Understanding the unique geochemical behavior of Sc in the interaction with clay minerals

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ABSTRACT

Regolith-hosted rare earth elements (REEs) deposits received great attention due to the increasing incorporation of REEs in modern technologies. In lateritic Sc deposits and ion-adsorption deposits (IADs), Sc behaves quite differently from other REEs: REEs adsorb as outer-sphere complexes on clay surface in IADs while Sc could enter the lattice of clay minerals in lateritic Sc deposits. The unique behavior of Sc has not been well understood yet. Here, by using first-principles molecular dynamics techniques, we show that the complexation mechanisms of Y$^{3+}$ and Sc$^{3+}$ on clay edge surfaces are distinctly different. Y$^{3+}$ preferentially adsorbs on Al(OH)$_2$SiO site with its coordination water protonated. Sc$^{3+}$ is found to behave similarly to other first-row transition metals (e.g. Ni$^{2+}$) due to its smaller ionic radius and prefers adsorbing on the vacancy site, from where Sc$^{3+}$ can be readily incorporated in the clay lattice. The H$_2$O ligands of Sc$^{3+}$ get deprotonated upon complexation, providing new binding sites for further enrichment of Sc$^{3+}$. These processes prevent Sc$^{3+}$ from being leached during weathering and lead to the formation of Sc-rich clay minerals found in lateritic deposits. Based on these results, it is revealed that the small ionic radius and high affinity to enter the vacancy on edge surfaces make Sc compatible with clay minerals and are the origin of its unique geochemical behavior.

Keywords: Scandium, rare earth elements, clay minerals, complexation mechanisms, first principles molecular dynamics
INTRODUCTION

Rare earth elements (REEs, i.e. scandium, yttrium, and 15 lanthanoids) are finding increasing use in modern high-tech industries such as electronics manufacture, green energy technologies, and military applications (Chakhmouradian and Wall, 2012; Williams-Jones and Vasyukova, 2018) and they have been classified as strategic and critical elements worldwide (Haxel, 2002; Gulley et al., 2018; Zhai et al., 2019). Among different REEs deposits, regolith-hosted deposits have received significant attention due to the enrichment and ease of extraction of high-value elements (Zhou et al., 2020). Ion-adsorption deposits (IADs) developed in South China are currently the dominant sources for heavy REEs (Hoshino et al., 2016) while the lateritic deposits recently found in Australia are regarded as a potential long-term Sc resources (Jaireth et al., 2014; Chassé et al., 2016; Chassé et al., 2019). Clay minerals played a pivotal role during the formation of these deposits (Li et al., 2017; Chassé et al., 2019; Borst et al., 2020; Elliott, 2020; Li and Zhou, 2020). In IADs, REEs were believed to be weakly adsorbed on clay minerals (i.e. in outer-sphere complexes) due to their easy-extraction nature (Bao and Zhao, 2008; Borst et al., 2020). In lateritic Sc deposits, however, Sc was found to be incorporated in the lattice of clay minerals before its association with goethite (Chassé et al., 2019).

The unique behavior of Sc compared with other REEs regarding the interaction with clay minerals is still poorly understood. Sc and other REEs exhibit very high hydration
enthalpy (Rizkalla and Choppin, 1991; Cotton, 2013) and therefore, they all form outer-sphere complexes on clay basal surfaces. Thus, it can be deduced that the uniqueness of Sc originates from its interaction with clay edge surface. However, the role clay edges played in the partition of REEs remains unclear. Recently, Borst et al. (2020) presented X-ray absorption fine structure (EXAFS) evidence confirming that outer-sphere complexes on basal surface are the dominant forms of REEs in IAD. The existence of inner-sphere complexes on clay edges, however, cannot be excluded by the authors, especially when the pH increment with depth was considered (Li et al., 2019; Li et al., 2020; Huang et al., 2021). Indeed, there are a number of experimental studies that support the existence of inner sphere complexes on clay edges in mildly acidic to basic conditions (Stumpf et al., 2002; Kowal-Fouchard et al., 2004; Takahashi et al., 2004; Verma et al., 2014; Zhou et al., 2021; Zhou et al., 2022). Using polarized EXAFS technique, Schlegel and Finck et al. investigated the complexation of $Y^{3+}$ and $Lu^{3+}$ on hectorites and suggested the existence of inner-sphere complexes on the edge surfaces that coordinated to both octahedral and tetrahedral sheets (Schlegel, 2008; Finck et al., 2009; Finck et al., 2017). The structures of such inner-sphere complexes, however, were not unambiguously determined. For example, both six- and eight-fold coordinations have been suggested for $Y^{3+}$ (Schlegel, 2008; Finck et al., 2017). The complexation mechanism of $Sc^{3+}$ on clay edge surfaces has not been studied to the best of our knowledge. Similar to $Sc^{3+}$, $Ni^{2+}$ could be enriched in phyllosilicates in lateritic deposits, where $Ni^{2+}$ is incorporated in the lattice of
clay minerals (Butt and Cluzel, 2013). It was found that clay edge surfaces acted as both complexation and nucleation sites for the formation of Ni-bearing clay minerals in lateritic Ni deposits (Dähn et al., 2002; Dähn et al., 2003; Zhang et al., 2019b; Liu et al., 2022).

