Surface complexation of heavy metal cations on clay edges: insights from first principles molecular dynamics simulation of Ni(II)

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Abstract

Aiming at an atomistic mechanism of heavy metal cation complexing on clay surfaces, we carried out systematic first principles molecular dynamics (FPMD) simulations to investigate the structures, free energies and acidity constants of Ni(II) complexes formed on edge surfaces of 2:1 phyllosilicates. Three representative complexes were studied, including monodentate complex on the $\equiv\text{SiO}$ site, bidentate complex on the $\equiv\text{Al}(\text{OH})_2$ site, and tetradentate complex on the octahedral vacancy where Ni(II) fits well into the lattice. The complexes structures were characterized in detail. Computed free energy values indicate that the tetradentate complex is significantly more stable than the other two. The calculated acidity constants indicate that the tetradentate complex can get deprotonated ($\text{pK}_a=8.4$) at the ambient conditions whereas the other two hardly deprotonate due to extremely high pK_a values. By comparing with the 2 Site Protolysis Non Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) model, the vacant site has been assigned to the strong site and the other two to the weak site, respectively. Thus a link has been built between atomistic simulations and macroscopic experiments and it is deduced that this should also apply to other heavy metal cations based on additional simulations of Co(II) and Cu(II) and previous simulations of Fe(II) and Cd(II)). This study forms a physical basis for understanding the transport and fixation of heavy metal elements in many geologic environments.

31 2:1-type clay minerals play important roles in the migration and retardation of heavy metal
32 elements and nuclides in nature (Bergaya and Lagaly, 2013; Evans, 1989; Sposito and
33 Greathouse, 1999). Because of their high adsorptive capacity, low cost, and chemical stability,
34 clay materials are extensively used in environmental engineering for removal of heavy metal
35 pollutants and are considered as efficient barrier materials in nuclear waste repositories for
36 retardation of radionuclides (Wagner, 2013; Yuan et al., 2013). Therefore, the molecular-scale
37 adsorption mechanism of heavy metal cations on clay minerals is crucial for understanding the
38 relevant interface geochemistry and developing efficient environmental materials.

39 A large number of batch sorption experiments have shown that the sorption of divalent heavy
40 metal cations, such as Ni(II), Zn(II), Cu(II), Co(II), Pb(II), and Cd(II) on 2:1 type phyllosilicates
41 consists of two processes (Baeyens and Bradbury, 1997; Barbier et al., 2000; Bradbury and
42 Baeyens, 2005a; Gupta and Bhattacharyya, 2006; Ikhsan et al., 2005; Jaisi et al., 2008; Stadler
43 and Schindler, 1993; Zachara et al., 1993). At low pH (e.g., 3~6 for Cd(II), Cu(II), Ni(II) and
44 Zn(II)) (Gu et al., 2010), cation exchange on the permanently charged basal/interlayer surfaces is
45 responsible for the adsorption, which is dependent on the layer charge density; at higher pH,
46 surface complexation on the variably charged edge surfaces is the major adsorption pattern and
47 this stage is greatly pH dependent (Abollino et al., 2008; Bourg et al., 2007; Gu et al., 2010;
48 Peacock and Sherman, 2005; Tan et al., 2010; Tournassat et al., 2013). In the past two decades,
49 the 2SPNE SC/EC (i.e., 2 site protolysis non electrostatic surface complexation and cation
50 exchange) model has been extensively and successfully applied to characterize the sorption of
51 many metal cations (e.g., Ni(II), Zn(II), Cd(II), Fe(II), Eu(III), Cm(III)) on 2:1-type clay
52 minerals (Baeyens and Bradbury, 1997; Bradbury and Baeyens, 1997, 1999, 2005a, b; Bradbury

et al., 2005; Soltermann et al., 2014; Soltermann et al., 2013). For the complexation on edge surface, in the modelling of sorption isotherm, two types of edge sites have been used to fit the adsorption data, commonly referred to be the strong site (S^{SOH}) and the weak site (S^{W^1OH}) (Baeyens and Bradbury, 1997). The strong site has a high binding affinity and a low site capacity (2 mmol/kg), while the weak site has a lower affinity and a higher site capacity (40 mmol/kg) (Baeyens and Bradbury, 1997).

Advanced spectroscopic methods have been broadly used to derive possible complexing sites for heavy metal cations. For example, Schlegel et al. (1999) investigated the sorption of Co(II) on edge surfaces of hectorite by polarized EXAFS (extended X-ray absorption fine structure) technique and found the formation of mononuclear complexes (Schlegel et al., 1999). EXAFS study indicated that Ni(II) formed inner-sphere mononuclear complexes at montmorillonite edges via corner-sharing pattern between Si tetrahedra and Ni(II) octahedra and edge-sharing pattern between Al octahedra and Ni(II) octahedra (Dähn et al., 2003). By modelling Zn(II) sorption isotherm with the 2SPNE SC/EC model and measuring EXAFS spectra, Dähn et al. have demonstrated the existence of two types of edge complexing sites, which agrees with the concept of the strong/weak site (Dähn et al., 2011). Atomistic simulations and measured EXAFS spectra suggested that Zn(II) was incorporated into the octahedra on clay edges at low loading and formed inner-sphere complexes on octahedral sites at medium loading (Churakov and Dähn, 2012). Schlegel and Manceau (2013) reported that Cu(II) formed inner-sphere complexes via the edge- and corner-sharing linkages in the continuity of octahedral and tetrahedral sheets, respectively (Schlegel and Manceau, 2013). To date, what the strong and weak site refer to and their complexing structures and protonation states are still unclear. It is hard to establish a direct link between spectroscopic results and the 2SPNE SC/EC model.

