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Acid-Base Properties of Kaolinite, Montmorillonite and Illite at Marine Ionic Strength

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Abstract

In marginal marine settings, understanding the role that clay minerals play in the transfer of metal cations from the water column to the seafloor is important if the composition of modern muds in the ocean is used as a proxy for the precursors of ancient shale deposits. In this study, we conducted potentiometric titrations of three naturally abundant clay minerals (kaolinite, montmorillonite and illite) in 0.56 M NaCl electrolyte solutions to ascertain the surface reactivity of each clay mineral at seawater ionic strength. Our results demonstrate that all three clay minerals were increasingly anionic as pH increases from 3 to 9, with montmorillonite having the highest negative-charge. The potentiometric titrations and adsorption data were modeled using both non-electrostatic (NEM) and electrostatic (constant-capacitance model, CCM) surface complexation models (SCMs). A two-site surface complexation model that included one basal siloxane surface site ($\equiv\text{X}^-$) and one amphoteric edge site ($\equiv\text{SOH}$), provided an excellent fit for the protonation data of each mineral. Cd(II) adsorption experiments were conducted to quantify the magnitude of cation adsorption, which showed that 10 g montmorillonite, illite, and kaolinite powder could bind an equivalent of 4.2×10^{-6} M, 3.8×10^{-6} M, and 3.6×10^{-6} M of Cd, respectively, under conditions relevant to seawater (initial Cd concentration of 8.9×10^{-6} M, and pH=8). To place this value into the context of modern riverine clay inputs to the ocean, 13.5×10^9 tons of total suspended sediment are deposited annually (Milliman and Meade, 1983) of which 10 to 25% is clay (Manheim et al., 1970; Schroeder et al., 2015). The total amount of Cd adsorbed to suspended clay minerals entering the modern oceans could then amount to approximately 10^4 to 10^5 tons per year. The results of this study highlight the potential role of clay minerals in transporting metals from the ocean water column to the seafloor.

Keywords: kaolinite; montmorillonite; illite; acid-base titration; adsorption; surface complexation model

1. Introduction

Clays are a group of hydrous aluminum silicate minerals with a sheet-like structure and a particle size of $< 2 \mu\text{m}$. They are common products of weathering and low-temperature hydrothermal alteration, and are a major component of fine-grained sedimentary rocks, such as shale, mudstone, siltstone and fine-grained metamorphic rock including slate and phyllite. From an environmental perspective, clays contribute to the transport and sedimentation of trace metals in rivers and estuaries (Elbaz-Poulichet et al., 1987; Konhauser et al., 1998; Sung, 1995), and they are important in the enhanced burial of organic carbon in marine sediments via adsorption and flocculation (Kennedy et al., 2002; 2014; Shchepetkina et al., 2017).

The main clay mineral groups are kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, montmorillonite $[(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and illite $[(\text{Al}_2)(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2 \cdot \text{K}_{1-x}]$ (Kerr, 1952; Duc et al., 2005a; Playter et al., 2017), and compositionally, they are comprised of two distinct layers. The first is composed of Si tetrahedral in which the Si^{4+} cation is bonded to four oxygen atoms, while the second layer is composed of Al hydroxide where an Al^{3+} cation is located at the center of an octahedron; in some clay minerals, the center cation of the octahedral sheet can undergo isomorphic substitution by Mg^{2+} . The tetrahedral and octahedral sheets are joined to form either 1:1 or 2:1 clay minerals. Kaolinite is a 1:1 clay mineral in which hydrogen bonding holds together the OH^- groups of one layer with the O^{2-} of the other. Subsequently, the structure is fixed

and cations cannot enter between the structural units (Ikhsan et al., 1999; Liu et al., 2013). Montmorillonite and illite are 2:1 type clay minerals in which the O^{2-} groups of one sheet are adjacent to the O^{2-} groups of another (Ikhsan et al., 2005; Delhorme et al., 2010). These clays have varying chemical compositions because substitution of divalent cations for trivalent cations in the octahedral layer and trivalent cations for tetravalent Si in the tetrahedral layers, which gives rise to permanent structural charge on the composite layer (Davis and Kent, 1990; Sposito et al., 1999; Srivastava et al., 2005; Guillot et al., 2009; Delhorme et al., 2010). Another source of charge in clay mineral structures is non-ideal octahedral occupancy (Mermut and Lagaly, 2001). For example, Hofmann and Klemen (1950) suggested that Li^+ can migrate from the interlayer to vacant octahedral sites, which results in the neutralization of the negative charge originating in the octahedral sheet owing to cation substitution.

The charge imbalance in clays is neutralized by the adsorption of cations to the outer surfaces of clay mineral particles or directly onto the tetrahedral sheets of adjoining clay mineral units. The strength with which the adsorbed cations are bound varies with the type of cation and its position on the clay mineral particle surface. On the surface edges, the cations are exchangeable with other cations in the environment. However, bonding is especially strong for the cations in the interlayer spaces (Thomas et al., 1999; Sinitsyn et al., 2000; Ikhsan et al., 2005; Delhorme et al., 2010). Furthermore, in swelling clay minerals, such as montmorillonite, the adjacent octahedral sheets are often weakly bonded, allowing for cations and water molecules to enter the interlayer space, which can result in swelling and changes to the clay mineral charge.