Here, we demonstrate that the unique behavior of Sc originates from its high affinity to enter the vacancy on clay edges using ab initio molecular dynamics (AIMD) technique. AIMD method has proven to be powerful in quantifying the structural and thermodynamical properties of mineral-cation interactions (Alexandrov and Rosso, 2015; Kubicki, 2016; Leung et al., 2018; Liu et al., 2022). We determined the complexation structures and the associated free energy changes of Sc$^{3+}$ on montmorillonite (010) edge and made comparison with Y$^{3+}$. Y$^{3+}$ is enriched in IADs in South China (Zhou et al., 2020) and here it is selected as an example of heavy REEs. The complexation free energies of Sc$^{3+}$ and Y$^{3+}$ on (010) surface were calculated using the method of constraint. The acidity constants of their surface complexes were calculated using AIMD based vertical energy gap method to determine their protonation states in common pH conditions. The results suggest that Y$^{3+}$ would preferentially adsorb on the Al(OH)$_2$SiO site in a pentagonal bipyramid geometry with its coordination water protonated. In contrast, Sc$^{3+}$ is embedded into the vacancy with all the coordination water deprotonated and the complexation free energy is significantly higher than its complex on the Al(OH)$_2$ site. Complexation of Y$^{3+}$ prohibits its further adsorption on the edge surface while Sc$^{3+}$ complexed provides addi-
tional binding sites for further complexation. This process contributes to the enrichment of Sc and leads to the formation of Sc-rich clay minerals found in the lateritic Sc deposits. The findings presented in this study provide an atomic level insight into the unique geochemistry of Sc$^{3+}$ and forms a microscopic basis for development of efficient REEs extraction techniques.

**COMPUTATIONAL METHODS**

**Atomistic model**

The clay (010) and (110) edge surface models were taken from previous studies (Zhang et al., 2020) and contained $3 \times 1 \times 1$ unit cells. 15 water molecules were placed in the interlayer region to represent the monolayer hydrate state, corresponding to a basal spacing of 12.5 Å. One isomorphic substitution of Mg for Al was imposed and one Li$^+$ was used as the counterion in the interlayer region. The surface model was placed in 3D periodically repeated orthorhombic box and surmounted by a ~15 Å thick solution region that contains 86 water molecules. The dimensions of the simulation box were 25 Å × 15.54 Å × 12.5 Å.

**AIMD simulations**

All AIMD simulations were carried out using the CP2K/QUICKSTEP package (VandeVondele et al., 2005; Kühne et al., 2020) where the electronic structures were calculated with density functional theory (DFT). With the dual-basis set Gaussian and plane wave (GPW) scheme (Lippert et al., 1997), the electronic wavefunctions were construct-
ed using a double-\(\zeta\) Gaussian-type orbital basis (VandeVondele and Hutter, 2007) with polarization functions (DZVP) and the electron density was represented with the plane-wave basis expanded to 360 Ry. The core electron states were described using Goedecker-Teter-Hutter (GTH) pseudopotentials (Goedecker et al., 1996). The exchange-correlation was accounted for with Perdew–Burke–Ernzerhof (PBE) functional (Perdew et al., 1997). The DFT-D3 functional was adopted for van der Waals corrections (Grimme et al., 2010). Wave functions were optimized to a tolerance of 1.0E-6.