Atomistic simulations have been proven powerful techniques to investigate the mineral-water interfaces (Alexandrov and Rosso, 2013; Boily, 2012; Cygan et al., 2009; Cygan et al., 2004; Greathouse et al., 2015; Greathouse et al., 2000; Greenwell et al., 2006; Kalinichev et al., 2007; Kwon and Newton, 2016; Leung and Criscenti, 2012; Newton et al., 2016; Rustad et al., 2003; Wang et al., 2005; Watts et al., 2014). As a state-of-the-art technique, first principles molecular dynamics (FPMD) simulation can accurately describe microscopic processes and reactive events (Car and Parrinello, 1985; Marx and Hutter, 2009; VandeVondele et al., 2005a) and it has been broadly applied to explore the interfacial properties of clay minerals (Arumugam and Becker, 2014; Boek and Sprik, 2003; Churakov, 2007; Kosakowski and Georg, 2010; Liu et al., 2012b; Liu et al., 2012c; Rosso et al., 2001; Suter et al., 2008; Suter et al., 2015; Suter et al., 2012; Tunega et al., 2002). In recent years, the FPMD-based vertical energy gap method for pKa calculations has been developed (Costanzo et al., 2011; Sulpizi and Sprik, 2008) and successfully applied in acidity estimates of functional groups on surfaces of layered minerals (Liu et al., 2013a; Liu et al., 2015; Liu et al., 2013b; Tazi et al., 2012). For 2:1 type clay minerals, previous pKa calculations have indicated that $\equiv\text{SiOH}$, $\equiv\text{Al}(\text{OH})_2$, and the octahedral vacancy are the major complexing sites for heavy metal cations (Liu et al., 2014; Liu et al., 2013b; Tazi et al., 2012). The common isomorphic substitutions, i.e. $\equiv\text{AlOH}$ on the tetrahedral sheet and $\equiv\text{MgOH}_2$ on the octahedral sheet, have too high pKa values (15.1 for $\equiv\text{AlOH}$ and 13.2 for $\equiv\text{MgOH}_2$ on (010) edge) (Liu et al., 2014; Liu et al., 2013b). These sites are protonated at ambient condition and therefore are not effective complexing sites. To the best of our knowledge, the FPMD simulations of complexation of cations on clay edges are very scarce (Churakov and Dähn, 2012; Liu et al., 2012a). For instance, Liu et al. (2014) investigated the inner-sphere complexations of Fe(II) on clay edges with FPMD simulations, and the corresponding complexing structures were

obtained. Recently, we employed FPMD simulations about Cd(II) complexes adsorbed on edge surfaces of 2:1 phyllosilicates; the complexing structures and free energies were derived (Zhang et al., 2016). It has shown that the free energy of tetradentate complex on the vacant site is significantly higher than those of monodentate complex on the $\equiv\text{SiO}$ and bidentate complex on the $\equiv\text{Al}(\text{OH})_2$ site. Thus we assigned the vacant site to strong site and the other two to weak site in the 2SPNE SC/EC model. However, the complexing mechanisms for other heavy metal cations are still lacking.

Nickel (Ni) is a widespread toxic transition metal, and ^{63}Ni is one important radioactive nuclide generated from nuclear fuels by fission. Furthermore, Ni(II) can be taken as a chemical analogue for other divalent heavy metal cations (e.g., Cu(II), Zn(II), Co(II), and Fe(II)) because of their identical valence and similar ionic sizes. Therefore it attracts significant attention in environmental sciences and geochemistry (Bradbury and Baeyens, 1999; Hummel and Curti, 2003; Marcussen et al., 2009; Peltier et al., 2010; Ren et al., 2013; Roberts et al., 1999; Scheidegger et al., 1996a; Scheidegger et al., 1996b; Yang et al., 2015).

In the present study, systematic FPMD simulations were conducted for a molecular level understanding of complexing mechanism of heavy metal cations on clay edges by selecting Ni(II) as the model cation. The simulations indicate that stable complexes can form on the three sites: monodentate complex on the $\equiv\text{SiO}$, bidentate complex on the $\equiv\text{Al}(\text{OH})_2$, and tetradentate complex on the vacant site. The calculated desorption free energies show that the octahedral vacancy is the most favorable complexing site where Ni(II) is embedded into the lattice. According to the concepts in the 2SPNE SC/EC sorption model, the vacant site is assigned to the strong site and the other two to the weak site. pKa values of surface complexes were calculated to reveal the protonation states. FPMD simulations were also carried out for complexes of Co(II)

and Cu(II) adsorbed on the vacant site. By integrating these complexes with those investigated previously (including Fe(II) and Cd(II)), we suggest that the assignment of surface sites should be applicable to other divalent heavy metal cations and other clay minerals. This study builds a direct link between atomistic simulations and macroscopic experiments, and the implication for geochemistry and environmental sciences has been discussed. .

2. METHOD

2.1. Models

Several studies have confirmed that (010) and (110) facets are the major edges of dioctahedral clays (Hartman and Perdok, 1955a, b, c; White and Zelazny, 1988). In this study, (010) edge surface was taken as the model surface to investigate the structures, free energies, and pKa values of Ni(II) complexes. The structures of Ni(II) complexes adsorbed on the (110) surface were also simulated. The surface model was taken from our previous studies (Liu et al., 2012b; Liu et al., 2013b) built on the basis of structural data in Viani et al (Viani et al., 2002). No isomorphic substitution was included. There are two unit cells contained in this model (Figure 1). All models were placed in 3D periodically repeated orthorhombic boxes with a solution region of 15 Å. 45 water molecules were inserted in the solution region (Figure 1), and this approximately reproduced the density of bulk water at the ambient conditions.

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140 Figure 1. The used models for Ni(II) complexing on (010) edge surface. These snapshots are
 141 derived from simulations. A: $\equiv\text{SiO}$ site; B: $\equiv\text{Al}(\text{OH})_2$ site; and C: vacant site. Cations are shown
 142 as balls; solid parts and water molecules are shown as sticks. O = red, H = white, Al = purple, Si
 143 = yellow, and Ni = blue.