Potentiometric titrations are used to characterize and quantify the density of proton active

functional groups of clay minerals (Tournassat et al., 2004a, b; Duc et al., 2006). These groups participate in protonation/deprotonation reactions and reflect the buffering capacity of the clay mineral over a given pH range (Gu and Evans, 2007, 2008; Kriaa et al., 2009; Gu et al., 2010). While a variety of clay minerals have been previously studied, there are two issues that still need to be resolved. First, significant differences in the proton reactivity and calculated thermodynamic protonation constants (K_a) have been reported. For example, models of titrations of a Wyoming smectite, from the Source Clays Repository (SWy-2; Costanzo, 2001), by Barbier et al. (2000) calculated a log K_a of -5.26 for the deprotonation of generalized edge hydroxyl groups, $\equiv\text{SOH}$, on the clay mineral, while Schroth and Sposito (1998) reported a log K_a of -7.2 for the same generalized functional groups. Possible causes for such discrepancies include: the sensitivity of acid-base properties of clay minerals to sample preparation (e.g., the washing procedure and storage conditions), the analytical conditions selected for the potentiometric titrations (Duc et al., 2005a, b), partial dissolution of the clay mineral during titration (Bibi et al., 2014), and re-adsorption and hydrolysis of dissolved species involving H^+ and OH^- that additionally impact the titrant budget and ultimately the protonation-deprotonation reactions (Baeyens and Bradbury, 1997; Duc et al., 2006).

Second, the majority of the experimental studies on clay reactivity have been performed in low ionic strength solutions, and the impact of high ionic strength on their capacity to adsorb metals is not well constrained. Previous studies have suggested that ionic strength has a major influence on the adsorption of metals to clay mineral by affecting the clay mineral surface charge (Balistrieri and Murray, 1981; Dzombak and Morel, 1990; Wanner et al., 1994; Gao and Mucci, 2001; Jara et al., 2005). For example, Wanner et al. (1994) showed that surface proton concentration on

Na-montmorillonite is inversely dependent on ionic strength in the acidic pH range due to structural-charge surface sites. Baeyens and Bradbury (1997) observed that background electrolyte concentration of 0.5 M can reduce the proton exchange of Na-montmorillonite to 2% (pH=3) and 10% (pH=2), respectively, compared to a background electrolyte concentration of 0.1 M. While Gao and Mucci (2001) reported that both the surface acidity constants and the specific capacitance of goethite increases with increasing ionic strength. Gu et al. (2010) indicated that ionic strength had a major impact on the distribution of the surface species $\equiv X^- \cdot H^+$ and $\equiv X^- \cdot Na^+$ for Na-montmorillonite, which has an impact on the intrinsic metal binding constants. In this study, the adsorption behavior of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) onto montmorillonite at the lower pH range was greatly affected by ionic strength, considering this type of adsorption is a cation exchange reaction occurring at the permanently charged basal surfaces.

In principal, the protonation constants and site concentrations determined in low ionic strength experiments can be extrapolated to higher ionic strength by: (a) accounting for changes in ion activities using activity coefficients, and (b) accounting for changes in the mineral electric field using electrostatic surface complexation models. In reality, these models often fail to accurately predict protonation and/or metal adsorption behavior at high ionic strengths, such as that of seawater (*ca.* 0.56 M). Therefore, the purpose of this study was to develop and test models that describe the surface charge properties, protonation behavior, and metal adsorption capacity of clay minerals at seawater conditions. Specifically, we quantified the proton and cadmium (Cd) adsorption affinities of three clay minerals, kaolinite, montmorillonite, and illite, at seawater ionic strength to determine their importance in regulating metal concentrations in the ocean and

particularly in marginal marine settings. We had three objectives: (1) to characterize the surface acid-base properties of three clay minerals in an electrolyte solution of 0.56 M NaCl using surface complexation modelling (SCM); (2) to create an integrated SCM model which could also account for Cd(II) binding to the surface of each type of clay mineral; and (3) to determine which clay mineral had the greatest capacity for metal adsorption under marine conditions. For each type of clay mineral, the total number of surface sites density and, consequently, the surface ionization constants were calculated using SCM.

2. Materials and methods

2.1. Preparation of clay mineral powders

Kaolinite (KGa-2), montmorillonite (SWy-2), and illite (IMt-2) were acquired from the Clay Mineral Society (CMS; University of Purdue, West Lafayette). Each clay mineral was ground using a mortar and pestle, passed through a 100-mesh sieve, and then stored in plastic bottles for subsequent use. The clay minerals were prepared following a procedure similar to that used by Gu et al. (2010): clay minerals were washed three times by first soaking for 2 h in a 1 M NaCl solution at a pH of 3.0, then centrifuged at 8,100 g for 10 min to pellet the clay mineral powders, and the supernatant pH was measured between each wash to ensure the supernatant solution pH value had dropped to 3. If pH 3 had not been reached, additional acid washes were performed. The clay minerals were then washed once in non-acidified solutions of 1 M NaCl, gradually decreasing the ionic strength from 1.0 to 0.56 to saturate clay minerals with Na⁺. After the final three washes in 0.56 M NaCl, the clay minerals were oven dried at 65°C for 48 h, and stored in sealed centrifuge

143 tubes for later use.

144

145 2.2. Zeta potential measurements

146 Zeta potential measurements were conducted as described by Liu et al. (2015) to assess the net
147 surface charge properties of each clay mineral. Acid washed and non-acid washed clay minerals (as
148 described above), were suspended in 0.56 M NaCl solutions, and then diluted with Milli-Q water 10
149 times to reduce the electrolyte concentration, in order to accurately measure zeta potential. The pH
150 levels of the solutions were then adjusted to cover pH 3-9, at intervals of 1 pH unit. The pH was
151 adjusted using aliquots of either HCl (0.012, 0.12 and 1.2 M) or NaOH (0.019, 0.19 and 1.9 M),
152 while being continuously stirred, until the pH stabilized. Zeta potential analyses were performed
153 using a Malvern Instruments Zetasizer Nano Series instrument. For control measurements, a 10x
154 dilution of 0.56 M NaCl solution without clay minerals was used.

