SECTION 1: INTRODUCTION AND BACKGROUNdD

Radiation exposure through consumption of radium-bearing groundwater represents an ongoing threat to human health worldwide (xxx). Radium (Ra) is a naturally-occurring radionuclide commonly found in soils, aquifer solids, and natural waters, and possesses 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 (?) (xxx), but most is contributed from soilds to porewater through alpha recoil during transmutation of mineral-bound parent isotopes.

Ongoing alpha recoil progressively elevates porewater Ra activities until hydrologic flushing removes the equilibrating solution, or secular equilibrium with parent radionuclides is achieved. Most aquifer systems contain low but adequate (e.g. U, Th, <5 mg/kgxxx?) parent radionuclide and sufficiently favorable hydrological conditions to facilitate delivery of measurable Ra to solution, albeit often at levels marginally above the detection limit of modern instrumentation. Nevertheless, some aquifers possess hazardous levels of Radium….

* Groundwater activities are typically low, but isotopes are useful for examining groundwater sources, including subterranean discharge, etc
* Naturally-occurring, elevated levels are observed in some parts of the US (Penssylvania –refs), and abroad (middle east, other places)…these are human health threats, with total radiation exceeding xxx-xxx Bq/L
* Anthropogenic activities are redistributing naturally occurring radioactive materials (NORM), much of it existing as Ra, from deep brine aqufiers, most notably from the recent proliferation of hydraulic fracturing
* Legacy contamination also poses a risk to groundwater, including uranium mine tailings, which often contain high activiites of Ra that is easily leached to the deeper subsurface.

~~Since the advent of the nuclear age, the fate of anthropogenic and naturally generated radioactive isotopes in the environment has been a major focus of groundwater transport studies due to the significant human and environmental health hazards they present.~~ One isotope of concern is radium, which was used as a phosphorescent compound historically, but sees little, if any industrial use today. The primary source of radium in groundwater is through natural production by the decay of its parent products, uranium and thorium. While a natural radium signal exists in nearly all ground waters, it is significantly elevated in ground waters that are liberated from deep formations by anthropogenic processes such as hydrocarbon extraction or uranium mining. Hydraulic fracturing, in particular, has recently raised some concerns where radium concentrations exceed 120 Bq/L in produced well waters (Barbot, Vidic, Gregory, & Vidic, 2013). Improper storage or handling of the wastes could result in radium contamination of groundwater, posing a radiological risk to local populations. An understanding of how radium would migrate under these scenarios is important during planning for hydraulic fracturing operations.

Radium isotopes also have been used as naturally occurring environmental tracers. A well-established example uses a mass balance of radium 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 radium isotopes is tuned to reach a target off shore end member (Moore, 2003). This model SGD fluxes match well with other measurement methods, but is unable to resolve groundwater behavior within the estuarine systems (Burnett et al., 2002). Radium 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 experience rapid changes in solution salinity, pH, and redox state, making radium transport through them more complicated. Indeed, variations of radium release from estuarine groundwater have already been observed (Hughes, Wilson, & Moore, 2015). In addition to its use as a groundwater tracer, radium has also been identified as a marker for historic spills associated with hydrocarbon extraction (Lauer & Vengosh, 2016). This is possible when the radium isotopic signature of produced water significantly differs from that of local groundwater (Warner, Christie, Jackson, & Vengosh, 2013). Successful implementation of this method requires a comprehensive accounting of radium 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 Ra is known to co-precipitate with Sr and Ba-bearing minerals, their high solubility (log K’s = xxx, xxx respectively (refs)) constrains precipitation in most aquifer systems. Hence, Ra adsorption to mineral solids imparts the greatest chemical control on soluble Ra transport in groundwater systems (refs). 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 and sulfate are observed, but these solution species dominate above pH 9 and when ligand activities are high (greater than xxx M). .

Numerous studies have examined Ra (ad)sorption to natural sediments and specific minerals by measuring and comparing distribution coefficients, Kd (refs). In general, iron (hydr)oxides, manganese oxides, and some clays minerals are found to be the most potent sorbents of Ra (L. Ames, McGarrah, & Walker, 1983; Bassot, Stammose, & Benitah, 2005; Beneš, Strejc, Lukavec, & Borovec, 1984; Fesenko, Carvalho, Martin, Moore, & Yankovich, 2014; Nirdosh, Trembley, & Johnson, 1990). 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 similar systems, even when only a synthetic iron oxide was considered (Beck & Cochran, 2013).

Recently, A more sophisticated approach for modeling Ra adsorption to minerals was considred by Sajih et al, who used surface complexation modeling to…… SCM accounts for variations in solution and solid phase chemicstry that impart important controls on adsorption, including surface charge, surface area, xxx, xxxx and xxx. SCM’s are often informed by spectroscopic measurments or ab intio modeling of sorbate coordination with a mineral surface (refs)….. More recent work has modeled data from radium sorption to ferrihydrite and goethite using a tetradentate binding site surface complexation model with good success (Sajih et al., 2014). The sorption of other group II ions to montmorillonites and other clay minerals is well studied and modeled (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). Lastly, there is very little data examining the sorption of radium to reduced minerals that form during natural cycling of certain groundwaters. 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.

