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METAL SORPTION ON KAOLINITE

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## ABSTRACT

A key issue in performance assessment of low-level radioactive waste sites is predicting the transport and retardation of radionuclides through local soils under a variety of hydrologic and geochemical conditions. Improved transport codes should include a mechanistic model of radionuclide retardation. We have been investigating metal sorption ( $Cs^+$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ ) on a simple clay mineral (kaolinite) to better understand the geochemical interactions of common soil minerals with contaminated groundwaters. Our studies include detailed characterizations of kaolinite surfaces, experimental adsorption measurements, surface complexation modeling, and theoretical simulations of cation sorption. The aluminol edge (010) site has been identified as the most likely site for metal sorption on kaolinite in natural solutions. Relative metal binding strengths decrease from  $Ba^{2+}$  to  $Sr^{2+}$  to  $Cs^+$ , with some portion sorbed on both kaolinite edges and basal surfaces. Some  $Cs^+$  also appears to be irreversibly sorbed on both sites. Molecular dynamics simulations suggest that  $Cs^+$  is sorbed at aluminol (010) edge sites as an inner-sphere complex and weakly sorbed as an outer-sphere complex on (001) basal surfaces. These results provide the basis to understand and predict metal sorption onto kaolinite, and a framework to characterize sorption processes on more complex clay minerals.

## INTRODUCTION

Transport and attenuation of radionuclide contaminants in subsurface environments are largely controlled by the sorptive properties of common soil minerals (e.g., clays, Fe-oxyhydroxides). Since a good mechanistic understanding of sorbate-mineral surface interactions is lacking, heavy reliance is placed on experimental measurements of solid-solution distribution coefficients ( $K_D$ ) for use in hydrogeochemical transport codes to predict the transport and retardation of dissolved radionuclides. These transport codes are the basis for Performance Assessment (PA) calculations by the Nuclear Regulatory Commission (NRC) and other

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regulatory agencies for the licensing of Low Level Waste (LLW) disposal sites or decommissioning of civilian nuclear facilities. However, current PA models use simplified conceptual models for radionuclide retardation that are based on linear and reversible  $K_D$ 's, and often do not consider other geochemical parameters which affect radionuclide transport and attenuation (e.g., temperature, pH, fluid composition, ionic strength, mineral substrate, organic complexation, etc.). Once radionuclide sorption and desorption mechanisms are better understood, more appropriate retardation models can be incorporated into the PA codes to allow for improved estimates of the potential for dose to the public.

This project is designed to provide mechanistic and kinetic data about the sorption behavior of metals with complex mineral surfaces and is based upon our earlier metal ( $Cs^+$  and  $Cd^{2+}$ ) sorption measurements on silica, corundum and kaolinite<sup>1</sup>, and the Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron (XPS) spectroscopic work characterizing the sorption of  $Cs^+$  onto the multiple surface and interlayer sites of clay minerals<sup>2</sup>. Unraveling the mechanistic controls on sorption under diverse geochemical conditions is necessary to predict metal transport and retardation in soils. Our multifocus approach to measure, characterize and model alkali and alkaline earth sorption onto a simple clay, kaolinite, establishes a framework for discerning how other radionuclides bind to more complex clay minerals (e.g., smectites). It also positions us to scale-up our results to predict radionuclide movement in real-world, site-specific scenarios. In this paper, we report on results obtained using scanning force microscopy (SFM), proton or metal adsorption titrations and atomistic modeling to characterize solvated metal interactions with kaolinite surfaces.

## METHODS

Because of the structural and compositional complexity of natural soil phases, we chose to use KGa1 kaolinite ( $Al_2Si_2O_5(OH)_4$ ) because it is a simple, well-crystallized clay mineral and because of its near-stoichiometric composition<sup>3</sup>. The kaolinite unit cell can be simply described as a gibbsite-like sheet of octahedrally coordinated Al bound to a siloxane sheet of tetrahedrally coordinated Si through shared oxygens. Kaolinite sheets are loosely bound in the (001) direction

by hydroxyl groups from the basal octahedral sheet forming hydrogen bonds with the oxygens of the basal siloxane sheet.