144 Our previous study has shown that for Al(III) cations at (010) edge surface of 2:1
 145 phyllosilicates, both 5- and 6-fold coordination states are possible and the latter one is more
 146 stable (Liu et al., 2012b). In the present study, all the edge Al(III) were assumed to be 6-fold
 147 coordinated. Three edge complexing sites were studied, i.e., $\equiv\text{SiO}$, $\equiv\text{Al}(\text{OH})_2$, and the outermost
 148 octahedral vacant site. For the investigated Ni(II) complexes, each binding group was initially
 149 deprotonated (i.e. $\equiv\text{SiO}$, $\equiv\text{AlOH}$, and O_{apical}). The stoichiometry of each simulated box for Ni(II)

complex was $\text{Al}_8\text{Si}_{16}\text{O}_{56}\text{H}_{23}\cdot\text{Ni}\cdot(\text{H}_2\text{O})_{45}$ and the charge was +1. In CP2K/QUICKSTEP code (VandeVondele et al., 2005a), a background charge was added to neutralize the net charge. Because of the 6-fold coordination of Ni(II) in aqueous solution (Neilson and Enderby, 1978; Ohtaki and Radnai, 1993), different numbers of water ligands were placed as the initial configurations: $\equiv\text{SiO}-\text{Ni}(\text{H}_2\text{O})_5$, $\equiv\text{Al}(\text{OH})_2-\text{Ni}(\text{H}_2\text{O})_4$, and $(\equiv\text{O}_{\text{apical}})_2(\equiv\text{AlOH})_2-\text{Ni}(\text{H}_2\text{O})_2$, respectively.

For the five water ligands of $\equiv\text{SiO}-\text{Ni}(\text{H}_2\text{O})_5$, the rightmost one is separated from the surface by Ni(II) (denoted as “outer” in Figure 2A) and the other four are equivalent (denoted as “inner” in Figure 2A). For the bidentate complex, the four water ligands can be divided into two types (denoted as “outer” and “inner” respectively in Figure 2B). For each type, the two ligands are reasonably presumed to have the same pKa value. For the complex on the outermost vacant octahedron, the two OH₂ ligands should be equivalent (denoted as $\text{Ni}(\text{H}_2\text{O})^{\text{V}}$).

To validate our computational setup, the pKa of Ni(II) aqua cation (i.e. $\text{Ni}(\text{H}_2\text{O})_6^{2+}$) was also calculated. The cell used is a cubic periodic box of a side length of 9.86 Å, which contains a $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and 26 solvent water molecules.

2.2. First principles MD

The CP2K/QUICKSTEP simulation package (VandeVondele et al., 2005a) was used to carry out all FPMD calculations. In this package, the implementation of DFT (density functional theory) electronic structure calculations was achieved by combining a Gaussian basis set with an auxiliary plane wave (GPW) (Lippert et al., 1997). The PBE functional (Perdew et al., 1996) was applied and Goedecker-Teter-Hutter pseudopotentials (Goedecker et al., 1996) were used to calculate the interactions between core and valence states. DZVP basis sets were employed for

all elements. The cutoff for electron density was set to be 280 Ry. Spin polarization calculations were performed with the high-spin states of Ni(II), Co(II), and Cu(II). Previous study has shown that both GGA and the hybrid functional can describe the structures of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ well (Mares et al., 2011). PBE and B3LYP (Becke, 1993; Lee et al., 1988) produced the same Ni-O bond (2.086 Å) in vacuo and very similar Ni-O bonds in COSMO solvation models (2.076 VS. 2.074 Å), which agree well with experiments (2.05~2.10 Å) (Mares et al., 2011). By using PBE (Perdew et al., 1996) and the hybrid functional HSE06 (Heyd et al., 2003; Krukau et al., 2006), we calculated the binding energies with small clusters (i.e., $\text{Ni}(\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O} \rightarrow \text{Ni}(\text{H}_2\text{O})_6^{2+}$). The results showed that the two functionals give very similar structures and binding energies (see the Electronic Annex for details). Furthermore, the accurate prediction of pKa in our study (10.4 VS. the experimental range 9.86-10.5, see below) also backups the good performance of PBE.

Born-Oppenheimer MD were performed with a wave function optimization tolerance of 1.0E-6 and a time step of 0.5 fs. The temperature was controlled at 330 K via the Nosé-Hoover chain thermostat. This slightly elevated temperature was to avoid the glassy behavior of DFT liquid water (VandeVondele et al., 2005b). For all of the simulations, a production run lasts for 5.0-20.0 ps after a prior equilibration stage for at least 3.0 ps. In the free energy calculations, the forces of the constraint at some points can reach a reasonable convergence in 5.0 ps, while longer durations are needed at some others. The statistics of results were collected every 5 fs.

2.3. Method of constraint

A series of constrained FPMD simulations were conducted to enforce the breakages the Ni(II)- $\text{O}_{\text{surface}}$ bonds for each complex on (010) surface. The free energy change (ΔF) was calculated by

193 integrating the mean force (f) along the reaction coordinate (Q) according to the thermodynamic
 194 integration relation (Sprik, 1998; Sprik and Ciccotti, 1998).

$$195 \quad \Delta F(Q) = -\int_{Q_0}^Q dQ' f(Q')$$

196 (1)

197 For the complex $\equiv\text{SiO-Ni}(\text{H}_2\text{O})_5$, the distance between Ni(II) and the dangling O of the $\equiv\text{SiO}$
 198 group was chosen as the Q . For the complex on the $\equiv\text{Al}(\text{OH})_2$ and vacant site, the CN
 199 (coordination numbers) of Ni(II) with respect to the O of the two $\equiv\text{AlOH}$ groups was selected as
 200 the Q .

201 Here the CN was quantified by:

$$202 \quad n = \sum_i \frac{1 - (r_i / r_c)^{12}}{1 - (r_i / r_c)^{24}} \quad (2)$$

203 Here n , r_i , and r_c denote the CN, the distance between Ni(II) and O of $\equiv\text{AlOH}$ group, and the
 204 cutoff, respectively. In this study, $r_c = 2.8 \text{ \AA}$ was used.

