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. They can present a significant human and environmental health hazards. 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 is then natural production by the decay of its parent products, uranium and thorium. While a natural radium signal exists in nearly all ground waters, it primarily presents a hazard 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, 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). The method constructs a simple conservative mixing model of local groundwater containing naturally occurring radium isotopes to reach a desired off shore end member (Moore, 2003). While many of the predictions of this model have matched well with other methods, it is not able to resolve groundwater behavior within the estuarine systems. Unfortunately, the assumption of conservative behavior that is assumed in the near shore system is questionable in estuarine aquifers, especially given that radium isotopes are retarded by the presence of iron and manganese oxides (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). Aside from a natural groundwater tracer, radium has also been identified as a possible marker for historic spills associated with hydrocarbon extraction (Lauer & Vengosh, 2016). This is possible because the radium isotopic signature of many shales differs significantly from that of local shallow groundwater (Warner, Christie, Jackson, & Vengosh, 2013). Making full use radium as a tracer in both of these scenarios demands careful accounting of the critical processes controlling transport.

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 and manganese oxides dominate radium retention (Bassot, Stammose, & Benitah, 2005; Beneš, Strejc, Lukavec, & Borovec, 1984; 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., 2014a). The sorption of other group II ions to montmorillonites and other clay minerals is well studied (Bas, 2006), 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. Understanding the full suite of minerals controlling radium transport will be key in predicting its behavior.

The literature contains a limited set of data studying radium sorption to most minerals, with radiotoxicity often cited as the reason for these limitations (Sajih et al., 2014a). A popular technique for circumventing these hazards is the use of analog compounds, which share some of the same chemical characteristics as radium, but present fewer human health hazards. Barium, which is in the same family as radium, has been considered and cited as an analog for radium in the environment (P. C. Zhang et al., 2001). Barium has been used to remove radium from produced waters from hydraulic fracturing, as the chemicals will coprecipitate in the presence of sulfate, and have relatively similar solubility products (T. Zhang, Gregory, Hammack, & Vidic, 2014), suggesting this can be a valid approach, particularly when attempting experiments requiring a high loading of sorbate. Previous work compared radium and barium sorption for similar experimental conditions (though significantly higher barium loading), finding some similarities for ferrihydrite, but some differences for goethite. Another study compared radium and barium uptake of carbonate minerals, also finding distinct differences in sorption behavior (Jones et al., 2011). These differences underscore the importance of studying radium specifically, only relying on chemical analogs when considerations of safety limit experimental activities.

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 primarily focused on the importance of iron oxides, but have not considered the role of clay minerals with exchangeable cations, or the importance of reduced iron minerals, both of which are commonly found in many aquifers. 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 models, showing that exchange reactions result in the enhanced sorption of radium in the montmorillonite, as 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. 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.

Lastly, 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% hydrogen 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. Lastly, the pyrite was allowed to air dry in the anaerobic glove bag with a dessicant. The pyrite composition was 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, and then the pH was checked and re-titrated to the desired value. 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 time points, as well as a desorption experiment described in the supporting information. 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 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). The relevant reactions are shown in table 1 (at the end of the paper), along with protonation constants from literature. Experimental sorption data was fit only by varying radium sorption reaction constants. Site densities were set using the BET surface area for the iron minerals, exchangeable sites for the clay were determined by the cation exchange capacity reported by Clay Society, and site densities were set from literature values (Mike H. Bradbury, Baeyens, Geckeis, & Rabung, 2005). 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.

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 2. 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. The extent of sorption increases with increasing pH for both iron oxides. It is worth noting that goethite shows limited 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 and its corresponding analogues 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 compiles selected experimental results from the literature, using calculated Kd values as a marker for 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., 2014a). 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.

Larger differences appear when examining radium adsorption to goethite, which has more available data in the literature. These results are displayed in table 2, 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., 2014b). One factor affecting this may be the differences in solution ionic strength. INSERT COMPARISON OF SURFACE AREAS AS JUSTIFICATION? 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 described experimental method, which should more closely match goethites found in natural settings (Schwertmann & Cornell, 2000). Reconciling these differences is crucial for understanding the importance of goethite in controlling radium sorption.

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 2. 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, however, the total extent of sorption 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 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 2, and were performed under similar solution conditions, but with different solid to solution ratios. Again, 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 (Ames, 1983), while the present experiments, which had the lowest solid loading, had the largest extent of sorption. The comparable 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 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). Unfortunately, there is little data examining the impact of pH on montmorillonite sorption of radium.

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 it seems clear that the existence of any kind of persistent iron oxide coating, or clay minerals with exchangeable cations will dominate sorption processes.