155

156 2.3. Potentiometric titrations

157 Potentiometric titrations of kaolinite, montmorillonite, and illite were conducted using a Man-Tech
158 Associates QC-Titrate autotitrator. The pH electrode was calibrated using commercial pH buffers
159 (Thermo Fisher Scientific; pH 2.0, 3.0, 4.0, 7.0, 10.0) and put into flasks containing the sample
160 slurry along with a magnetic stir bar, titrant dispenser, thermocouple and an Argon (Ar) gas line. For
161 each titration, 0.3 g of clay mineral powder (KGa-2, SWy-2, and IMt-2) was suspended in
162 approximately 35 mL of electrolyte solution (0.56 M NaCl) in a wide-mouth Pyrex beaker (for a
163 final clay mineral powder concentration of approximately 10 g/L), and purged with Ar for 30 min

prior to, and throughout, the titrations to maintain a CO₂-free atmosphere in the flask. Before each titration, the suspension was acidified to pH 3.0 with 2 M HCl, and titrations were then performed alkalimetrically between a pH range of 3.0 to 11.1. The incremental volume of base added, and corresponding pH changes were recorded for each titration step. Each addition of base occurred only after a pH electrode stability of 0.1 mV/s was attained. Titrations were conducted a minimum of five times for each of the clay minerals. Blank titrations were performed for machine calibration, using only the 0.56 M NaCl background solutions. Once a pH of approximately 11 was reached, reverse ‘down-pH’ titrations were performed, decreasing the suspension pH to 3 with aliquots of 0.01 M HCl in order to assess possible hysteresis in the titration curves, a test to ensure the reversibility of the titration process (Duc et al., 2005b).

2.4. Cd adsorption experiments

Batch Cd adsorption experiments were performed under an open atmosphere with initial aqueous Cd concentrations of 8.9×10^{-6} M and 8.9×10^{-7} M; Cd adsorption onto each clay mineral was measured as a function of pH and used to determine adsorption stability constants. To do so, 10 g/L of KGa-2, SWy-2, and IMt-2 were each suspended in a 0.56 M NaCl solution. A 1,000 ppm Cd commercial standard solution (Thermo Fisher Scientific) was diluted in a solution of 0.56 M NaCl to prepare a 100 mg/L stock solution. The Cd-bearing stock solution was acidified to pH 3 to prevent potential Cd precipitation. Aliquots (10 mL) were spiked with Cd and then adjusted to the starting pH (between pH 3-10, in 1 pH unit intervals) using small aliquots of concentrated HCl or NaOH. The test tubes were then placed on a rotary shaker for 24 h. After 24 h, the final pH of each

solution was measured, the solutions were centrifuged at 12,000 g for 15 min to pellet the clay minerals, and the supernatant was decanted and filtered through 0.45 μm membranes. Filtered supernatants were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES).

The concentration of Cd adsorbed to the clay minerals was calculated by difference between the initial and final aqueous Cd concentrations. Control experiments were conducted without clay minerals to determine if Cd adsorbed to the experimental apparatus. The analytical uncertainty of the ICP-OES for measuring Cd at experimental concentrations was determined to be $\pm 2\%$ by repeat analysis of standards.

Cd desorption experiments were conducted for all three clay minerals to test the reversibility of Cd adsorption behavior. Immediately after the adsorption experiments, the Cd-loaded clay pellets were collected and re-suspended in 0.56 M NaCl solutions. The solutions were acidified to pH 3 by the addition 2 M HCl. The suspensions were gently agitated for 24 h, and centrifuged and filtered as previously described. The filtered suspensions were then analyzed for Cd concentration by ICP-OES. The amount of Cd measured was compared to the concentration of Cd adsorbed to calculate the percent of Cd recovered.

3. Model for proton and metal adsorption

SCM have been widely used as an equilibrium-based approach to interpret and predict the protonation and metal adsorption behavior of surfaces such as clay minerals. The SCM approaches previously used for cation adsorption on clay mineral surfaces in single adsorbate systems were

206 predominately non-electrostatic models (NEM), and were conducted at relatively low ionic
207 strengths compared to seawater: kaolinite at ionic strength 0.001 to 0.1 (Huertas et al., 1998); illite
208 at ionic strength 0.01, 0.1 and 0.5 (Bradbury and Baeyens, 2009); and montmorillonite at ionic
209 strength 0.1 (Soltermann et al., 2014). The NEM approach excludes explicit electrostatic terms from
210 the mass law equations for surface equilibria, such that all chemical and electrostatic interactions
211 are implicitly included in the equilibrium constant for each surface reaction (Serrano et al., 2009).
212 Electrostatic surface complexation models have also been used for clays. These models include the
213 constant capacitance model (CCM) for illite, kaolinite, and montmorillonite at ionic strength 0.01 to
214 0.1 (Gu and Evans, 2007, Gu and Evans, 2008 and Gu et al. 2010), diffuse double layer model
215 (DDL) for kaolinite at ionic strength 0.001 to 0.1 (Landry et al., 2009; Schaller et al., 2009; Reich et
216 al., 2010) and montmorillonite at ionic strength 0.01 (Marcussen et al., 2009). In contrast, CCM and
217 other electrostatic double-layer models consider the electrostatic interactions between the ion and
218 the surface, and surface complexes are considered to have a spatial distribution of charge that can be
219 attributed to electrostatic planes (Serrano et al., 2009).

