SECTION 1: INTRODUCTION AND BACKGROUND

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 primarily a concern in lower flux 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 due to the elevated presence of radium in produced waters, with concentrations in excess of 120 Bq/L (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.

In parallel to these risks, the radium isotopes also have been leveraged as naturally occurring environmental tracers. The primary 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 desired off shore end member (Moore, 2003). This model matches well with other 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 if there are spatial and temporal transport heterogeneities (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 has 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 radium isotope ratios can delineate between produced water from deep formations and local groundwater (Warner, Christie, Jackson, & Vengosh, 2013). Improved models of radium isotope transport enable better usage of the radium isotope suite to trace critical groundwater processes.

Radium isotope transport is dominated by advection and diffusion, where specific mineral phases control the aqueous radium concentration through sorption. Radium weakly forms complexes with carbonate and sulfate ions at pH values greater than 9, but is free radium for most environmental conditions (Grivé, Duro, Colàs, & Giffaut, 2015). Previous work has studied sorption by measuring and comparing distribution coefficients, Kd, finding that iron oxides, manganese oxides, and some clays dominate radium retention (L. Ames, McGarrah, & Walker, 1983; Bassot, Stammose, & Benitah, 2005; Beneš, Strejc, Lukavec, & Borovec, 1984; Fesenko, Carvalho, Martin, Moore, & Yankovich, 2014; Nirdosh, Trembley, & Johnson, 1990). While a useful indicator for the extent of radium retention in a given system, these coefficients are primarily empirical and are not easily adapted to dynamic systems or systems with differing mineral composition. 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). 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 radiotoxicity of radium has limited its range of study, thus analog compounds possessing similar chemistry, but lower health risks are used (Sajih et al., 2014). Barium, which is in the same family as radium, is commonly used as an analog for radium in the environment (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. Previous work, however, compared radium and barium sorption for similar experimental conditions (though significantly higher barium loading), finding some similarities for ferrihydrite, but some differences for goethite (Sajih et al., 2014). Another study compared radium and barium uptake of carbonate minerals, also finding distinct differences in sorption behavior (Jones et al., 2011). Comparison of barium and strontium also show significant differences in sorption to clay minerals (Grutter, HR, Rossler, & Keil, 1994). These differences underscore the importance of studying radium specifically, only relying on chemical analogs when considerations of safety limit experimental activities or the behavior is shown to be sufficiently similar.

The objective of this work is to develop further understanding of radium sorption behavior and develop simple models of radium sorption that can be used in a wide range of groundwater studies. 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 been almost completely ignored. 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 simple surface complexation models. The results show that pH plays a crucial role in determining sorption extent, and that while iron oxides do show extensive sorption under certain conditions, the most dominant mineral is in fact sodium montmorillonite. This result is mirrored in the surface complexation modeling, suggesting that exchange reactions with inner layer cations drive the enhanced sorption of radium in the 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 was provided by the MIT Environmental, Health, and Safety office, and acidified to 3% using HCl.

2.1 MINERAL PREPARATION

Both ferrihydrite and goethite minerals were prepared using standard methods (Schwertmann & Cornell, 2000). Briefly, ferrihydrite was precipitated by dissolving Fe(III)Cl3 in water, and rapidly titrating the solution to pH 7-8, followed by centrifugation and washing to remove background electrolytes. The iron content of prepared ferrhydrite slurry was characterized using the ferrozine method (Stookey, 1970), and aliquots of the slurry were added directly to the experiments. Goethite was prepared by slow oxidation of an initially O2 free solution of Fe(II)Cl2 and 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 70 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 cleaned clay was then washed and centrifuged 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), which came in a large ore form. The pyrite was ground using mortar and pestle, and then the 45-250 um size fraction were sieved out. The pyrite was 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 washed with DI water to remove the remaining acid. Lastly, the pyrite was allowed to air dry in the anaerobic glove bag with a dessicant. The pyrite composition was also confirmed through XRD.

2.2 SORPTION EXPERIMENTAL SETUP

200 mL serum vials 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 Radium-226 Stock. Experiments using pyrite were performed in an anaerobic glove bag with oxygen free solutions, while all others were performed in lab air. The pH was titrated to 3,5,7 or 9 +/- 0.05, and then the bottle was sealed with a butyl stopper. Bottles were shaken for 24 hours, as p The pH was then checked and re-titrated to the desired value. If the pH deviated more than 0.1 pH units, then the bottle was allowed to equilibrate for 15 minutes, and the re-titration process repeated. HCl and NaOH at high concentrations were used for all titrations, so that volume additions did not exceed 5% of the original volume. Once re-titration was complete, the samples were filtered using 0.22 um polyethersulfone filters, which was shown not to significantly sorb radium. 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 techniques. 10 mL of sample (5 mL of Sodium montmorillonite supernatant due to filtration difficulty) 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.

Many supernatant samples using ferrihydrite at pH 9 were below this 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 simply placed in scintillation vials, and counted directly on the counter, with the resulting counts being adjusted for ferrihydrite loss during filtration. The physical arrangement arrangement closely matches that of the multinuclide standard, so no geometry corrections were used.

