Molecular Dynamics Simulation of Ion Adsorption and Ligand Exchange on an Orthoclase Surface

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ABSTRACT: Orthoclase (K-feldspar) is one of the natural inorganic materials, which shows remarkable potential toward removing heavy metal ions from aqueous solutions. Understanding the interactions of the orthoclase and metal ions is important in the treatment of saline wastewater. In this paper, molecular dynamics simulations were used to prove the adsorption of different ions onto orthoclase. The adsorption isotherms show that orthoclase has remarkable efficiency in the removal of cations at low ion concentrations. Aluminol groups are the preferential adsorption sites of cations due to higher negative charges. The adsorption types and adsorption sites are influenced by the valence, radius, and hydration stability of ions. Monovalent cations can be adsorbed in the cavities, whereas divalent cations cannot. The hydrated cation may form an outer-sphere complex or an inner-sphere complex in association with the loss of hydration water. Na⁺, K⁺, and Ca²⁺ ions mainly undergo inner-sphere adsorption and Mg²⁺ ions prefer outer-sphere adsorption. On the basis of simulation results, the mechanism of ion removal in the presence of orthoclase is demonstrated at a molecular level.

INTRODUCTION

The presence of various organic and inorganic pollutants in earth’s water supplies is a serious threat to human life and the environment due to their toxicity. Several techniques such as adsorption, extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, ion exchange, and membrane processes are proposed for the handling of wastewater pollution and removing heavy metals from industrial wastewater. The selection of alternative low-cost materials such as adsorbents for the removal of inorganic ions has been emphasized.1−8 Recently, clay minerals are being widely used for wastewater handling9−12 because of the features such as high ion exchange capacity, a large surface area, chemical and mechanical stability, low cost, easy manipulation, as well as high abundance and harmlessness to the environment. Many research studies showed that Pb(II), Ni(II), Cd(II), Cu(II), Zn(II), and U(V) ions may be removed by natural minerals from aqueous solutions.6−13 The evaluation of clay efficiency in the removal of metals is expected to deepen the knowledge about the mechanisms.

The distribution of ions is determined by the competition between water and ions for adsorption sites.14−17 The interfacial water structure has a significant effect on the adsorption of colloidal particles and ions. It was demonstrated that the properties of water close to the solid surfaces are different from those in the solution. For instance, the self-diffusion coefficient of water reduces significantly in a calcite hydration layer.14−21 Cs⁺ ions prefer to be adsorbed in inner-sphere coordination close to the smectite surface because of the large ionic radius and low hydration energy of Cs⁺.22 Not only was the dipole orientation of water molecules on the surface investigated, but those in the interlayer of minerals also...
was studied.23−36 The dipole of water molecules plays an important role in determining the basal spacing and the formation of stable H-bonding networks at a mineral surface.30 Thus, it is necessary to understand the mechanism of H2O−ion−mineral interaction.

In particular, feldspars are one of the natural inorganic materials and show remarkable potential toward removing heavy metal ions from aqueous solutions. Natural feldspars have many advantages, such as high removal efficiency of heavy metal ions, low cost, huge quantity, and environmental friendliness.

In the past decades, there have been numerous experimental studies on the structure, component, and properties of feldspar surface. The high-resolution in situ X-ray specular reflectivity was used by Fenter and co-workers to measure the structures of an orthoclase (K-feldspar) cleavage surface in contact with deionized water.18,19 Fenter et al. observed that the activation energies for orthoclase dissolution were in proportion to the Al site density of orthoclase.15 The Al tetrahedral site is often found to be the reactive site.37−39 Al-Anber reported that the maximum removal of Fe(III) ions from aqueous solutions was 93% using natural feldspar.4 Meanwhile, it was found that orthoclase could sequester U(VI) preferentially from the contaminated water solution in its capillary-size intragrain fractures.12,13 The mobility of charged aqueous species decreases as it approaches the surface.12 Recent experimental study by Maryam et al. focused on the adsorption of As(V) on feldspar mineral.7 The results indicated that the feldspars with higher aluminum content show higher adsorption capacity. It is due to the electrostatic forces between As(V) and the terminal aluminol groups of feldspar in an acidic medium.7 Thus, it could be seen that adsorption, ion exchange, and the interfacial structure are closely related to the component and the structure of orthoclase.