220 In this study, both NEM and CCM surface complexation models were developed using the
221 computer program FITEQL 4.0 (Herbelin and Westall, 1999). The CCM was chosen as it describes
222 proton and metal adsorption at high ionic strength systems (Jara et al., 2005), and the NEM
223 approach was chosen to make a comparison with the results of the CCM approach.

224 Previous research has found two types of adsorption sites on clay mineral surfaces (Lagaly et
225 al., 2006; Gu and Evans, 2008; Liu et al., 2013). One, a permanent negatively charged site ($\equiv X^-$) on
226 basal siloxane surfaces, accounts for cation exchange reactions. The other is the amphoteric site

227 ($\equiv\text{SOH}$) on the clay mineral edges. The amphoteric sites have three protonation states, $-\text{OH}_2^+$, $-\text{OH}$,
 228 and $-\text{O}^-$, whose distribution depend on solution pH, leading to pH-dependent interfacial properties.

229 The permanent negatively charged sites, $\equiv\text{X}^-$, were assumed to be occupied by Na^+ cations
 230 from the background electrolyte, and can undergo the following exchange reaction:

232 The equilibrium constant for reaction (1) was described as:

$$233 \quad K_{\text{XNa}} = \frac{[\equiv\text{X}^- \cdot \text{Na}^+] \cdot a_{\text{H}^+} \cdot \gamma_{\text{H}^+}}{[\equiv\text{X}^- \cdot \text{H}^+] \cdot a_{\text{Na}^+} \cdot \gamma_{\text{Na}^+}} \quad (2)$$

235 The clay mineral edge sites can undergo both protonation and deprotonation reactions, where “S”
 236 can be either Si or Al cations:

239 The equilibrium constants for reactions (3) and (4) were described as:

$$240 \quad K_{(+)} = \frac{[\equiv\text{SOH}_2^+]}{[\equiv\text{SOH}^0] \cdot a_{\text{H}^+} \cdot \gamma_{\text{H}^+}} \exp(-F\psi_{\text{edge}}/RT) \quad (5)$$

$$241 \quad K_{(-)} = \frac{[\equiv\text{SO}^-] \cdot a_{\text{H}^+} \cdot \gamma_{\text{H}^+}}{[\equiv\text{SOH}^0]} \exp(-F\psi_{\text{edge}}/RT) \quad (6)$$

242 In our model, metal adsorption on the basal siloxane surfaces sites of clay minerals occurred
 243 through the following complexation reaction (Gu and Evans, 2007):

245 The Cd-site stability constant for reaction (7) was defined as:

$$K_{X_2Cd} = \frac{[\equiv X_2^- \cdot Cd^{2+}] \cdot [a_{Na^+}]^2 \cdot \gamma_{Na^+}^2}{[\equiv X^- \cdot Na^+]^2 \cdot a_{Cd^{2+}} \cdot \gamma_{Cd^{2+}}} \quad (8)$$

Reactions on the clay mineral edge sites were based on the following hypothesized adsorption reactions:

The Cd-site stability constant for the above reaction was defined as:

$$K_{SOCd^+} = \frac{[\equiv SOCd^+] \cdot a_{H^+} \cdot \gamma_{H^+}}{[\equiv SOH^0] \cdot a_{Cd^{2+}} \cdot \gamma_{Cd^{2+}}} \exp(-F\psi_{edge}/RT) \quad (10)$$

where $\exp(-F\psi_{edge}/RT)$ is the electrostatic term, F the Faraday constant (C/mol), ψ the surface potential (V), R the molar gas constant (C/mol/K), T the absolute temperature (K), and γ the aqueous activity coefficient calculated from the Davies equation (Davies, 1938). The Davies equation was applied because estimated constants using this approximation agree well with measured values in high ionic strength solutions (Millero and Schreiber, 1982; Gao and Mucci, 2001). In all of the equations above, $\psi_{edge} = 0$ for an uncharged edge surface, which was used for the NEM approach (Bourg et al., 2007).

The least square fitting program FITEQL 4.0 (Herbelin and Westall, 1999) was used to model the potentiometric titration data, and solve, for a predetermined number of surface sites, the site acidity constants (expressed as pKa, equivalent to $-\log K_a$) and corresponding site concentrations that best describe the excess charge data. Variance values (V(Y)) of $0.1 < V(Y) < 20$, indicate a good fit to the experimental data (Westall, 1982). The equilibrium constants for surface protonation reactions and site densities determined by modeling the titration data were then used as fixed values

for calculating metal binding constants (K_M) from batch metal adsorption experiments. Calculations also considered six aqueous Cd hydrolysis reactions, three cadmium carbonate complexes (Table 1; Baes and Mesmer, 1976; Stipp et al., 1993), as well as aqueous cadmium chloride complexes (Table 1; Zirino and Yamamoto, 1972). The aqueous equilibrium constants of all these metal complexes were adjusted to 0.56 M ionic strength using the Davies equation (Davies, 1938). All the parameters and surface reaction used in modeling the Cd adsorption to individual clay mineral are shown in Table 1. The double-layer capacitance (C/m^2) is an experimentally accessible quantity only, based on N_2 adsorption onto a strictly water-free clay mineral (James and Parks, 1982; Stadler and Schindler, 1993). Therefore, it is reasonable to use capacitance as a flexible parameter to minimize the given error. In this study, a range of capacitance values were used from previous studies, and a good fit value was obtained from Srivastava et al. (2005), Ikhsan et al. (2005), and Gu and Evans (2007) for kaolinite, montmorillonite and illite, respectively.