All pH-dependent surface charge measurements were made in background electrolyte solutions of 0.1 M NaCl. Sorption isotherms were measured for  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  (as an analog for  $\text{Ra}^{2+}$ ) using a Mettler DL 12 titrator in 0.01-1.0M NaCl background electrolyte solutions. Solution aliquots were taken after pH stabilization and were analyzed for metals by Directly Coupled Plasma (DCP) or Inductively Coupled Plasma (ICP) spectroscopy. Sorption was calculated by difference from starting solutions. SFM topographic images were obtained in air using a Park Scientific Instrument Autoprobe LS in contact mode with PSI Ultralever<sup>TM</sup> tips. Empirical molecular modeling was performed on a UNIX workstation using software provided by the Catalysis and Sorption Project consortium and Molecular Simulations Inc. (MSI, San Diego, CA). Interatomic force field parameters for energy calculations were based on MSI tabulations that have been optimized for crystalline, layered aluminosilicate systems<sup>4</sup>.

## RESULTS AND DISCUSSION

### Surface Charge and Sorption Sites

The surface charge and metal sorption properties of kaolinite were found to be pH-dependent, reflecting the acid-base properties of constituent Si- and Al-oxide and hydroxides. The amphoteric properties of aluminol and silanol on the edges and basal planes have been characterized with acid-base potentiometric titrations using a triple layer model (TLM) to describe surface charge. Optimized TLM parameters for kaolinite surface acidity constants (pK) and its constituent oxides (quartz and corundum), show that Si sites in kaolinite behave like those in  $\text{SiO}_2$  ( $\text{pK}_{\text{Si, Quartz}} = 5.4$  vs.  $\text{pK}_{\text{Si, KGa1}} = 5.7$ ) while Al sites in kaolinite become more acidic than corresponding sites in  $\text{Al}_2\text{O}_3$  ( $\text{pK}_{\text{Al, Corundum}} = 10.9$  vs.  $\text{pK}_{\text{Al, KGa1}} = 3.8$ ). Regressed surface charge equilibrium constants and site densities for KGa1, using a multisite reactivity model (both Al and Si on edge and basal plane sites), suggests either that the siloxane basal plane plays a greater role in overall surface charge than would be expected for fully satisfied siloxane bonds or that the number of pH-dependent edge sites are underestimated<sup>4</sup>. It is common to assume that edge site

densities contribute little to pH-dependent surface charge because edges are thought to amount to only 10% of the total surface area for layered silicate minerals (postulated basal plane to edge aspect ratio of 10:1).

Since metal sorption onto kaolinite is a function of the charge distribution on the surfaces as well as the absolute proportions of exposed planes of differing surface charge, we initiated SFM studies of KGa1 particle surfaces. These microtopographic measurements of kaolinite crystals have shown that up to 50% of kaolinite edges sites are exposed<sup>5</sup> (i.e., proportions of basal to edge surface areas of KGa1 particles range from 2:1 to 10:1). Most of the KGa1 surface charge is attributed to a combination of exposed Al- and Si-sites on the basal plane and edges, and can be related to aluminol or silanol bonds which can accept or donate protons<sup>4</sup>. Moreover, these results explain surface charge titration results without calling upon proton sorption or desorption from the siloxane basal plane.