Born-Oppenheimer type molecular dynamics (BOMD) simulations were carried out in NVT ensemble with temperature controlled at 300 K using a Nosé-Hoover chain thermostat. For each simulation, a production run was performed for over 15.0 ps after an equilibration run for at least 5.0 ps.

Constrained AIMD

The complexation free energy was calculated with constrained AIMD (Sprik and Ciccotti, 1998). In this method, the free energy profile was obtained by integrating the mean forces along a specified reaction coordinate. In this study, the distance from \(\text{Sc}^{3+}/\text{Y}^{3+}\) to the plane defined by three surface oxygen atoms (i.e., two O in AlOH and one O in SiO(H)) was selected as the reaction coordinate. A similar reaction coordinate has been shown to be able to describe the desorption processes of REEs from mineral surface (Leung et al., 2021). The outer-sphere form was taken as the final state of the desorption process.
pKa calculations

The intrinsic pKas of Sc\textsuperscript{3+}/Y\textsuperscript{3+} surface complexes were evaluated with the half-reaction scheme of the vertical energy gap method (Sulpizi and Sprik, 2008; Cheng et al., 2009; Costanzo et al., 2011; Cheng and Sprik, 2012). The deprotonation free energy was calculated as the integral of the ensemble averages of the vertical energy gaps along the alchemical path from reactant state to product state. We refer the readers to our previous papers for the details (Cheng et al., 2014).

RESULTS AND DISCUSSION

Complex structures

There are several sites possible for complexing transition metal cations (e.g. Cd\textsuperscript{2+} and Ni\textsuperscript{2+}) on clay edge surfaces, including the SiO site, the Al(OH)\textsubscript{2} site, and the vacancy site, with the latter two being more favorable (Alexandrov and Rosso, 2013; Zhang et al., 2017). Possible Sc\textsuperscript{3+}/Y\textsuperscript{3+} complexes on (010) surface were firstly probed with free AIMD simulations. Y\textsuperscript{3+} and Sc\textsuperscript{3+} were initially placed on the Al(OH)\textsubscript{2} and vacancy sites (Fig. 1a). During the simulation, Y\textsuperscript{3+} initially complexed on the vacancy site gradually transferred to the Al(OH)\textsubscript{2}SiO site (Fig. 1b). This complexation site has not been reported for other transition metals like Ni\textsuperscript{2+} and Cd\textsuperscript{2+} (Zhang et al., 2016; Zhang et al., 2017), which could be explained by the larger ionic radius of Y\textsuperscript{3+}. The average Y\textsuperscript{3+}-O distance on this site was 2.36 Å. On this site, Y\textsuperscript{3+} was seven-fold coordinated (i.e., four H\textsubscript{2}O ligands, two
AlOHs, and one SiO) in a slightly irregular pentagonal bipyramid cage. Y$^{3+}$ located slightly above the octahedral plane on this site, similar to the structure suggested by Schlegel (2008). On Al(OH)$_2$ site, Y$^{3+}$ was eight-fold coordinated with six H$_2$Os and two AlOHs in a square antiprism geometry (Fig. 1c), where Y$^{3+}$ resided on the octahedral plane. Such a coordination environment could minimize the inter-ligand repulsions (Thompson, 1979) and resembles the structure predicted for the Y$^{3+}$ aqua ion (Díaz-Moreno et al., 2000; Liu et al., 2012). The average Y$^{3+}$-O distance was 2.41 Å, which was in good agreement with the values reported for the eight-fold coordinated Y$^{3+}$ in previous studies (i.e., 2.35 Å~2.46 Å) (Matsubara et al., 1990; Díaz-Moreno et al., 2000; Ikeda et al., 2004; Liu et al., 2012).