4. Results

4.1. Zeta potential

The surface area (determined through N_2 adsorption) and cation exchange capacity (CEC) of each of the clay minerals, provided by the CMS, were: $23.50 \pm 0.06 \text{ m}^2/\text{g}$ and $3.3 \text{ meq}/100 \text{ g}$ for kaolinite (KGa-2), and $31.82 \pm 0.22 \text{ m}^2/\text{g}$ and $76.4 \text{ meq}/100 \text{ g}$ for montmorillonite (SWy-2) (CMS), and $45 \text{ m}^2/\text{g}$ and $27 \text{ meq}/100\text{g}$ for illite (IMt-2), respectively (Kriaa et al., 2009).

The surface charges of kaolinite (KGa-2), montmorillonite (SWy-2), and illite (IMt-2) were measured as a function of pH (Fig. 1). All three types of clay minerals exhibited an increasingly

negative surface charge with increasing pH. Montmorillonite was the most anionic over the entire pH range studied, followed by illite and then kaolinite. This order was in accordance with the CEC of the three clay minerals as provided by the CMS (e.g., 76.4 meq/100 g for montmorillonite; 27 meq/100 g for illite; 3.3 meq/100 g for kaolinite; Ikhsan et al., 2005; Kriaa et al., 2009). The zeta potentials of montmorillonite and illite showed only slight increases in negative charge when the pH was increased from 3 to 9, with values ranging from -40 to -47 mV and -30 to -42 mV, respectively. In contrast, the zeta potential for kaolinite showed a strong increase in the negative charge from 0 to -33 mV over the same pH range.

4.2. Potentiometric titrations

Fig. 2 shows potentiometric titration data obtained over the pH range of 3 to 11 in solutions of 0.56 M NaCl for kaolinite, montmorillonite and illite. Only data from pH 4 to 10 were used to model the excess charge (in millimoles per gram of clay mineral powder) due to a combination of uncertainty in electrode calibration and errors in the calculated values for H^+ or OH^- consumed at the extreme ends of the pH range (Baeyens and Bradbury, 1997; Smith et al., 1999; Lalonde et al., 2008). Additionally, pH 4-10 brackets most relevant aqueous environments, including seawater. In Fig. 2, the slope at any given point can be interpreted as the instantaneous buffering capacity for the clay mineral. In other words, the slope indicates the consumption of protons in millimoles per unit of pH. The alkalimetric (forward) and acidimetric (reverse) titrations for all three types of clay minerals did not exhibit significant differences (Fig. S1), implying that reversibility of the proton adsorption/desorption reactions on the clay minerals occurs within the timescale of the experiments,

and that the titration process did not irreversibly damage the clay minerals.

A two-site NEM model, including one basal siloxane surface site ($\equiv X^-$) and one amphoteric edge site ($\equiv SOH$), provided excellent fits to the titration data of all three clay minerals. The best-fit values for the surface acidity constants and corresponding site densities are summarized in Table 1. The fit data showed that the $\equiv X^-$ and $\equiv SO^-/\equiv SOH_2^+$ groups of kaolinite have pK_a values of 4.15 ± 0.02 and $8.67 \pm 0.13/-6.49 \pm 0.68$, those of montmorillonite are 2.15 ± 0.35 and $8.57 \pm 0.01/-5.17 \pm 0.10$, and those of illite are 3.74 ± 0.11 and $8.68 \pm 0.14/-5.91 \pm 0.19$, respectively. A summation of the concentration of surface sites across the analyzed pH range revealed that the clay mineral powders have averages of 0.95 ± 0.05 , 1.90 ± 0.23 , and 0.60 ± 0.08 mmol/g (dry weight) for kaolinite, montmorillonite and illite, respectively. Montmorillonite possessed higher densities of both $\equiv X^-$ and $\equiv SOH$ sites, followed by kaolinite and illite (Fig. S2), consistent with the fact that swelling clay minerals, such as montmorillonite, have higher cation exchange capacities. In addition, all three clay minerals possessed higher densities of $\equiv X^-$ than $\equiv SOH$ sites.

The NEM describes ion adsorption while excluding electrostatic terms from the mass law equations for surface equilibria, making it a less parameterized model for the interpretation of surface reactivity. To describe the effects of electrostatic forces, we also used a CCM, whereby the electric double layer at the clay mineral/water interface was assumed to be a flat capacitor and all the surface complexes are inner-sphere complexes (Gu et al., 2010). CCM using FITEQL was successful when two sites (including one basal siloxane surface site, $\equiv X^-$, and one amphoteric edge site, $\equiv SOH$) were considered. As shown in Table 1, the electrostatic term (CCM) had an impact on the calculated pK_a values of the surface species $\equiv X^-$, $\equiv SO^-$ and SOH_2^+ for all three clay minerals.

Meanwhile, site densities of both $\equiv X^-$ and $\equiv SOH$ obtained by the CCM were in agreement with the results obtained using the NEM for kaolinite and illite, while site densities of $\equiv SOH$ obtained by CCM for montmorillonite were higher than the values obtained by NEM.

4.3. Cd adsorption

4.3.1. Kaolinite

The adsorption of Cd onto 10 g/L kaolinite in solutions of 0.56 M NaCl is shown as a function of pH for the 8.9×10^{-7} M and 8.9×10^{-6} M Cd experiments (Fig. 3A). In all experiments with kaolinite (both low and high Cd concentration), Cd adsorption increased with increasing pH from 3 to 8.5 (data above pH 8.5 were not considered reliable as appreciable loss of Cd due to the precipitation of cadmium carbonate solids was apparent at higher pH levels; Fig. 3 and S4), and less than 10% of Cd was observed to be removed below pH 6.5. Above pH 6.5, increased Cd adsorption was observed, with 60% of the total Cd removed at pH 8.5.