205 In the free energy calculations of complex on the vacant site, as CN decreased to 1.0 the
 206 complexing configuration is the same as that of $\equiv\text{Al}(\text{OH})_2\text{-(H}_2\text{O)}_4$. It is then inappropriate to
 207 control the remaining desorption process as constraining only one $\equiv\text{AlOH-Ni}$ bond cannot detach
 208 Ni(II) from the clay edge. As a consequence, this free energy can be reasonably considered as the
 209 sum of the free energies of two stages, i.e. from the tetradentate to the bidentate complex and
 210 from the bidentate to the outer-sphere complex (see the Section **3.2. Free energies of**
 211 **complexes**).

In our recent study (Zhang et al., 2016), by using the same technique and surface model, we calculated both desorption and adsorption processes of Cd(II) for the three sites to check the hysteresis, and found that for each site, the difference between two profiles was within only 0.7 kcal/mol. This indicates that the hysteresis effect in these calculations is negligible. Therefore, in this study we only calculated the desorption processes.

2.4. pKa calculation

The pKa values of Ni(II) hydrate ($\text{Ni}(\text{H}_2\text{O})_6^{2+}$) and complexes investigated were computed by using the half-reaction scheme of vertical energy gap method (Cheng et al., 2009; Costanzo et al., 2011). In this method, the proton of an acid site (denoted as AH) is gradually transformed into a dummy, i.e., a classical particle without any charge. The free energy change of the transformation is calculated according to:

$$\Delta_{dp}A = \int_0^1 d\eta \langle \Delta_{dp}E \rangle_{r\eta}$$

(3)

Here the subscript η means the coupling parameter that is increased from 0 (reactant, i.e. the protonated state) to 1 (product, i.e. the deprotonated state). $\Delta_{dp}E$ stands for the vertical energy gap which is defined as the difference of potential energies of the reactant and the product states. The averages of $\Delta_{dp}E$ are derived from the MD trajectories generated by sampling the restrained mapping Hamiltonian:

$$H_\eta = (1-\eta)H_R + \eta H_P + V_r$$

(4)

Here H_R and H_P refer to the reactant and product states, respectively. The restrained harmonic potential V_r is used to keep the dummy atom situating at a position resembling that in the reactant state:

$$V_r = \sum_{i=1}^{n_d} \frac{1}{2} k_d (d - d_0) + \sum_{i=1}^{n_\alpha} \frac{1}{2} k_\alpha (\alpha - \alpha_0) \quad (5)$$

The V_r is composed of the bonding and angle bending terms whose equilibrium values were d_0 and α_0 , respectively. The equilibrium values were obtained from the free simulations of their respective protonated states and the restraining parameters (k_d and k_α) were adopted according to the prescriptions in previous studies (Cheng et al., 2009; Sulpizi and Sprik, 2008). The details of V_r are listed in Table 1. For the pKa calculations of the complexes on the $\equiv\text{SiO}$ and $\equiv\text{Al}(\text{OH})_2$ sites, in the simulations of their deprotonated states we have observed that the OH ligands get a proton from solvent H_2O , which means the two complexes ($\equiv\text{SiO-Ni}(\text{H}_2\text{O})_5$ and $\equiv\text{Al}(\text{OH})_2\text{-(H}_2\text{O})_4$) does not dissociate in the environmental pH range. To quantify their hydrolysis, we calculated the pKa value for each of the OH_2 ligand (marked in Figure 2A and 2B). To prevent the dissociation, we had restrained all the O-H bonds of solvating water molecules additionally with harmonic potentials ($k_d=0.1$ a.u. and $d_0=1.89$ Bohr) in the simulations of deprotonated states. In practice, the integral in Equation (3) is evaluated with the three-point Simpson's rule and thus the simulations at $\eta=0.0, 0.5$, and 1.0 are required, respectively:

$$\Delta_{dp} A = \frac{1}{6} (\langle \Delta E \rangle_0 + \langle \Delta E \rangle_1) + \frac{2}{3} \langle \Delta E \rangle_{0.5} \quad (6)$$

The three point approximation usually can reach an effective compromise between the accuracy and computational cost (Sulpizi and Sprik, 2008) for many systems. Nevertheless, for some cases, the three-point formula is not enough because of the poor linearity of the energy

gaps. As a result, the simulations at $\eta=0.25$ and 0.75 are necessary, and therefore the free energy is estimated with the five-point formula:

$$\Delta_{dp}A = \frac{1}{12} \left(\langle \Delta E \rangle_0 + \langle \Delta E \rangle_1 + 4 \left(\langle \Delta E \rangle_{0.75} + \langle \Delta E \rangle_{0.25} \right) + 2 \langle \Delta E \rangle_{0.5} \right) \quad (7)$$

With the same method, one proton of a hydronium in the solution region of the same simulation box used for clay is gradually transformed into a dummy. The corresponding integral of deprotonation free energy is denoted as $\int_0^1 d\eta \langle \Delta_{dp} E_{\text{H}_3\text{O}^+} \rangle_{r\eta}$.

In the pKa calculation of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, the term $\int_0^1 d\eta \langle \Delta_{dp} E_{\text{H}_3\text{O}^+} \rangle_{r\eta}$ is 15.35 eV according to the previous report (Costanzo et al., 2011) which used the same cubic box (i.e. the side length = 9.86 Å).

The overall formula used to calculate pKa is:

$$2.30k_B T pK_a = \int_0^1 d\eta \langle \Delta_{dp} E \rangle_{r\eta} - \int_0^1 d\eta \langle \Delta_{dp} E_{\text{H}_3\text{O}^+} \rangle_{r\eta} + k_B T \ln[c^0 \Lambda_{\text{H}^+}^3] \quad (8)$$

Here $c^0 = 1\text{mol/L}$ is the unit molar concentration and Λ_{H^+} stands for the thermal wavelength of proton (Costanzo et al., 2011). The $k_B T \ln[c^0 \Lambda_{\text{H}^+}^3]$ is the translational entropy generated by the acid dissociation and it is approximated by the chemical potential of a free proton at standard concentration. This term is equal to -0.19 eV.