Sc$^{3+}$ was six-fold coordinated with four H$_2$Os and two AlOHs on the Al(OH)$_2$ site (Fig. 1d). Sc$^{3+}$ exhibited a regular octahedron coordination geometry and located at the mid-plane of the clay TOT sheet. The average Sc$^{3+}$-O distance was 2.13 Å. On the vacancy site, the two water ligands of Sc$^{3+}$ dissociated spontaneously during the simulation and thus the resulting stable structure was a slightly irregular octahedron where Sc$^{3+}$ was six-coordinated with four surface O atoms and two OHs (Fig. 1e). The average distances between Sc$^{3+}$ and apical O, O atoms of AlOH, and OH were 2.48 Å, 2.10 Å, and 1.99 Å, respectively. The spontaneous dissociation of the coordination water was consistent with its strong acidic nature as demonstrated in the following section.

The complexation structures of Sc$^{3+}$ and Y$^{3+}$ show that these two cations share a
same complexing site, i.e. the Al(OH)$_2$ site. Apart from this site, they also have different complexing sites, that is, vacancy site for Sc$^{3+}$ and Al(OH)$_2$SiO site for Y$^{3+}$. The complexation structures on these two sites are compared in Fig. 2. It can be seen that while Y$^{3+}$ is clearly off the edge plane, Sc$^{3+}$ resembles the lattice Al position, that is, Sc$^{3+}$ is embedded into the octahedral sheet (Fig. 2). In our previous study, we derived the complexation structures of transition metals on the vacancy site and found that cations including Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$ and Cu$^{2+}$ fit well in the vacancy while Cd$^{2+}$ is clearly off the vacancy center (Zhang et al., 2017; Zhang et al., 2019a). Based on these observations, it was proposed that cations smaller than Cd$^{2+}$ (e.g. Ni$^{2+}$) could enter the clay lattice. The complexation structure of Sc$^{3+}$ in Fig. 2 suggests that this rule also applies for Sc$^{3+}$: Sc$^{3+}$ is indeed smaller than Cd$^{2+}$ (i.e. 0.83 Å Vs. 1.03 Å) (Whittaker and Muntus, 1970). This indicates that Sc$^{3+}$ behaves similarly to first-row transition metals in interaction with clay minerals.

Besides (010) surface, (110) surface is also a major edge surface of clay minerals. Additional AIMD simulations show that the complexation structures of Sc$^{3+}$ and Y$^{3+}$ on (110) surface are similar to their counterparts on (010) surface (Online Material1 Fig. OM1). Y$^{3+}$ formed a pentagonal bipyramid complex bonded to both the octahedral sheet and tetrahedral sheet on the (AlOH)$_2$SiO site and a square antiprism complex on the (AlOH)(AlSiO) site on (110) surface (Online Material1 Fig. OM1). Sc$^{3+}$ formed octahedral complexes on both the (AlOH)(AlSiO) site and the vacancy site on (110) surface. On
the vacancy site, one H\textsubscript{2}O ligand of Sc\textsuperscript{3+} dissociated spontaneously during the AIMD simulation. Similar to the cases on (010) surface, Y\textsuperscript{3+} complexes on (110) surface are clearly off the edge plane while Sc\textsuperscript{3+} fits well in the octahedral vacancy on (110) surface and is embedded into the clay octahedral sheet.

The complexation structure of Lu\textsuperscript{3+} (i.e. the smallest lanthanide) on the vacancy site was also obtained from AIMD simulation. The complexation structure (Fig. 2c) clearly shows that Lu\textsuperscript{3+} formed a bidentate complex on the vacancy site and was away from the edge plane. Therefore similar to Y\textsuperscript{3+}, Lu\textsuperscript{3+} cannot enter the vacancy.

Based on the above structures, the stable surface complexes for Y\textsuperscript{3+} and Sc\textsuperscript{3+} on (010) surface are determined to be: seven-fold coordinated pentagonal bipyramid for Y\textsuperscript{3+} on Al(OH)\textsubscript{2}SiO site, eight-fold coordinated square antiprism for Y\textsuperscript{3+} on Al(OH)\textsubscript{2} site, and six-fold coordinated octahedra for Sc\textsuperscript{3+} on Al(OH)\textsubscript{2} and vacancy sites. To better understand the complexation mechanisms of Y\textsuperscript{3+} and Sc\textsuperscript{3+}, these structures were used as the initial configurations in the following sections to calculate the complexation free energies and pKas of these complexes.