Experimental Cd adsorption data were modeled by both NEM and CCM, using the site concentrations and acidity constants calculated from the potentiometric titrations. In experiments with a low initial Cd concentration (8.9×10^{-7} M), an excellent fit was achieved when just one amphoteric site and aqueous Cd chloride complexes were considered using the NEM approach (see Table 1 and Fig. 3). At the higher Cd concentration (8.9×10^{-6} M), it was necessary to invoke both basal siloxane surface sites $\equiv X^-$ and amphoteric edge sites $\equiv SOH$ to explain the observed Cd adsorption behavior by the NEM approach; the Cd-site stability constants are shown in Table 1. When using the CCM approach, the inclusion of both basal siloxane surface sites ($\equiv X^-$) and

amphoteric edge sites ($\equiv\text{SOH}$) were necessary to explain the observed Cd adsorption behavior at across the Cd range examined (8.9×10^{-7} to 8.9×10^{-6} M); the best-fit metal binding constants are shown in Table 1.

4.3.2. Montmorillonite

Fig. 3B shows the adsorption edge of Cd onto 10 g/L montmorillonite in 0.56 M NaCl for the 8.9×10^{-7} M and 8.9×10^{-6} M Cd experiments. Cd adsorption was minimal below pH 5, but increased to 15% in the pH range of 5-7, and then followed with a steeper increase in adsorption to pH 8.5, at which point approximately 60% of Cd was adsorbed.

A two-site metal adsorption model (both NEM and CCM), which included the permanently charged surface site $\equiv\text{X}^-$ from basal siloxane surfaces and one variably charged $\equiv\text{SO}^-$ site from amphoteric edge sites, was used to predict the relative proportions of each of these sites in the adsorption of Cd onto montmorillonite. Invoking two adsorbed surface species, $\equiv\text{XCd}^+$ and $\equiv\text{SOCd}^+$, resulted in a good fit to the batch adsorption data (Fig. 3A). The best-fit metal binding constants are shown in Table 1. The electrostatic term had a major impact on the Cd-site stability constant (as $\log K_{\text{Cd}}$) values, especially for the low Cd concentrations ($<8.9\times 10^{-7}$ M).

4.3.3. Illite

The adsorption behavior of Cd onto illite for the 8.9×10^{-7} M and 8.9×10^{-6} M Cd experiments is shown in Fig. 3C. Two phases of adsorption are observed in the adsorption edge. Below pH 4.5, almost no Cd was adsorbed, while above pH 4.5 the degree of adsorption increased to 55% at pH

8.5. For both the low Cd concentration (8.9×10^{-7} M) and high Cd concentration (8.9×10^{-6} M), either a two-site NEM or a CCM, which included both $\equiv X^-$ and $\equiv SO^-$ sites, provided an excellent fit (Fig. 3C) for the data. The corresponding Cd-site stability constants (as $\log K_{Cd}$) are shown in Table 1. A hypothesis is that CCM might better account for changes in ionic strength by adjusting the extent of the surface electric field; however, Cd adsorption behavior at more than one ionic strength would need to be tested to confirm this hypothesis.

4.4. Cd desorption

Over 90% of the adsorbed Cd was found to desorb from each of the clays (Fig. 3, open symbols). The remaining 10% may be attributed to losing a small amount of mass during the adsorption/desorption cycle. The desorption experiments suggest that the primary mechanism of metal removal from solution is reversible adsorption to clay mineral surfaces.

5. Discussion

Both the NEM and CCM protonation models provide good fits for the experimental titration data (Fig. 2). Majone et al. (1996) and Huertas et al. (1998) obtained similar results using kaolinite, with and without the inclusion of the electrostatic term in the surface model. The advantage of the NEM with respect to the CCM was its simpler mathematical formulation, which may be critical if the overall surface behaves like a multi-site one.

Experimental results and theoretical calculations from Bourg et al. (2007) and Liu et al. (2013) suggest that there are four functional groups associated with clay minerals: aluminol ($\equiv Al-OH_n$),

silanol ($\equiv\text{Si-OH}_n$), silica-alumina bridging ($\equiv\text{SiAl-OH}_n$), and alumina-alumina bridging ($\equiv\text{Al}_2\text{-OH}_n$). There are also free unbonded $-\text{O}$, $-\text{OH}$ or $-\text{OH}_2$ groups on the edge surfaces. For simplicity, we make no distinction between surface hydroxyl groups, so the constants calculated for $\equiv\text{SOH}$ sites represent an average contribution of amphoteric aluminol and silanol groups on the clay mineral edges.

The density of surface sites available for protonation and deprotonation reactions on our kaolinite and montmorillonite samples are higher in this study than those that have been previously reported (Table 2). For example, Schroth and Sposito (1996), Angove et al. (1997), and Gu and Evans (2008) reported that kaolinite possesses no more than 0.05 mmol/g of $\equiv\text{X}^-$ sites or $\equiv\text{SOH}$ sites $< \text{pH } 9$, while Srivastava et al. (2005) found that kaolinite has approximately 0.10 mmol/g of $\equiv\text{SOH}$ sites $< \text{pH } 10$. Our kaolinite sample had approximately an order of magnitude more $\equiv\text{X}^-$ sites and $\equiv\text{SOH}$ sites. For montmorillonite, Ikhsan et al. (2005) reported 0.39 mmol/g of $\equiv\text{X}^-$ sites and 0.06 mmol/g of $\equiv\text{SOH}$ sites within the pH range 4 to 9.5; while Stadler and Schindler (1993) and Gu et al. (2010) observed 0.60-0.71 mmol/g of $\equiv\text{X}^-$ sites and 0.20-0.35 mmol/g of $\equiv\text{SOH}$ sites at $< \text{pH } 9$. These values are lower than our experimental results of 1.02-1.07 mmol/g of $\equiv\text{X}^-$ sites and 0.88-1.39 mmol/g of $\equiv\text{SOH}$ sites. For illite, both $\equiv\text{X}^-$ sites and $\equiv\text{SOH}$ site densities are comparable to the previous findings of 0.06-0.54 mmol/g of $\equiv\text{X}^-$ sites and 0.05-0.41 mmol/g of $\equiv\text{SOH}$ sites within a similar pH range to the one used in this study for three types of illite samples (Kriaa et al., 2009). We suggest that the differences in the site density for kaolinite and montmorillonite are likely best explained by differences in titration conditions, i.e., most previous research conducted acid-base titrations at lower ionic strength solutions (less than 0.1 M). We chose high ionic strength