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 3, show that ferrihydrite complexation dominates over goethite, matching the relative extents of sorption observed in the sorption isotherms. It is traditional when modeling fererhydrite behavior to 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. Given the low levels of radium used in the experimental data set, it is not surprising that weak site behavior was not observed during ferrihydrite sorption. Other recent work examining radium sorption to ferrihydrite used a tetradentate reaction to fit experimental data (Sajih et al., 2014a; Sverjensky, 2006). In order to maintain comparisons with goethite and montmorillonite behavior, as well as to maintain the simplicity of the overall modeling approach, this method was not used. The same work also fitted their experimental data using more traditional models, which found complexation constants that were roughly 1-2 log units larger than found here. Given the significant differences in experimental set up in terms of solution and solid loading, this difference seems reasonable.

There is a limited data set that leverages surface complexation methods to understand radium sorption behavior to iron oxides, thus it can be instructive to examine other group II ions, such as strontium and barium, which have similar behavior. Strontium is typically shown to have much weaker interactions with iron oxides, reflected in significantly lower surface complexation constants, even when considering more advanced models of sorption (Carroll, Roberts, Criscenti, & O’Day, 2008; Small, Warren, & Roden, 1999). A different model using a charge distribution (CD) model, however, found similar levels of sorption between goethite and strontium, and predicted that it forms an outer sphere complex (Rahnemaie, Hiemstra, & van Riemsdijk, 2006). X-ray absorption spectroscopy studies of strontium behavior near an iron oxide reflect this, confirming that strontium forms outer sphere complexes with iron oxide surfaces (Axe, Bunker, Anderson, & Tyson, 1998; Sahai, Carroll, Roberts, & O’Day, 2000). Barium also has seen some limited study to iron oxides, finding also weaker complexation than radium, but also generally stronger than that of strontium (Sajih et al., 2014b). In addition, sorption to other iron oxides, such as magnetite, has been studied, again finding similar strengths of sorption (Catalette, Dumonceau, & Ollar, 1998). Overall, it is unclear whether or not the behavior of the group II elements on iron oxides can be easily extended to predict radium behavior beyond a general prediction that radium will also form outer sphere complexes with iron oxide surfaces.

Surface complexation modeling of radium behavior on sodium montmorillonite was also fit using a 1 site model, as seen in figure 4, and in the fitted reaction constants in table 3. Unlike the model for the iron oxides though, it was necessary to include an exchange reaction where radium displaced sodium in the inner layer of the clay. This is a commonly used technique 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, Keiler, & Morel, 1999). Previous models of metal sorption to clays used a more complex scheme for surface behavior, including multiple types of sites to represent surface sorption (M. H. Bradbury & Baeyens, 2002). While a two site model similar to these was considered, a single site model was sufficient to fit the experimental data well, and allows for comparison to iron oxide behavior. The presence of exchange 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.

COMPARE TO SORPTION OF BARIUM STRONTIUM. HOW DOES EXCHANGE COMPARE TO OTHER METALS??? 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. This matches with observations that increases in salinity result in radium displacement (Beck & Cochran, 2013; Fesenko, Carvalho, Martin, Moore, & Yankovich, 2014).

DISCUSSION OF PYRITE

SECTION 3.3: IMPLICATIONS FOR RADIUM AS TRACER

The presented experiments and associated modeling reveal that radium sorbs with varying extent to a variety of common oxidized iron minerals found in groundwater environments. Previous studies of iron oxides have shown that they play an important role as sorbents of radium, and we confirm this result. However, we also show that clay minerals, especially ones with significant cation exchange capacity, may play a similarly important, if not larger role in retarding radium transport compared to iron oxides alone, especially in more acidic groundwater systems, such as mining wastes where oxide sorption is limited. These results suggest that a broader range of minerals ought to be considered when building transport models of radium in natural groundwater settings.

Sulfide bearing iron minerals, which are common in reduced groundwaters may also play a more intricate role in radium transport than first indicated by the sorption results in this experiment. The experimental sulfide mineral was carefully cleaned to remove iron oxide coatings, however, natural variability in redox state of groundwater can drive the formation of oxidized iron coatings that could then enhance radium retention. This plays an important factor in groundwaters that experience natural or anthropogenically driven shifts in groundwater redox state. One area where this is crucial is in hydraulic fracturing, where anoxic shale brines are exposed to oxygenated water, which may result enhanced radium retention. The work here lays a path for improving models of radium transport, which can then be leveraged in efforts to use radium isotopes as a marker for hydraulic fracturing contamination. They would allow for predictions not only of the timing of contamination events but also methods to back calculate the source of such events.

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

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

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

Catalette, H., Dumonceau, J., & Ollar, P. (1998). Sorption of cesium, barium and europium on magnetite. *Journal of Contaminant Hydrology*, *35*(1-3), 151–159. doi:10.1016/S0169-7722(98)00123-5

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.

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

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

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

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

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

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

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

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., Livens, F. R., Vaughan, D. 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. doi: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. 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

Small, T. D., Warren, L. A., & Roden, E. E. (1999). Sorption of Strontium by Bacteria , Fe ( III ) Oxide , and Bacteria - Fe ( III ) Oxide Composites, *33*(24), 4465–4470.

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

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

Table 2: 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.