**Complexation free energies**

The stabilities of the four surface complexes were probed by calculating the free energy changes from the inner-sphere states to the outer-sphere states. The free energies were obtained by using the constrained AIMD method and the distances between
Y$^{3+}$/Sc$^{3+}$ and the edge surface plane were selected as the reaction coordinate. The first
and second pKas of Sc$^{3+}$ aqua ion are 4.3 and 5.4 respectively (Baes and Mesmer, 1976),
indicating that Sc$^{3+}$ is doubly deprotonated in near neutral pH environment. In contrast,
the first pKa of Y$^{3+}$ aqua ion is 7.7 (Baes and Mesmer, 1976), that is, the H$_2$O ligands of
Y$^{3+}$ hardly deprotonate in mildly acidic pH. Therefore, Y$^{3+}$ and Sc(OH)$_2^+$ were used in
the free energy calculations. The obtained free energy curves and representative interme-
diate structures are shown in Fig. 3.

On the Al(OH)$_2$ site, Y$^{3+}$ was bidentately coordinated and formed a square antiprism
coordination at $d = 1.95$ Å (Fig. 3). As Y$^{3+}$ left the surface, the free energy curve gradu-
ally went up (Fig. 3a). At $d = 2.8$ Å, one Y$^{3+}$-OH bond broke and Y$^{3+}$ transformed into a
monodentate complex in mono-capped trigonal prismatic geometry (Fig. 3c). As the dis-
tance increased to 3.1 Å, one solvent water molecule entered the hydration shell of Y$^{3+}$
and the free energy curve started to decrease. At $d = 3.6$ Å, Y$^{3+}$ transformed to an out-
er-sphere complex in pentagonal bipyramid coordination. The free energy curve reached
the local minima at this distance and the corresponding free energy change was 22.4
kcal/mol, indicating that Y$^{3+}$ complexed on the Al(OH)$_2$ site is fairly stable.

On the Al(OH)$_2$SiO site, the desorption of Y$^{3+}$ included three successive bond
breaking events (Fig. 3c), that is, the breakage of the two Y$^{3+}$-AlOH bonds and the
Y$^{3+}$-SiO bond (at $d = 1.8$ Å, 2.2 Å and 2.8 Å respectively). At the initial state (i.e., $d = 1.4$
Å), Y$^{3+}$ formed a tridentate complex in pentagonal bipyramid geometry. As the distance
increased to 1.8 Å, one Y$^{3+}$-AlOH bond broke and the coordination shell of Y$^{3+}$ transformed into an octahedron. With the further increasing of the distance, two solvent water molecules entered the hydration shell of Y$^{3+}$ successively at 2.2 Å and 2.4 Å and Y$^{3+}$ changed into the pentagonal bipyramid coordination. At d = 2.8 Å, Y$^{3+}$ coordinated with another solvent water molecule and the Y$^{3+}$-SiO bond broke. The free energy curve started to decrease at this distance and reached the local minima at d = 3.4 Å, where Y$^{3+}$ formed an outer-sphere complex in a mono-capped trigonal prism. The free energy change for the desorption process of Y$^{3+}$ from Al(OH)$_2$SiO site was calculated to be 29.8 kcal/mol. This value suggests that Y$^{3+}$ complexed on the Al(OH)$_2$SiO site is substantially more stable than that on the Al(OH)$_2$ site and Y$^{3+}$ would preferentially adsorb on the Al(OH)$_2$SiO site. Y$^{3+}$ is bonded to one SiO group and two AlOH groups on the Al(OH)$_2$SiO site. The AlOH groups also belong to the Al(OH)$_2$ site and the complex on Al(OH)$_2$SiO occupies the binding sites of Al(OH)$_2$. Therefore, complexation on the Al(OH)$_2$ site actually hardly happen due to the strong steric repulsions imposed by Y$^{3+}$ complex on the Al(OH)$_2$SiO site. This is in agreement with the previous EXAFS measurement which suggested Y$^{3+}$ was tilted away from the mid-plane of the clay TOT sheet (Schlegel, 2008).