Table 1. The parameters used in restraining the dummy atoms (harmonic potentials in Equation 4). H_d represents the dummy atom. n_d and n_α mean the number of restrained bonds and angles, respectively. d_0 stands for equilibrium bond lengths (in Bohr), and α_0 stands for equilibrium angles (in radian). The meaning of each acid group is described in the text.

Acid groups	n_d	d_0	k_d	n_α	α_0	k_α
$\equiv Ni-OHH_d$ (aqua ion)	1	1.89	0.1	2	1.83 (H-O- H_d)	0.1
					2.00 (Ni-O- H_d)	0.1
$\equiv SiO-Ni-OHH_d$	1	1.89	0.1	2	1.83 (H-O- H_d)	0.1
					2.06 (Ni-O- H_d)	0.1
$\equiv Al(OH)_2-Ni-OHH_d$	1	1.89	0.1	2	1.80 (H-O- H_d)	0.1
					2.09 (Ni-O- H_d)	0.1
$\equiv Ni-OHH_d^V$	1	1.89	0.1	2	1.82 (H-O- H_d)	0.1
					1.82 (Ni-O- H_d)	0.1
$\equiv H_2H_dO^+$	3	1.89	1.0	2	1.94 (H-O- H_d)	0.1
		1.89			1.94 (H-O- H_d)	0.1
		1.89				0.1

3. RESULTS

3.1. Surface complexes

In the free FPMD simulations, stable Ni(II) complexes formed on the three sites. The equilibrium structures (Figure 2) are similar to their counterparts of Fe(II) derived in our previous FPMD studies (Liu et al., 2014; Liu et al., 2013b), i.e. monodentate complex on the $\equiv SiO$ site, bidentate complex on the $\equiv Al(OH)_2$ site, and tetradentate complex on the vacant site.

280 The bond length of Ni-O in the monodentate complex is 2.01 Å (Figure 2A). For the complex
 281 on the $\equiv\text{Al}(\text{OH})_2$ site, the two Ni-O bonds are equivalent with the bond length of 2.03 Å (Figure
 282 2B). For the complex on the vacant site, the MD trajectory clearly shows that Ni(II) occupies a
 283 site equivalent to that of Al(III) cations on octahedral sheet, which thus forms an epitaxial
 284 octahedron (Figure 2C and 2D). The $\text{Ni-O}^{\text{inner}}$ (i.e. two apical O) bonds are longer than the Ni-
 285 O^{outer} bonds (i.e. two $\equiv\text{AlOH}$) (2.21 Å *VS.* 2.02 Å) (Figure 2C and 2D). These bonds are longer
 286 than those of Al-O in lattice (1.94 Å), which is consistent with the fact that the hydration shell of
 287 Ni(II) is larger than that of Al(III) ($R_{\text{Ni-O}} = 2.07$ Å and $R_{\text{Al-O}} = 1.90$ Å) (Ohtaki and Radnai,
 288 1993).

289
 290 Figure 2. The snapshots of equilibrium structures of Ni(II) complexes adsorbed on the (010)
 291 interface. A: $\equiv\text{SiO}$ site; B: $\equiv\text{Al}(\text{OH})_2$ site; C: vacant site (side view); D: vacant site (top view).
 292 For clarity, solvent water molecules have been removed. Ni(II) cations are shown as balls; clay

293 substrates and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, Ni
294 = blue, and dummy atom = Black.

295 **3.2. Free energies of complexes**

296 The free-energy curves for the desorption processes of the three Ni(II) complexes are shown in
297 Figure 3 and the forces of constraint are included in the Electronic Annex.. The free-energy
298 values are collected in Table 2.

299

300 Figure 3. The calculated free-energy profiles for desorption of Ni(II) complexes on (A) $\equiv\text{SiO}$,

301 (B) $\equiv\text{Al(OH)}_2$, and (C) vacant site. The curves are used to guide eyes.

302 Table 2. Desorption free energies of the three Ni(II) complexes.

Sites	ΔF (kcal/mol)
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$\equiv\text{SiO}$	15.8 ± 0.9
$\equiv\text{Al}(\text{OH})_2$	31.5 ± 1.6
vacant site	58.3 ± 2.1

The statistical error is calculated by using the thermodynamic integration equation (Equation 1). The statistical error in force is calculated as the semi-difference between the force values only using the first half and the second half of trajectory.

For Ni(II) complex on the $\equiv\text{SiO}$ site, the desorption free energy is 15.8 kcal/mol (Table 2). Figure 4 illustrates the initial and final configurations obtained from the constrained simulations. It can be seen that the complexing structure at the distance of 2.0 Å (Figure 4A) is almost the same as that in the free MD simulation. As the distance increases to 3.1 Å, one solvent water molecule enters the solvation shell of Ni(II) (Figure 4B), and an outer-sphere complexing pattern forms (see Figure 4B), which is thus taken as the end of desorption (see the force curve in Annex).

Figure 4. Snapshots in the free energy calculations for the complexing on the $\equiv\text{SiO}$ site. (A) The initial structure (2.0 Å); (B) The final structure (3.1 Å). For clarity, solvent water molecules have been removed. Green dotted line represents the hydrogen bonds. Cations are shown as balls.

Solid parts and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, and Ni = blue.