Molecular modeling techniques were used to better understand, at an atomistic level, specific site acidity at edge and basal plane sites in kaolinite. Specifically, Molecular Electrostatic Potential (MEP) calculations, which represent the net summation of the atomic partial charges at the mineral cluster surface, were performed using the observed crystallographic structure of kaolinite<sup>5</sup> and energy minimized positions for hydroxyl groups on selected surfaces. The MEP surface depicts the most favorable sites for ionic sorption on kaolinite. MEP results show that there is a significant difference in the electrostatic potential of edge and basal surface sites<sup>5</sup>. That is, siloxane and gibbsite basal planes (001) are not as negatively charged as edge silanol or aluminol sites (010). Furthermore, the aluminol edge sites are more reactive for cation sorption (greater negative electrostatic charge) than the edge silanol sites. In summary, the combination of calculated charge distributions from potentiometric titrations, measured proportions of edge and basal plane areas from SFM images, and atomistic MEP surface charge densities provides a consistent picture of distinct crystallographic sites that control kaolinite surface charge and reactivity. That is, aluminol edge sites are preferred metal sorption sites over edge silanol or basal Si- or Al- sites. It should be noted that a small permanent negative charge may exist on the basal planes due to ionic substitutions in the octahedral or tetrahedral layers.

### Metal Sorption

Sorption isotherms for  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  onto kaolinite surfaces at 25°C are shown in Figure 1, where  $\text{>Me}$  denotes sorbed metal and the solid line is a best fit using a constant capacitance surface complexation model. Note that at a given pH, the relative binding strength of  $\text{Ba}^{2+}$  to kaolinite is significantly stronger than that measured for  $\text{Sr}^{2+}$  ( $\text{pK}_{\text{Sr}} = 6.44$  vs.  $\text{pK}_{\text{Ba}} = 6.02$ ). Both metals demonstrate the same pH-dependent sorption isotherm at high pH, but significant pH-independent sorption occurs in acid solutions ( $\text{pH} < 7$ ). The most likely explanation is that metal binding in acid solutions occurs at the basal siloxane layer because of a small permanent, and pH-independent, charge arising from minor substitution of  $\text{Al}^{3+}$  and/or  $\text{Fe}^{3+}$  for tetrahedral  $\text{Si}^{4+}$ .

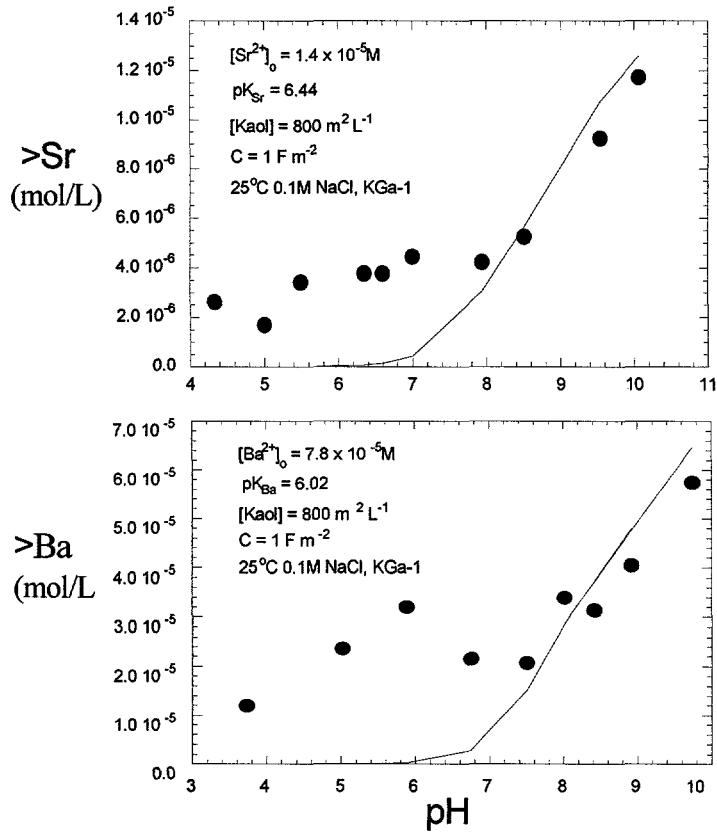


Figure 1. Sorption isotherms for Sr and Ba onto kaolinite; line is best fit for constant capacitance surface complexation model.