Sc(OH)$_2^+$ formed a stable bidentate complex on the Al(OH)$_2$ site with a distance of 1.8 Å from the surface (Fig. 3d). This distance is shorter than the value obtained for Y$^{3+}$ (i.e., 1.80 Å V.S. 1.95 Å), in agreement with its smaller ionic radius (0.83 Å V.S. 1.10 Å).
(Whittaker and Muntus, 1970). During the desorption process, the two Sc$^{3+}$-AlOH bonds dissociated successively at $d = 2.4$ Å and 2.9 Å respectively. The coordination shell of Sc$^{3+}$ was compensated by two solvent water molecules after Sc$^{3+}$-AlOH dissociations and Sc$^{3+}$ kept the octahedral geometry during the entire desorption process. The local minima on the free energy curve located at $d = 3.6$ Å, where Sc(OH)$_2^+$ formed a stable outer-sphere complex (Fig. 3b). The free energy required for Sc(OH)$_2^+$ to reach this state was 14.8 kcal/mol.

The detachment of Sc(OH)$_2^+$ from the vacancy site was more complicated than that on the Al(OH)$_2$ site. At the distance of 0.7 Å from the surface plane, Sc$^{3+}$ was incorporated in the octahedral sheet and located near the center of the vacancy (Fig. 3d). As Sc(OH)$_2^+$ left the surface, the bonds between Sc$^{3+}$ and the two apical O atoms gradually broke. At $d = 1.4$ Å, Sc(OH)$_2^+$ coordinated with one SiOH group and located slightly off the octahedral plane. One solvent water molecule entered the coordination shell of Sc$^{3+}$ at this distance and Sc$^{3+}$ kept its octahedral coordination geometry. As the distance further increased to 2.0 Å, Sc(OH)$_2^+$ transferred onto the Al(OH)$_2$ site spontaneously and captured another water molecule (Fig. 3d). Therefore, the desorption process of Sc(OH)$_2^+$ from the vacancy site can be regarded as a combination of two sub-steps, that is, transfer of Sc(OH)$_2^+$ from the vacancy site to the Al(OH)$_2$ site and the desorption of Sc(OH)$_2^+$ from the Al(OH)$_2$ site. Therefore, the corresponding free energy data after $d = 2.0$ Å was taken from that of Sc(OH)$_2^+$ on the Al(OH)$_2$ site. The free energy change for the detach-
ment of Sc(OH)$_2^+$ from the vacancy site was 32.4 kcal/mol (Fig. 3b), which was significantly higher than the value obtained for Sc(OH)$_2^+$ on the Al(OH)$_2$ site, implying that Sc(OH)$_2^+$ would adsorb preferentially on the vacancy site. Similarly, the free energy required for Ni$^{2+}$ desorption from the vacancy site was determined to be 58.3 kcal/mol in the previous study, which was significantly higher than the value on the Al(OH)$_2$ site (31.5 kcal/mol) (Zhang et al., 2017).

**Hydrolysis of surface complexes**

The first and the second pKas of Y$^{3+}$/Sc$^{3+}$ complexes on different sites calculated using the vertical energy gap method were collected in Table 1. We found that Sc$^{3+}$ complexed on the vacancy site is the most acidic, with the first and second pKas of -6.5 and -0.2 respectively. Such low pKas were consistent with the spontaneous dissociations of water ligands mentioned above. These values were clearly separated from the pKas obtained for other Sc$^{3+}$ and Y$^{3+}$ complexes, i.e. 7.2~8.4. The moderate pKa values for Sc$^{3+}$ complex on Al(OH)$_2$ site, Y$^{3+}$ complexes on Al(OH)$_2$ and Al(OH)$_2$SiO sites indicate that these complexes could hydrolyze in neutral and basic environments and therefore, both the protonated and deprotonated forms could exist in common pH range. In contrast, for Sc$^{3+}$ complexed on the vacancy site, only the doubly deprotonated form is possible due to the very low pKas.

The first pKas of Sc$^{3+}$ and Y$^{3+}$ aqua ions were measured to be 4.3 and 7.7, respectively (Baes and Mesmer, 1976). Based on the calculated pKas, it can be found that com-
plexation on the vacancy site significantly decreased the pKa of Sc$^{3+}$. Such a decrease was also found in our prior study for Ni$^{2+}$ complexed on this site (i.e. 8.4 V.S. 10.4) (Zhang et al., 2017). For Y$^{3+}$, however, complexation on clay edge had little influence on its pKa (i.e. 7.2–8.2 V.S. 7.7).