[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, which allows 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). In the case of sodium montmorillonite which has been shown to exchange cations, we also posed an exchange reaction following previous models of clay sorption behavior using a selectivity coefficient (Michael H. Bradbury & Baeyens, 2005). 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 covers radium carbonate, sulfate, and hydroxide complexes, and 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 through 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. It is worth noting that goethite shows limited, if any, sorption at acidic pHs, and that ferrihydrite shows the most sorption at pH 9 compared to all of the other minerals.

There is an abundance of prior work examining sorption of radium to iron oxides such as ferrihydrite and goethite, however comparison between these previous works can be difficult, due to differences in solution composition and solid solution ratio. 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.

For ferrihydrite, surprisingly little data exists, with only two sources reporting any sort of isotherm data. The experimental results presented here match within an order of magnitude of the Kd values calculated in other work (Beck & Cochran, 2013; Sajih et al., 2014). While the pH of these points is similar, a variety of solution conditions were used, with both other studies using significantly larger amounts of background electrolyte. The K­d found in this work is the largest of the collected data sets, but was also performed with the lowest ionic strength background solution, which matches with previous results suggesting that increased salinity will reduce radium sorption extent (Gonneea et al., 2008). It is worth noting that 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 significant differences in sorption extent compared to previous research, generally observing a larger extent of sorption for solutions of comparable pH (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. A much weaker pH dependence is observed for montmorillonite sorption as compared to the iron oxides. The total extent of sorption, however, is significantly larger 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. 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 the iron oxides, there is only a limited set of experimental data with which to compare the gathered experimental data. The two data points are reported in table 1, and were performed under similar solution conditions, but with different solid to solution ratios. As with goethite, there are significant differences in the order of magnitude in the calculated Kd value. Experiments with the highest solid loading showed the least extent of sorption (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 clays society measured 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 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 some limited sorption.

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 reaction constants and suggested reactions, which can be found in table 2, show that ferrihydrite complexation dominates over goethite, matching the relative extents of sorption observed in the sorption isotherms. Traditional models of ferrihydrite behavior use a two site model, with a strong and weak site, where the strong site represents sorption at low levels of sorbate, and the weak site represents sorption at high levels of sorbate (Dzombak & Morel, 1990). This type of model was considered when fitting the experimental data, however, there was no sensitivity found for the reaction constant for the weak site, and only a single site and single reaction were needed. Given 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, with two tetradentate reactions to fit experimental data (Sajih et al., 2014; Sverjensky, 2006). While fitting with the same model was performed using similar amounts of surface sites, the overall fit was not noticeably better than with a single monodentate reaction. The same work also fitted their experimental data using a two site model, which found complexation constants that were roughly 1-2 log units larger than found here. It is well understood that ferrhydrite structure can vary depending on the very specific synthesis conditions, so it is not surprising to see some variance.

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 the interactions of the analog compounds barium and strontium with iron oxides. 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 study specific radium behavior, comparing with model predicted behavior based on analogs. This further motivates the need to develop the data set constraining radium behavior 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. 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 certainly 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, even after accounting for exchange, which matches with the sorption isotherm results.

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 up to 398. The calculated selectivity coefficient for radium here 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 radium binding found here is significantly stronger than that found for other 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 therefore 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 owing 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, using surface complexation modeling only 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 surface behavior, 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 is more complex, and better understanding is best gained through 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, however, they also indicate that it is crucial to consider the role of montmorillonites, and other clays that have exchangeable cations in the inner layer, as they presented the most extensive sorbents of all the considered minerals. Pyrite showed minimal sorption at best, however, it may play a limited role in controlling sorption in anoxic environments, or when iron oxide coatings form on the pyrite surface. 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 exchange reaction, which provided the dominant mechanism for sorbing radium with montmorillonite. 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 more comprehensive 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). Studies of radium behavior in batch reactors so far have provided a first basis with which to develop these models of transport, and this work contributes further to this body of work by highlighting critical minerals that control transport, as well as providing constants to constrain radium behavior. Further study, particularly probing radium behavior at these surfaces, and during transport, would be instrumental in further 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. doi: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. doi: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. doi:10.1021/es304638h

Bas, E. (2006). Adsorption behavior of strontium on binary mineral mixtures of Montmorillonite and Kaolinite, *64*, 957–964. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi:10.1016/j.gca.2005.06.031

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. doi: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. doi: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

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. doi: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. doi: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.

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. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi:10.1021/acs.estlett.6b00118

Moore, W. S. (2003). Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. *Biogeochemistry*, *66*(1), 75–93. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. doi: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. (2014). Adsorption of radium and barium on goethite and ferrihydrite: A kinetic and surface complexation modelling study. *Geochimica et Cosmochimica Acta*, *146*, 150–163. doi: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. doi:10.1002/9783527613229

Stookey, L. L. (1970). Ferrozine---a new spectrophotometric reagent for iron. *Analytical Chemistry*, *42*(7), 779–781. doi: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. doi: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. doi:10.1007/s10967-013-2740-3

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. doi: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. doi: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. doi: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. doi: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. doi:10.1021/es405168b

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.