The desorption free energy of the $\equiv\text{Al}(\text{OH})_2\text{-Ni}(\text{H}_2\text{O})_4$ complex is 31.5 kcal/mol (Table 2), indicating that Ni(II) complexing on $\equiv\text{Al}(\text{OH})_2$ site is more possible than that on the $\equiv\text{SiO}$ site. As CN decreases to 1.1, the cation captures one solvent water molecule, and thus it transforms into a monodentate complex (i.e. $\equiv\text{Al}(\text{OH})\text{-Ni}(\text{H}_2\text{O})_5$) (Figure 5B). This configuration gives rise to a local minimum (18.2 kcal/mol) on the free energy curve (see the Figure 3B). At CN=0.05, a second water molecule becomes the ligand of Ni(II) and an outer-sphere complex forms, that denotes the end of the desorption process (see Figure 5C and force curve in Annex). From the local minimum to the end, the corresponding free energy is 13.3 kcal/mol.

Figure 5. Snapshots in the free energy calculations for the complexing on the $\equiv\text{Al}(\text{OH})_2$ site at CN= (A) 1.95, (B) 1.1, and (C) 0.05. For clarity, solvent water molecules have been removed. Green dotted line represents the hydrogen bond. Cations are shown as balls. Solid parts and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, and Ni = blue.

For the complex on the vacant site, as CN decreases, Ni(II) gradually leaves the $\equiv\text{AlOH}$ groups. The structures at CN = 1.95 and 1.0 are displayed in Figure 6. At CN = 1.0 Ni(II) cation gets out of the vacancy and instead binds with another $\equiv\text{AlOH}$ group, thus yielding a complex of $\equiv\text{Al}(\text{OH})_2\text{-Ni}(\text{H}_2\text{O})_4$ that is the same as the bidentate one as shown above. The desorption

process can be viewed as a combination of two stages, i.e., the transformation from the vacant site to the $\equiv\text{Al}(\text{OH})_2$ site ($\Delta F = 26.8$ kcal/mol) and the desorption from the $\equiv\text{Al}(\text{OH})_2$ site ($\Delta F = 31.5$ kcal/mol) (Figure 3C). Therefore, the total free energy on the vacant site is 58.3 kcal/mol (Table 2). This value is significantly higher than those of the monodentate and bidentate ones, which implies that Ni(II) preferentially adsorbs on the vacant site.

Figure 6. Snapshots in the free energy calculations for the complexing on the vacant site at CN= (A) 1.95 and (B) 1.0. For clarity, solvent water molecules have been removed. Cations are shown as balls. Solid parts and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, and Ni = blue.

3.3. pKa values of surface complexes

Table 3 lists the obtained free energy changes and pKa values of Ni(II) aqua-ion and the three surface complexes. The errors of pKa values range from 0.7 to 1.4, indicating a reasonable convergence in the simulation duration.

The computed pKa of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ is 10.4. This value agrees well with the experimental results that range from 9.86 to 10.5 (Baes and Mesmer, 1976), which validates the simulation setup.

The predicted pKa values of complexes on the $\equiv\text{SiO}$ and $\equiv\text{Al}(\text{OH})_2$ site are 16.6 and 14.5, respectively, indicating that the two surface complexes hardly dissociate under normal pH condition. The derived pKa of $\text{Ni}(\text{H}_2\text{O})^{\text{V}}$ is 8.4, implying that the complex on the vacant site can deprotonate in the common pH range. A representative snapshot of the complexing structure upon deprotonation is shown in Figure 7. It can be seen that the $\text{Ni}(\text{II})\text{-OH}$ group accepts hydrogen bonds from both surface $\equiv\text{Al-OH}_2$ and one solvent water molecule, and this configuration stays in the whole simulation period (~ 20 ps).

Table 3. Calculated free energies (in eV) and pKa values of surface complexes. $\text{Ni}(\text{H}_2\text{O})^{\text{H}}$ means hydrated cation $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. $\text{Ni}(\text{H}_2\text{O})^{\text{Si}}$ and $\text{Ni}(\text{H}_2\text{O})^{\text{Al}}$ stand for the complexes on the $\equiv\text{SiO}$ and $\equiv\text{Al}(\text{OH})_2$ site, respectively. $\text{H}_3\text{O}^{+\text{Si}}$, $\text{H}_3\text{O}^{+\text{Al}}$, and $\text{H}_3\text{O}^{+\text{V}}$ denote the hydronium for the complex on the $\equiv\text{SiO}$, $\equiv\text{Al}(\text{OH})_2$, and vacant site, respectively.

Groups	$\eta=0.0$	$\eta=0.25$	$\eta=0.5$	$\eta=0.75$	$\eta=1.0$	ΔA	pKa
$\text{Ni}(\text{H}_2\text{O})^{\text{H}}$	18.40 $\pm$ 0.01	17.19 $\pm$ 0.01	16.47 $\pm$ 0.01	15.92 $\pm$ 0.02	10.85 $\pm$ 0.29	16.22 $\pm$ 0.04	10.4 $\pm$ 0.7
$\text{Ni}(\text{H}_2\text{O})^{\text{Si}}$	20.85 $\pm$ 0.00	19.96 $\pm$ 0.04	18.65 $\pm$ 0.04	17.71 $\pm$ 0.03	12.20 $\pm$ 0.13	18.42 $\pm$ 0.04	16.6 $\pm$ 1.0
$\text{H}_3\text{O}^{+\text{Si}}$	19.97 $\pm$ 0.03	-	17.48 $\pm$ 0.01	-	13.29 $\pm$ 0.03	17.19 $\pm$ 0.02	-
$\text{Ni}(\text{H}_2\text{O})^{\text{Al}}$	20.32 $\pm$ 0.00	19.59 $\pm$ 0.06	18.86 $\pm$ 0.02	17.09 $\pm$ 0.01	11.82 $\pm$ 0.22	18.04 $\pm$ 0.04	14.5 $\pm$ 1.2
$\text{H}_3\text{O}^{+\text{Al}}$	19.78 $\pm$ 0.06		17.17 $\pm$ 0.02	-	13.20 $\pm$ 0.02	16.94 $\pm$ 0.03	-
$\text{Ni}(\text{H}_2\text{O})^{\text{V}}$	20.32 $\pm$ 0.02	19.34 $\pm$ 0.06	18.36 $\pm$ 0.01	17.01 $\pm$ 0.01	14.11 $\pm$ 0.14	18.05 $\pm$ 0.04	8.4 $\pm$ 1.4
$\text{H}_3\text{O}^{+\text{V}}$	19.87 $\pm$ 0.04	-	17.78 $\pm$ 0.05	-	13.08 $\pm$ 0.02	17.35 $\pm$ 0.04	-

The error in pKa is estimated as the sum of the error in the deprotonation free energy of the acid group and of that in the deprotonation free energy of the hydronium. Statistical error in the free energy is calculated as the semi-difference between the values employing the first half or the second half of the trajectory only.