Measured  $\text{Cs}^+$  sorption isotherms onto kaolinite surfaces at 25°C and in three background electrolyte solutions (0.01-1.0 M NaCl) are shown in Figure 2. These titrations were conducted from low to high pH and then reversed from high to low pH. At each ionic strength (IS), there is clear hysteresis in the sorption behavior.  $\text{Cs}^+$  is irreversibly sorbed by kaolinite, particularly at  $\text{pH} < 6$ . In addition, we see that as the IS of  $\text{Na}^+$  increases by two orders of magnitude, the sorbed  $\text{Cs}^+$  decreases by about an order of magnitude and that the absolute concentration of  $\text{Na}^+$  is 5-6 orders of magnitude greater than that of  $\text{Cs}^+$ . Since  $\text{Na}^+$  is considered to always sorb as an outer-

sphere complex, the results in 1.0 M NaCl suggest that there is a minimum concentration of irreversibly sorbed Cs<sup>+</sup> that sorbs as an inner-sphere complex. The facts that Cs<sup>+</sup> is displaced by Na<sup>+</sup> and desorption becomes less pH-dependent with increasing ionic strength, suggest that a large fraction of the Cs<sup>+</sup> is bound as an outer-sphere complex. The most likely binding site is the siloxane basal surface which might have a small pH-independent residual charge. However, the pH-dependence of Cs<sup>+</sup> sorption at all ionic strengths suggests that some Cs<sup>+</sup> is also bound as an inner-sphere complex, probably to the pH-dependent aluminol edge site.

