Murphy, R., & Strongin, D. (2009). Surface reactivity of pyrite and related sulfides. *Surface Science Reports*, *64*(1), 1–45. http://doi.org/10.1016/j.surfrep.2008.09.002

Naveau, A., Monteil-Rivera, F., Dumonceau, J., Catalette, H., & Simoni, E. (2006). Sorption of Sr(II) and Eu(III) onto pyrite under different redox potential conditions. *Journal of Colloid and Interface Science*, *293*(1), 27–35. http://doi.org/10.1016/j.jcis.2005.06.049

Naveau, A., Monteil-Rivera, F., Guillon, E., & Dumonceau, J. (2007). Interactions of aqueous selenium (-II) and (IV) with metallic sulfide surfaces. *Environmental Science and Technology*, *41*(15), 5376–5382. http://doi.org/10.1021/es0704481

Nirdosh, I., Trembley, W., & Johnson, C. (1990). Adsorption-desorption studies on the 226Ra-hydrated metal oxide systems. *Hydrometallurgy*, *24*(2), 237–248. http://doi.org/10.1016/0304-386X(90)90089-K

Parkhurst, D. L., & Appela, C. A. J. (2013). *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*. *U.S. Geological Survey Techniques and Methods*. Retrieved from http://pubs.usgs.gov/tm/06/a43/

Rahnemaie, R., Hiemstra, T., & van Riemsdijk, W. H. (2006). Inner- and outer-sphere complexation of ions at the goethite-solution interface. *Journal of Colloid and Interface Science*, *297*(2), 379–388. http://doi.org/10.1016/j.jcis.2005.11.003

Rama, & Moore, W. S. (1996). Using the radium quartet for evaluating groundwater input and water exchange in salt marshes. *Geochimica et Cosmochimica Acta*, *60*(23), 4645–4652. http://doi.org/10.1016/S0016-7037(96)00289-X

Sahai, N., Carroll, S. A., Roberts, S., & O’Day, P. A. (2000). X-Ray Absorption Spectroscopy of Strontium(II) Coordination. *Journal of Colloid and Interface Science*, *222*(2), 198–212. http://doi.org/10.1006/jcis.1999.6562

Sajih, M., Bryan, N. D. D., Livens, F. R. R., Vaughan, D. J. J., Descostes, M., Phrommavanh, V., … Morris, K. (2014a). Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study. *Geochimica et Cosmochimica Acta*, *146*, 150–163. http://doi.org/10.1016/j.gca.2014.10.008

Sajih, M., Bryan, N. D., Livens, F. R., Vaughan, D. J., Descostes, M., Phrommavanh, V., … Morris, K. (2014b). Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study: SUPPLEMENTARY DATA. *Geochimica et Cosmochimica Acta*, *146*, 150–163. http://doi.org/10.1016/j.gca.2014.10.008

Schwertmann, U., & Cornell, R. (2000). *Iron Oxides in the Laboratary*. *Wiley-VCH Verlag Gmbh*. Weinheim, Germany: Wiley-VCH Verlag GmbH. http://doi.org/10.1002/9783527613229

Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. *Analytical Chemistry*, *42*(7), 779–781. http://doi.org/10.1021/ac60289a016

Sverjensky, D. A. (2006). Prediction of the speciation of alkaline earths adsorbed on mineral surfaces in salt solutions. *Geochimica et Cosmochimica Acta*, *70*(10), 2427–2453. http://doi.org/10.1016/j.gca.2006.01.006

Tamamura, S., Takada, T., Tomita, J., Nagao, S., Fukushi, K., & Yamamoto, M. (2013). Salinity dependence of 226Ra adsorption on montmorillonite and kaolinite. *Journal of Radioanalytical and Nuclear Chemistry*, *299*(1), 569–575. http://doi.org/10.1007/s10967-013-2740-3

Tournassat, C., Grangeon, S., Leroy, P., & Giffaut, E. (2013). Modeling specific ph dependent sorption of divalent metals on montmorillonite surfaces. a review of pitfalls, recent achievements and current challenges. *American Journal of Science*, *313*(5), 395–451. http://doi.org/10.2475/05.2013.01

Warner, N. R., Christie, C. a., Jackson, R. B., & Vengosh, A. (2013). Impacts of shale gas wastewater disposal on water quality in Western Pennsylvania. *Environmental Science and Technology*, *47*, 11849–11857. http://doi.org/10.1021/es402165b

Wersin, P., Hochella, M. F., Persson, P., Redden, G., Leckie, J. O., & Harris, D. W. (1994). Interaction between aqueous uranium (VI) and sulfide minerals: Spectroscopic evidence for sorption and reduction. *Geochimica et Cosmochimica Acta*, *58*(13), 2829–2843. http://doi.org/10.1016/0016-7037(94)90117-1

Zachara, J. M., Smith, S. C., McKinley, J. P., & Resch, C. T. (1993). Cadmium Sorption on Specimen and Soil Smectites in Sodium and Calcium Electrolytes. *Soil Science Society of America Journal*, *57*(6), 1491. http://doi.org/10.2136/sssaj1993.03615995005700060017x

Zhang, P. C., Brady, P. V., Arthur, S. E., Zhou, W. Q., Sawyer, D., & Hesterberg, D. A. (2001). Adsorption of barium(II) on montmorillonite: An EXAFS study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *190*(3), 239–249. http://doi.org/10.1016/S0927-7757(01)00592-1

Zhang, T., Gregory, K., Hammack, R. W., & Vidic, R. D. (2014). 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. *Environmental Science and Technology*, *48*(8), 4596–4603. http://doi.org/10.1021/es405168b