Figure 7. The snapshot of equilibrium structure of Ni(II) complex adsorbed on the vacant site upon deprotonation. For clarity, solvent water molecules have been removed. Green dotted line represents the hydrogen bonds. Cations are shown as balls. Solid parts and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, and Ni = blue.

4. DISCUSSIONS

4.1. Complexing mechanism of Ni(II)

The calculated free-energy values indicate that Ni(II) adsorbs on the three edge sites spontaneously. The octahedral vacancy is the most favored site where Ni(II) is embedded into lattice, and the complexing on the $\equiv\text{Al}(\text{OH})_2$ site is more favorable than on the $\equiv\text{SiO}$ site. Additional simulations show that the structures of complexes adsorbed on (110) surface are similar to the case on (010) edge (Figure 8). Ni(II) forms a monodentate complex on the $\equiv\text{SiO}$ site, a bidentate complex on the $\equiv\text{AlOH}\equiv\text{AlSiO}$ site, and a tetradentate complex on the octahedral vacancy. It can be found that Ni(II) fits well into the vacancy on (110) edge like a lattice cation (Figure 8C and D). That means, the complex on vacancy has significantly higher free energy and therefore, the vacancy is the most favored complexing site. According to these results, the vacant site can be assigned to the strong site, and the other two to the weak sites. The pKa calculations indicate that only the complex on the vacant octahedron can hydrolyze (i.e. pKa

= 8.4) in the common pH range, while the other two always remain protonated. Comparison with the pKa of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in aqueous solution (10.4) indicates that complexing on the vacant site slightly lowers the pKa, whereas those on the $\equiv\text{SiO}$ and $\equiv\text{Al}(\text{OH})_2$ sites significantly enhance the pKa. This coincides with the result of 2SPNE SC/EC. In the modelling of Ni(II) sorption on montmorillonite, the fitted pKa values of surface complexes on the strong sites are 9.4 and 9.1 for Na-montmorillonite and Ca-montmorillonite respectively (Bradbury and Baeyens, 2005b), while no hydrolysis is needed to take into account for complexes on weak sites (Bradbury and Baeyens, 2005b). This agreement further backups the assignment of surface sites discussed above.

Figure 8. The snapshots of equilibrium structures of Ni(II) complexes adsorbed on the (110) interface. A: $\equiv\text{SiO}$ site; B: $\equiv\text{AlOH}\equiv\text{AlSiO}$ site; C: vacant site (side view); D: vacant site (top view). For clarity, solvent water molecules have been removed. Ni(II) cations are shown as balls; clay substrates and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, Ni = blue.

On the basis of the above discussion, the mechanism for initial complexation can be derived. Ni(II) first adsorbs on the outermost octahedral vacancies which corresponds to the strong site in 2SPNE SC/EC model, and as environmental pH increases some complexes get deprotonated. As the vacant sites are gradually saturated, Ni(II) starts to form bidentate complex on the $\equiv\text{Al}(\text{OH})_2$ site and then monodentate complex on the $\equiv\text{SiO}$ site and the two sites correspond to the weak site in the sorption model. Ni(II) adsorbed on $\equiv\text{Al}(\text{OH})_2$ can share one OH with the Ni(II) on the vacant site. In that case, the free energy and pKa of the Ni(II) on $\equiv\text{Al}(\text{OH})_2$ are different from the values derived above: the complexation will be weaker than without Ni(II) on vacancy and also, this can weaken the effect of complexation on the hydrolysis of Ni(II) (i.e. its pKa will be lower than 14.5). Further adsorption at high pH such as multinuclear complexation and nucleation are also very important for understanding the fate of Ni(II). These issues will be addressed in our future studies.

Our model contains eight $\equiv\text{SiO}$ sites, four $\equiv\text{Al}(\text{OH})_2$ sites, and four vacant sites, thus the ratio of weak site to strong site is 3:1. This is different from that in the 2 SPNESC/CE sorption model (20:1). Although there is a qualitative consistence in both studies that the weak site is much more abundant than the strong site, to expect a full agreement is obviously impossible. First, it is hard to quantitatively describe different complexing sites by the current experimental techniques because of the high complexity of clay edges. The estimates in sorption model were determined solely by the measured isotherm without any molecular-level basis. Second, the present surface is a periodic model. In reality, clay particles usually have different facets, and therefore the real site capacities are hard to represent with one single surface. Third, for the most common substitution in montmorillonite (Mg for Al on octahedral sheet), we have shown that $\equiv\text{Mg}(\text{OH})_2$ has a high pKa of 13.0 (Liu et al., 2013b) and therefore, it almost doesn't deprotonate within the

common pH range (4~9), indicating that this group is not responsible for edge complexation. Because of the strong repulsion from the two protons of $\equiv\text{MgOH}_2$, foreign cations cannot approach the vacant site. As a result, one such substitution reduces a strong site (i.e. vacancy) and a weak site (i.e. $\equiv\text{Al}(\text{OH})_2$) respectively, thus the relative population of strong site in sorption model decreases drastically.