for our experiments because we were interested in addressing conditions relevant to estuarine and open marine environments. Nonetheless, the values for protonation constants (pK_a values) obtained from surface complexation models are similar in magnitude to those found by previous research (Table 2) (Angove et al., 1997; Srivastava et al., 2005; Gu and Evans, 2007 & 2008; Kriaa et al., 2009; Gu et al., 2010). The widespread distribution of the pK_a values might be due to the inclusion of only two types of adsorption site (basal siloxane surface site $\equiv\text{X}^-$ and amphoteric edge site $\equiv\text{SOH}$) that does not account for the heterogeneity in clay minerals and is, therefore, an oversimplification of the system (Schindler et al., 1987; Angove et al., 1997).

Collectively, our results show that clay minerals display an overall net negative charge at the pH of seawater (*ca.* 8), but the degree of negative charge depends on the intrinsic structure of the clay mineral. 2:1 type clay minerals, such as montmorillonite and illite, in which an octahedral sheet is sandwiched between two tetrahedral sheets, have vastly greater surface areas than do 1:1 clay minerals, such as kaolinite. Further, the interlayer cations in 2:1 clays (i.e., K⁺, Al³⁺, Mg²⁺) give rise to isomorphic substitution and higher cation exchange capacity. Conversely, 1:1 type clay minerals, such as kaolinite, have almost no substitution of interlayer cations, and the unit layers are held tightly together as a result of hydrogen bonding. Therefore, the net negative charge is lower and the cation-binding characteristics are weaker than those of 2:1 clays.

Differences in the net surface charge of the three clay minerals translate into different metal adsorption capacities. For instance, we determined that 10 g montmorillonite, illite and kaolinite (containing 2.46, 0.63, and 1.01 mmol/g of edge sites from CCM, respectively) can bind an equivalent of 4.7×10^{-4} g, 4.3×10^{-4} g, and 4.0×10^{-4} g of Cd (from an initial Cd concentration of

434 8.9×10^{-6} M, 0.56 M NaCl electrolyte solution and pH=8), respectively. Illite shows greater Cd
435 adsorption capacity than kaolinite, which may due to the greater CEC of illite, or isomorphous
436 substitution within tetrahedral sheets on the basal faces for illite (Beene et al., 1991; Garnham et al.,
437 1993).

438 Irrespective of the clay mineral, adsorption of Cd varied with pH. Our results indicated that Cd
439 adsorbs onto all three types of clay minerals in two distinct phases: (1) at pH less than 7, adsorption
440 occurs via cation exchange onto permanent charge sites on basal siloxane surfaces; and (2) at higher
441 pH, adsorption occurs on amphoteric edge sites. This observation correlates well with previous
442 studies; for example, Lackovic et al. (2003) found that the adsorption of Cd onto kaolinite was best
443 modeled by the outer-sphere complexation of Cd onto two $\equiv X^-$ sites on the siloxane faces
444 ($\equiv X_2^{2-} - Cd^{2+}$) at lower pH and bidentate inner-sphere complexation onto $\equiv SOH$ edge sites
445 ($\equiv (SO)_2Cd^0$) above pH 7.5. Marcussen et al. (2009) suggested that the adsorption of Ni to
446 montmorillonite at pH < 6.6 is nonspecific via a permanent negatively charged surface site, while at
447 pH > 6.6, the degree of Ni adsorption increased with increasing pH, which is typical for specific
448 adsorption to hydrous oxide surfaces. Gu and Evans (2007) modeled metal adsorption onto illite
449 with three surface binding sites ($\equiv X_2^- \cdot Cd^{2+}$, $\equiv X^- \cdot CdOH^+$, $\equiv SOCd^+$), and observed that $\equiv X^-$ is
450 the main negatively charged adsorption site between pH 3 to 7. The edge species $\equiv SO^-$ did not
451 become the predominant metal adsorption site until pH > 7 at an ionic strength of 0.1.

452 In our study, the speciation diagrams for Cd adsorption onto all three clay minerals (Fig. S5-S8)
453 showed that $\equiv XCd^+$ was the dominant Cd binding coordination between pH 3 to 6. The difference in
454 the extent of Cd adsorption between kaolinite, montmorillonite and illite might result from cation

exchange on the interlayer sites. This hypothesis is supported by the effects of the cation exchange capacity of the three clay minerals (shown above), the strong competition by Na^+ , and the relative inaccessibility of some interlayer sites make many exchange sites unavailable for Cd adsorption under the conditions of these experiments. Below pH 6, the adsorption edge for the Cd – kaolinite system is different from those of montmorillonite and illite, with adsorption increasing steadily. However, above pH 6, Cd adsorption was lower onto kaolinite and illite than montmorillonite.