**IMPLICATIONS**

According to the structures, free energies, and the pKas of surface complexes, an atomic level understanding of the complexation mechanisms of Sc$^{3+}$ and Y$^{3+}$ can be obtained. Y$^{3+}$ prefers adsorbing on the Al(OH)$_2$SiO site as a pentagonal bipyramid complex. Complexation on this site prohibits the complexation of Y$^{3+}$ on the Al(OH)$_2$ site due to the consumption of the AlOH binding sites. The H$_2$O ligands of Y$^{3+}$ keeps protonated upon complexation, especially in the acidic to slightly basic environment found in IADs.

Sc$^{3+}$ behaves differently from Y$^{3+}$ in that it preferentially adsorbs on the vacancy site and forms an octahedral complex that fits well in the vacancy. The free energy required to desorb Sc$^{3+}$ from this site is obviously higher than that on the Al(OH)$_2$ site, suggesting that detachment of Sc$^{3+}$ from clay edge surfaces hardly occur. Different from Y$^{3+}$, complexation of Sc$^{3+}$ on the vacancy site significantly reduces the pKas of its H$_2$O ligands and results in the deprotonation of these ligands. All of the aforementioned characteristics were also observed for Ni$^{2+}$, which could be readily incorporated in the octahedral sheet (Zhang et al., 2017). Moreover, the pKas of H$_2$O ligands of Ni$^{2+}$ also decreased upon
complexation on the vacancy site, which makes the deprotonation easier (Zhang et al., 2017). The OH groups formed after the deprotonation of H$_2$O ligands were found to be able to complex additional Ni$^{2+}$, leading to the formation of multinuclear complexes and even the nucleation of hydroxide or phyllosilicates (Zhang et al., 2019a; Zhang et al., 2019b). Thus, one can expect that similar processes also happen to Sc$^{3+}$, that is, Sc$^{3+}$ could form multinuclear complexes on clay edge surfaces. During the supergene weathering of Sc-bearing silicates (e.g. amphibole and clinopyroxene (Chassé et al., 2019)), the thus-formed multinuclear complexes can be readily silicificated due to the abundance of Si in fluids.

During the formation of lateritic Sc deposits, Sc$^{3+}$ was found to be enriched in the clay phase (up to hundreds of ppm) (Chassé et al., 2019). The findings presented here provide an atomic level clue for understanding the formation of the Sc-rich clays: during the weathering process, Sc$^{3+}$ released from parent rocks preferentially adsorbs on the vacancy site on clay edges; the H$_2$O ligands of Sc$^{3+}$ readily get deprotonated upon complexation, providing new binding sites for complexation of additional Sc$^{3+}$; this process leads to the nucleation and growth of Sc-rich clays, which can effectively prevent Sc from being leached.

Overall, the results obtained in the present study suggest that Y$^{3+}$ and Sc$^{3+}$ have distinctly different complexation mechanisms on clay edge surfaces. This difference arises from the smaller ionic radius of Sc$^{3+}$ and its high affinity to the vacancy on clay edge,
which makes Sc compatible with clay minerals and behave similarly to some transition
metals (e.g. Ni$^{2+}$) at the atomic level (i.e. complexation sites, relative stabilities, and hy-
drolysis). These effects together contribute to the unique geochemical behavior of Sc ob-
served in the deposits.
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2(46), 9133-9143.

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Endnote:

1Online Material.
FIGURE 1. Complexation of Sc$^{3+}$/Y$^{3+}$ on clay (010) surface. (a) Simulation box showing the clay surface and solution region. (b) and (c) Complexation structures of Y$^{3+}$ on the Al(OH)$_2$SiO site and the Al(OH)$_2$ site, respectively. (d) and (e) Complexation structures of Sc$^{3+}$ on the Al(OH)$_2$ site and the vacancy site, respectively. O = red, H = white, Si = yellow, Al = pink, Mg = green, Y = cyan, Sc = brown, and Li = purple. Surface O atoms in coordination polyhedra are colored in blue. For clarity, solvent water molecules in (b)-(e) are not shown.
FIGURE 2. Comparison of Sc$^{3+}$/Y$^{3+}$/Lu$^{3+}$ complexes on clay (010) surface. (a) Sc$^{3+}$ complex on the vacancy site. (b) Y$^{3+}$ complex on the Al(OH)$_2$SiO site. (c) Lu$^{3+}$ complex on the vacancy site. Lu is colored in ice-blue and other atoms are color-coded by ele-
ments as described in Figure 1. The blue dash lines mark the position of the center of the vacancy.