4.2. Implication for heavy metal complexation

Our previous study has shown that Cd(II) preferentially adsorbs on the vacant site on clay edges (Zhang et al., 2016), and the present study shows that the complexing structures of Cd(II) and Ni(II) are different: Cd(II) does not occupy the lattice position though it forms stable complex at the octahedral vacancy (see Figure 9A). This difference is due to the much larger radius of Cd(II) (e.g., for aqua-cations, $R_{\text{Cd-O}} = 2.29 \text{ \AA}$ and Ni(II) $R_{\text{Ni-O}} = 2.07 \text{ \AA}$) (Ohtaki and Radnai, 1993).

The complexing structure of Fe(II) adsorbed on the vacant site which has been shown in earlier study (Liu et al., 2014) is similar to that of Ni(II). Additional simulations of Co(II) and Cu(II) complexes on the vacant site were conducted and the equilibrium structures were derived (Figure 9B and 9C). They both formed tetradentate complexes similar to Ni(II) and Fe(II). Co(II) has an octahedral complexing configuration (Figure 9B), while Cu(II) is five-fold coordinated (Figure 9C). This is consistent with the previous studies in aqueous solutions that have shown that penta-coordinated Cu(II) is predominant (Frank et al., 2015; La Penna et al., 2015; Liu et al., 2010; Pasquarello et al., 2001). It can be seen that these cations fit well into the empty octahedra because of their similar ionic radii, thus the corresponding complexes should have significantly higher free energies than the others. Therefore, these cations should have very similar complexing mechanisms. In addition, it is reasonable to deduce that divalent cations with larger

size than Cd(II) cannot be embedded into the lattice position, while those in the fourth period can occupy a lattice position equivalent to Al(III).

Figure 9. The snapshots of equilibrium structures of different cations adsorbed on the vacant sites of (010) interface. A: Cd(II), B: Co(II), and C: Cu(II). For clarity, solvent water molecules have been removed. Cations are shown as balls. Solid parts and water ligands are shown as sticks. O = red, H = white, Si = yellow, Al = purple, Cd = gold, Co = cyan, and Cu = orange.

We have shown that Fe(II), Co(II), and Cu(II) fit well into the empty octahedra just like Ni(II), and therefore their complexes adsorbed on this site should have significantly higher free energies

than on the others. Though Cd(II) does not occupy a lattice position, its complex on the vacant site shows much higher free energy. Therefore, for all of these divalent cations, the vacant site can be described by the strong site used in the 2SPNE SC/EC model. This study builds a link between batch experiments and atomistic simulations for complexation of metal cations on clay edges. Together with our previous studies on edge surfaces (Liu et al., 2014; Liu et al., 2012b; Liu et al., 2013b), we provide atomic-level understanding of interface chemistry of clay edges including hydration structures, surface acidities, and complexation of heavy metal cations.

4.3. Environmental and geochemical significance

Our study indicates that the outermost octahedral vacancy of 2:1-type clay minerals (e.g. montmorillonite, illite and mixed-layer clays) has the highest binding affinity for divalent heavy metal cations. This finding is of significant environmental and geochemical implications. For 1:1-type clay minerals, e.g. kaolinite, its octahedral sheet is similar to that of 2:1-type. Consequently, the Al-O octahedral vacancy on edge surfaces of kaolinite should also be the most possible complexing site for heavy metal cations. In soils and aquifers, clay minerals distribute widely as important components, while the level of heavy metal is normally lower than that in lab experiments. Therefore, heavy metal cations can be effectively immobilized on the vacant sites due to the very high desorption free energy. Recently, it has been shown that frayed edge on micaceous minerals (i.e. partially expanded wedge between non-swelling and swelling interlayer regions (Nakao et al., 2008)) can have very high affinity to some toxic metal cations such as Cs⁺ (Fuller et al., 2015; Rosso et al., 2001; Zaunbrecher et al., 2015). Although overlooked in previous studies, frayed edge can also be important for adsorption of heavy metal cations. This issue deserves more simulation studies.

Nickel laterites account for a large proportion of global Ni resources (Golightly, 1981). In this type of deposit, Ni can be very rich in phyllosilicates, e.g. smectites and talc (Butt and Cluzel, 2013; Golightly, 1981) and it is suggested that Ni enters the octahedral layers (Gaudin et al., 2005). Our finding here provides a microscopic clue for understanding that scenario. Ni cations fit well into the lattice and the 1st shell water readily gets deprotonated in common pH range (pKa is about 8.0). The OH groups generated from the hydrolysis can serve as the anchoring sites for the following adsorbed cations. This leads to the further nucleation/growth and therefore, Ni is effectively incorporated into the crystal structures of phyllosilicate phases.

5. CONCLUSION

By employing FPMD simulations, we revealed the complexing mechanisms of Ni(II) on clay edge surfaces. Three representative complexes were investigated, i.e. monodentate complex on $\equiv\text{SiO}$ site, bidentate complex on $\equiv\text{Al}(\text{OH})_2$ site, and tetradentate complex on vacant site where Ni(II) was embedded into the lattice. The desorption free energies calculated from constrained FPMD simulations indicate that the tetradentate complex is significantly more stable than the other two. Therefore, we assign the vacant site and the other two sites to the strong site and the weak site, respectively. On the basis of additional simulations, we deduce that other divalent heavy metal cations should have the similar complexing mechanisms. pKa calculations show that Ni(II) complex on the vacant site can be deprotonated while complexes on other sites remain protonated in common pH range. The microscopic and thermodynamic mechanisms derived in this study contribute to understanding the fate of heavy metal elements in natural and engineering environments.

ACKNOWLEDGMENT

500 The authors acknowledge National Science Foundation of China (Nos. 41222015, 41273074,
501 41425009, and 41572027), Special Program for Applied Research on Super Computation of the
502 NSFC-Guangdong Joint Fund (the second phase), the Foundation for the Author of National
503 Excellent Doctoral Dissertation of PR China (No. 201228), the Newton International Fellow
504 Program and financial support from the State Key Laboratory for Mineral Deposits Research.
505 We are also grateful to the High Performance Computing Center of Nanjing University for use of
506 the IBM Blade cluster system.

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