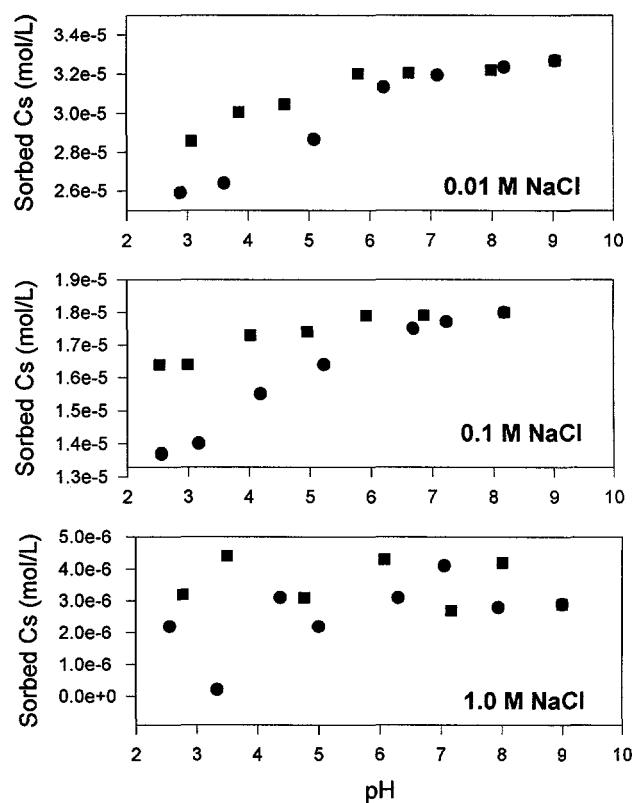


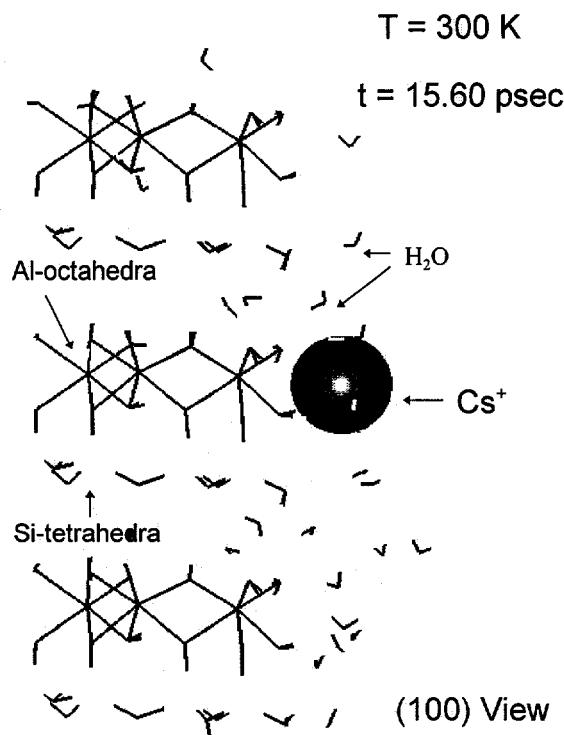
Figure 2. Sorption (circles) and desorption (squares) isotherms of Cs<sup>+</sup> onto kaolinite as a function of ionic strength at 25°C.

#### Molecular Modeling of Cesium Sorption

Several empirical molecular modeling techniques, including energy minimization and molecular dynamics (MD) codes, were used to simulate the interactions of dissolved cesium with a kaolinite surface. One Cs<sup>+</sup> atom, along with its waters of hydration, was positioned adjacent to either the (010) edge or the (001) basal aluminol surface of kaolinite prior to energy minimization. Simulations indicate that Cs<sup>+</sup> sorbs directly to the aluminol (010 edge) as an inner sphere complex (Figure 3). Note that the solvating water molecules are not positioned between the Cs<sup>+</sup> and the (010) edge of kaolinite, but rather coordinate to silanol and other unreacted edge sites. Energy minimization results for the (001) surface indicate that Cs<sup>+</sup> is coordinated to the basal aluminol plane as an outer sphere complex, with waters of hydration completely

surrounding the  $\text{Cs}^+$ . This contrasts sharply with the inner sphere configuration of  $\text{Cs}^+$  sorption at the (010) edge.

Two MD simulations at 300 K were performed using a solvated  $\text{Cs}^+$  positioned at either the (010) edge or the (001) aluminol basal surface<sup>5</sup>. Cesium, water molecules, and basal hydrogens were allowed to freely translate, while heavy kaolinite atoms were fixed. Over 20,000 time steps of 1 femtosecond each were calculated. The results for  $\text{Cs}^+$  initially positioned near the (010) edge were the same as shown on Figure 3. However, shortly after equilibration of the water molecules on the (001) surface,  $\text{Cs}^+$  (outer sphere complex) migrates toward the (010) edge and repositions itself as a an inner sphere complex coordinated to an aluminol site. Clearly, these computer simulations suggest that the edge aluminol site is the preferred  $\text{Cs}^+$  sorption site on a stoichiometric kaolinite.



**Figure 3. Inner-sphere sorption of  $\text{Cs}^+$  ion onto aluminol site at (010) edge of the kaolinite structure.**

## CONCLUSIONS

The surface charge and reactive sites of kaolinite were characterized by potentiometric titrations, SFM surface area measurements, and MEP calculations of long range electrostatic forces. These complementary studies have led to the identification of aluminol edge (010) sites as the most likely site for metal sorption. Relative metal binding strengths over all sites were found to decrease from  $\text{Ba}^{2+}$  to  $\text{Sr}^{2+}$  to  $\text{Cs}^+$ ; metals are sorbed on both kaolinite edges and basal surfaces. Some fraction of  $\text{Cs}^+$  also appears to be irreversibly sorbed. Empirical MD simulations suggest that  $\text{Cs}^+$  is sorbed at aluminol (010) edge sites as an inner-sphere complex and weakly sorbed as an outer-sphere complex on (001) basal surfaces. The computer simulations are consistent with

results of sorption/desorption isotherms as a function of ionic strength. These results provide the basis to understand and predict metal sorption onto kaolinite, and the general framework to characterize the sorption of other metals onto more complex soil minerals.

#### ACKNOWLEDGMENTS

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