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., 2014). 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 (T. Zhang, Gregory, Hammack, & Vidic, 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 radium analogue, also show significant differences in sorption to clay minerals (Grutter, HR, Rossler, & Keil, 1994). These differences underscore that using Ba as a chemical analog to approximate Ra adsorption may provide misleading results.

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. The objectives of this work are to therefore 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 (including high salinity brines) and 2) use surface complexation modeling to test mechanistic descriptions of Ra adsorption to mineral surfaces, 3) use SCM modeling to provide quantitative comparisons of Ra adsorption to different minerals. In this study, we first compare sorption of radium to ferrihydrite, goethite, sodium montmorillonite, and pyrite with a low salinity background solution, and then model that sorption through established surface complexation models. 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 montmorillionite is more extensive over a range of solution conditons 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.

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. Radium-226 stock in 3% HCl was provided by the MIT Environmental, Health, and Safety office.

2.1 MINERAL PREPARATION

Both ferrihydrite and goethite minerals were prepared using standard methods (Schwertmann & Cornell, 2000). Briefly, ferrihydrite was precipitated by dissolving FeCl3\*xxxH2O (?) 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 xxx mM Fe2+ and xxx mM bicarbonate using air over the course of 2 days. The resulting mineral was centrifuged and washed to remove background electrolyte, and then dried for 2 hours at 50 C(?). Both iron minerals were characterized using x-ray diffraction to confirm their composition.

Calcium montmorillonite STX-1b was ordered from the clay minerals society (clays.org). 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 the carbonates (Klute, Kunze, & Dixon, 1986). Since the mineral data from the clay society indicated low or negligible iron content, no iron oxide removal was performed. The clay was then centrifuged and equilibrated with the experimental background solution, resulting in a sodium montmorillonite. The clay was dried at 50 C overnight, and then carefully ground using mortar and pestle.

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.

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 226Ra 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., 2014), 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, 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 was complete, samples were allowed to re-equilibrate for several minutes, and then filtered using 0.22 um polyethersulfone filters, which did not sorb significantly quantities of Ra. Experimental error was quantified by measuring the standard deviation of triplicates for each data point.

2.3 ANALYTICAL TECHNIQUES

Solutions of radium were quantified using scintillation counting. 10 mL of sample were mixed with 10 mL of Ultima Gold XR (Perkin Elmer) and sealed for 30 days to allow radium-226 to reach a transient 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 radium-226 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. Radium-226 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 radium-226 standard curve used in the scintillation counting.

[DISCUSSION OF SURFACE AREA ANALYSIS]

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 more complex models established by the literature. The simple 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). The more advanced 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, cation exchange capacity measurements by the clays society, or literature 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, 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 may be driven by the significant differences in mineral surface area.

There is an abundance of prior work examining sorption of radium to iron oxides such as ferrihydrite and goethite (references); however direct comparison is problematic, owing to differences in solution composition and solid-solution ratio, which are known to impact fitting parameters (refs). 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., 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, xxx mM, others, xxx-xxx mM), which matches with previous results suggesting that increased salinity will reduce radium sorption extent (Gonneea et al., 2008). In our study, Ra adsorbed more extensively to ferrihiydrite than goethite across all solution conditions. One study compared radium sorption to hematite, ferryhydrite, 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.

Larger differences between sources appear when examining radium adsorption to goethite, which has more available data in the literature. These 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., 2014). One factor affecting this may be the differences in solution ionic strength or surface area of the synthesized goethite. Other possible differences may be driven by 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, and the calculated Kd values listed in table 1. The results are remarkably linear for the range of radium activities considered. The total extent of sorption to montmorillonite is significantly larger than iron oxides over the whole range of pH values. The only isotherm in this study showing a larger extent of sorption is ferrihydrite at pH 9, with all others having significantly less sorption. However, a much weaker pH dependence is observed for montmorillonite sorption. This result suggests that the dominant mechanism controlling montmorillonite sorption is not complexation with pH variable 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.

As with goethite, there are significant differences in the order of magnitude in the calculated Kd value. Previous studies using high amounts of solid (what are they?) resulted in less sorption compared to low amounts of solid (xxx mg/L, etc) (L. L. Ames, 1983), while the present experiments, which had the lowest solid loading , had the largest extent of sorption. 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 may drive some of this variation, as the reported surface area of the STx-1b used in this study is more than twice that of the SWy-1 used in the other study (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. Since the clays are also sourced from different regions, it’s possible there are significant variations in the chemical structure and metal ion loading that might also drive variations in sorption, which can be observed in the differences in Fe3+ content observed by the clay society when characterizing the clays. These differences would more likely affect exchange with the inner layer of the clay. Further study of radium retention to clays should try to focus on quantifying and modeling these differences.