If only Cd adsorption was taken into account at a single ionic strength, the electrostatic effects could be neglected with no practical difference in the calculated behavior (Majone et al., 1996). This is primarily due to the fact that the diffuse and intermediate potentials are slightly dependent on pH and Cd concentration so that the electrostatic effect is small (Majone et al., 1996). In the electrostatic model, the residual negative charge at the surface, due to the free forms $\equiv\text{SO}^-$ and $\equiv\text{X}^-$, is counterbalanced by the positive charge due to the sodium adsorption in the diffuse layer.

Considering the widespread distribution of clay minerals in marginal marine settings, it is easy to imagine that clay minerals could serve as a significant sink for trace metals. For instance, assuming 1 g of clay mineral is composed of approximately 45% kaolinite, 45% illite, and 10% montmorillonite (Stein et al., 1994; Gingeles et al., 2001), then a simple extrapolation suggests that 4.2×10^{-5} g $((1 \text{ g} \times 45\% \times 3.6 \times 10^{-6} \times (1/10) \text{ M} + 1 \text{ g} \times 45\% \times 3.8 \times 10^{-6} \times (1/10) \text{ M} + 1 \text{ g} \times 10\% \times 4.2 \times 10^{-6} \times (1/10) \text{ M}) \times 112.41)$ of Cd could potentially be bound to their surfaces. Of course, the mass is just an estimate because variations in clay mineral supply are dependent on landmass lithology, and as such, different coastal sediments will have different clay mineral assemblages (Stein et al., 1994; Gingeles et al., 2001).

476 Considering the total suspended sediment delivered by all rivers to the oceans annually (e.g.
477 13.5×10^9 tons; Milliman and Meade, 1983), of which 10 to 25% is clay (Manheim et al., 1970;
478 Schroeder et al., 2015), the total amount of Cd adsorbed to suspended clay minerals in the modern
479 oceans could amount to around 10^4 to 10^5 tons per year. This back-of-the-envelope calculation is not
480 meant to be an exact quantification because additional considerations would need to be included,
481 such as: (1) clay minerals will adsorb other metal cations due to competitive binding, (2) dissolved
482 Cd will be complexed by dissolved organic ligands (Byrne et al., 1988), and (3) some fraction of Cd
483 would be expected to precipitate as Cd carbonate minerals at seawater pH (Stipp et al., 1993). The
484 latter case was observed in our Cd precipitation control experiments. Nonetheless, our calculations
485 do point to the potential importance that clay minerals may play in the oceans with regards to trace
486 metal fluxes to the seafloor.

487 When reconstructing Cd behavior in oceans, it is generally accepted that the mobilization of
488 metals from particulate matter occurs when river-water mixes with seawater. For example,
489 Elbaz-Poulichet et al. (1987) found that the dissolved Cd concentrations in various estuaries display
490 a systematic increase in the mixing zone, which the authors suggested was caused by the increasing
491 ionic strength, a process enhanced by the remobilization of trace metals via resuspension of
492 particulate matter in the mixing zone. Thus, the issue of determining what fraction of the clay
493 mineral-bound Cd reaches the seafloor and measuring the clay mineral sedimentation rates needs to
494 be resolved.

495 Importantly, although most clay is deposited in estuaries and deltas, wave-induced resuspension,
496 and hypopycnal plumes associated with episodes of high fluvial outflow are capable of transporting

fine-grained sediment for tens of km offshore. Also, deltas tend to over-steepen and collapse giving rise to offshore-directed sediment-gravity flows that can travel hundreds of km. The variable ionic strength of the depositional waters associated with these processes and changing ionic strengths associated with sediment gravity flows suggest that the patterns of Cd storage associated with clay minerals is complex but potentially tractable.

Clay minerals bind significant concentrations of metals and may be ultimately an important contributor to trace metal deposition in shallow-marine environments. In this study, we used Cd as a proxy for divalent metals in the seawater column that may be bound to clay minerals at seawater relevant ionic strength. Future efforts will be needed experimentally determine if the adsorption of other trace metals onto both individual clay minerals, composites of clay minerals, and clay mineral-microorganism composites at seawater ionic strength, to constrain the role of micron-sized particles in the water column on trace metals deposition in marine settings.

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686 Fig. 1. Zeta potential measurements of kaolinite (filled diamonds), montmorillonite (filled triangles)
687 and illite (filled circles) exposed to 0.56 M NaCl as a function of pH. Error bars represent the
688 ± 1 -sigma standard deviation of 6 different runs, and the data are highly reproducible.

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Fig. 2. Titration curves of Na-saturated clay minerals (10 g/L, in the presence of 0.56 M NaCl solution): (A) kaolinite; (B) montmorillonite; (C) illite. Filled symbols are experimental data from alkalimetrically titrations, red lines are NEM, and black lines are CCM calculates using the

714 parameters given in Table 1.

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718 Fig. 3. Adsorption edges for 8.9×10^{-6} M (1 ppm) and 8.9×10^{-7} M (0.1 ppm) Cd^{2+} exposed in a 0.56
719 M NaCl ionic strength solution with 10 g/L of clay minerals: (A) Kaolinite; (B) Montmorillonite; (C)

720 Illite. Filled symbols represent adsorption data. Open symbols represent desorption data. Solid lines
721 represent best-fit models (red for NEM and black for CCM) of 8.9×10^{-6} M Cd adsorption data to the
722 clay minerals, while dashed lines represent best-fit models (red for NEM and black for CCM) of
723 8.9×10^{-7} M Cd adsorption data. Grey lines represent blank adsorption without any sorbent
724 (precipitation depends on pH).

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