FIGURE 3

FIGURE 3. Desorption of Y$^{3+}$/Sc(OH)$_2^+$ from clay edge surface. (a) and (b) Desorption free energy curves associated with the desorption of Y$^{3+}$ and Sc(OH)$_2^+$. (c) and (d) Snapshots showing the complexation structures during the desorption processes. Atoms are color-coded by elements as described in Figure 1.
**TABLE 1.** Calculated vertical energy gaps (in eV), thermodynamic integrals (in eV), and pKa values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>η=0.0</th>
<th>η=0.5</th>
<th>η=1.0</th>
<th>ΔA</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlY(H₂O)₅(H₂O)</td>
<td>20.32±0.01</td>
<td>18.02±0.03</td>
<td>13.65±0.01</td>
<td>17.67±0.02</td>
<td>8.0±0.8</td>
</tr>
<tr>
<td>AlY(H₂O)₃(OH)(H₂O)</td>
<td>20.33±0.04</td>
<td>18.15±0.05</td>
<td>13.03±0.02</td>
<td>17.66±0.04</td>
<td>7.8±1.2</td>
</tr>
<tr>
<td>AlH₃O⁺</td>
<td>19.54±0.01</td>
<td>17.34±0.04</td>
<td>13.12±0.04</td>
<td>17.00±0.03</td>
<td></td>
</tr>
<tr>
<td>AlSiY(H₂O)₃(H₂O)</td>
<td>20.12±0.05</td>
<td>18.07±0.04</td>
<td>13.42±0.01</td>
<td>17.64±0.04</td>
<td>8.2±1.0</td>
</tr>
<tr>
<td>AlSiY(H₂O)₂(OH)(H₂O)</td>
<td>20.36±0.04</td>
<td>17.85±0.01</td>
<td>13.70±0.03</td>
<td>17.58±0.02</td>
<td>7.2±0.7</td>
</tr>
<tr>
<td>AlSiH₃O⁺</td>
<td>19.66±0.04</td>
<td>17.11±0.01</td>
<td>13.67±0.04</td>
<td>16.96±0.02</td>
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</tr>
<tr>
<td>AlSc(H₂O)₃(H₂O)</td>
<td>19.69±0.01</td>
<td>17.76±0.04</td>
<td>14.33±0.05</td>
<td>17.51±0.04</td>
<td>8.4±1.0</td>
</tr>
<tr>
<td>AlSc(H₂O)₂(OH)(H₂O)</td>
<td>20.15±0.02</td>
<td>17.95±0.01</td>
<td>13.07±0.04</td>
<td>17.50±0.01</td>
<td>8.2±0.5</td>
</tr>
<tr>
<td>AlH₃O⁺</td>
<td>19.54±0.01</td>
<td>17.06±0.02</td>
<td>13.14±0.04</td>
<td>16.82±0.02</td>
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</tr>
<tr>
<td>VSc(H₂O)(H₂O)</td>
<td>19.34±0.05</td>
<td>17.52±0.02</td>
<td>12.89±0.02</td>
<td>17.05±0.03</td>
<td>-6.5±1.0</td>
</tr>
<tr>
<td>VSc(OH)(H₂O)</td>
<td>19.77±0.02</td>
<td>17.71±0.04</td>
<td>13.98±0.02</td>
<td>17.43±0.03</td>
<td>-0.2±1.0</td>
</tr>
<tr>
<td>VH₃O⁺</td>
<td>19.57±0.03</td>
<td>17.66±0.03</td>
<td>13.26±0.02</td>
<td>17.25±0.03</td>
<td></td>
</tr>
</tbody>
</table>

The superscript “Al”, “AlSi”, and “V” stand for complexes on the Al(OH)₂ site, Al(OH)₂SiO site, and vacancy site, respectively.