DISCUSSION OF KINETIC EXPERIMENT RESULTS

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. As with the other minerals, Kd values were fit, showing very linear response in the range of radium activities considered, and those values are reported in table 2. 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 3.2 SURFACE COMPLEXATION MODELING

Figure 3 compares the surface complexation modeling results for goethite and for ferrihydrite, both showing a good fit to the corresponding experimental data. The fitted reactions and constants, which can be found in table 2, show that Ra 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. Owing to the low levels of radium used in the experimental data set, it is not surprising that weak site behavior was not observed. 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 and did not observe noticibly better fits compared to using a single monodentate reaction. Moreover, the fitted constants were significantly different (nearly 20 log units smaller). 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. Although the disparity between these studies and the constant reported here is quite high, it is known that the structural properties (??) of ferrihydrite may vary substantially according to the method used for synthesis, which may account for some of the variance. 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., 2014), 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 monodentate reactions and an exchange reaction with the inner layer cations, as seen in figure 4, 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 used a similar scheme for surface behavior, including multiple types of sites to represent surface sorption using the strong and weak site formulation described for ferrihydrite (M. H. Bradbury & Baeyens, 2002). The model here also uses 2 sites, however the designation of “strong” and “weak” sites does not apply since both contribute to sorption at the modeled 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 nearly as well the two site model. 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, though with significantly fewer available surface sites (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 weakest 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 complexation model, and better understanding is best gained through direct measurement; x-ray absorption spectroscopic study as has been done with montmorillonite and iron oxides. Indeed, this complexity has been found when studying redox-active metals such as selenium and uranium, which oxidize the pyrite surface (Naveau, Monteil-Rivera, Guillon, & Dumonceau, 2007; Wersin et al., 1994). Further characterization of the pyrite surface properties is necessary to better constrain radium behavior with 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 …. 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). These complex interactions have significant implications for the use of radium as tracers in the natural environment for groundwater. 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. The composition of a given water’s salinity will also likely have an impact on the retention of radium on the mineral surfaces of the aquifers based on the different results for various metals.

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 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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TABLE 3: Reaction Stoichiometries and Associated log K

Ferrihydrite

1. FhyOH + H+ = FhyOH2+  log K = 7.92 Source: (Dzombak & Morel, 1990)
2. FhyOH = FhyO- + H+ log K = -8.93 Source: (Dzombak & Morel, 1990)
3. FhyOH + Ra+2 = FhyOHRa+2  log K = 5.7 Source: Data fitting

Goethite

1. GoeOH + H+ = GoeOH­­2+ log K = 4.8 Source: (Sverjensky, 2006)
2. GoeOH = GoeO- + H+ log K = -10.4 Source: (Sverjensky, 2006)
3. GoeOH + Ra+2 = GoeOHRa+2 log K = 3.5 Source: Data fitting

Sodium Montmorillonite

1. 2 Na-Clay + Ra+2 = Ra-Clay­2 + 2 Na+  log K = 0.15 Source: Data fitting
2. ClayOH + H+ = ClayOH2+  log K = 4.5 Source: (Michael H. Bradbury & Baeyens, 2005)
3. ClayOH = ClayO- + H+ log K = -7.9 Source: (Michael H. Bradbury & Baeyens, 2005)
4. ClayOH + Ra+2 = ClayOHRa+2 log K = 6.4 Source: Data fitting

Pyrite

1. PyrSH = PyrS- + H+ log K = 6.45 Source: (Naveau et al., 2006)
2. PyrS- + Ra+2 = PyrSRa+ log K = -6.4 Source: Data Fitting

Table 1: Fitted Kd values for sorption isotherms

|  |  |  |
| --- | --- | --- |
| Mineral | pH | Kd |
| Ferrihydrite | 3 | 229.89 |
|  | 5 | 471.37 |
|  | 7 | 2486.88 |
|  | 9 | 115932.70 |
| Goethite | 3 | 0 |
|  | 5 | 302.74 |
|  | 7 | 573.62 |
|  | 9 | 11697.99 |
| Sodium Montmorillonite | 3 | 6740.15 |
|  | 5 | 17749.39 |
|  | 7 | 21473.27 |
|  | 9 | 22894.86 |
| Pyrite | 3 | 0? |
|  | 5 | 0? |
|  | 7 | 536.20 |
|  | 9 | ~520 |

Figures are below

Figure 3. Sorption of Radium to ferrihydrite, sodium montmorillonite, goethite, and pyrite at pH 7. Best fit lines were fitted to each mineral to determine the distribution coefficient Kd.



Figure 1. Effect of pH on radium-226 sorption to ferrihydrite. The trends seen here (increasing sorption with increasing pH), are reflected in the other minerals as well.



Figure 4. Surface complexation model fits of experimental data. Top: Ferrihydrite, Bottom: Sodium montmorillonite.