Molecular simulations have become a powerful method for the explanation of experimental phenomena at a nanoscale.14−37 Kerisit et al. studied H2O−orthoclase interactions by molecular dynamics simulations.2 The electron density distribution, interfacial water structure, coordination number, and adsorption sites were in good agreement with experimental measurements. By far, there have been many computational MD studies about the interfacial effect.14,28−37 These studies computationally proved that the self-diffusion coefficient of water and those of electrolyte ions at the orthoclase surface are reduced within the range of approximately 5 nm. The presence of ions reduced the water diffusivity.3 Simulations of the adsorption of uranyl complexes at a H2O−orthoclase interface revealed a large favorable free energy of adsorption for UO2−24− and UO2CO3, which were chemically adsorbed to the surface. Uranium atoms formed chemical bonds with hydroxyl oxygen of the surface.5,30 K+ ions in the vicinity of adsorbing species dissolved from the surface into the aqueous solution when UO2−23− was adsorbed on the surface on the account of its net positive charge. However, neutral UO2CO3 adsorbed on the surface due to a net dipole of the surface functional groups.5,30 Cations and polar molecules were attracted to the orthoclase surface by long-range electrostatic forces. Consequently, cations and positive groups of polar molecules accumulated at the surface, and K+ ions were released. These processes are determined by the structure and composition of orthoclase. Ab initio calculations and NMR measurements showed that hydrolysis of Si−O−Al bonds is proton-promoted.38,39

Nowadays, more attention is being focused on the direct observations on the mineral surface. By molecular modeling, it is possible to extract information on structural properties, which are not easy to be obtained from experiments. In this paper, MD simulations were performed to investigate the process of ion adsorption and ion exchange in orthoclase. The influence of interfacial water on ion adsorption was also investigated. Our attention is focused on the interfacial structure, adsorption, distribution, and interaction of ions and water at the nanoscale. On the basis of simulation results, the mechanism of ion removal in the presence of orthoclase was demonstrated at a molecular level.

### RESULTS AND DISCUSSION

#### Distribution of Ions.

All of the atom-type symbols and atomic charges used in this work are shown in Table 1.

**Table 1. Atom-Type Symbols and Atomic Charges Used In This Work**

| species        | symbol | charge (e) |
|----------------|--------|------------|
| Si             | st     | 2.10000    |
| Al             | at     | 1.57500    |
| K+             | K      | 1.00000    |
| Na+            | Na     | 1.00000    |
| Mg2+           | Mg     | 2.00000    |
| Ca2+           | Ca     | 2.00000    |
| Cl−             | Cl−    | −1.00000   |
| water oxygen   | OW−    | −0.84760   |
| water hydrogen | HW     | 0.42380    |
| bridging oxygen (Si−O−Si) | ob | −1.05000 |
| bridging oxygen with substitution (Si−O−Al) | obts | −1.16875 |
| hydroxyl oxygen (Si−O−H) | ob | −0.95000 |
| hydroxyl oxygen with substitution (Al−O−H) | ohs | −1.06875 |
| hydroxyl hydrogen (Si/Al−O−H) | ho | 0.42500 |

Previous research showed that cations and polar molecules may be attracted to oppositely charged orthoclase surfaces by long-range electrostatic forces.30 A preferential accumulation of cations and positively charged end of polar molecules was near the surface.32 At the beginning of the simulations, all of the cations and Cl− ions were in the solution. At the end of the simulations, some cations accumulated on the orthoclase surface for all four systems.

The range in adsorbent−adsorbate specificity is reflected in the adsorption of ions at the particle−water interface. The adsorption types of ions could be divided into outer-sphere adsorption and inner-sphere adsorption. Outer-sphere adsorption is the case where one or more H2O molecules are interposed between the ions and surface. The inner-sphere adsorption is the case where no H2O molecules are interposed between the ions and surface (Figure 1).

As shown in Table 2, almost half of the cations (about 25 for the monovalent cations and 10−13 for the divalent cations) are in the Stern layer after 50 ns MD simulation. At the beginning of the simulations, K+ ions of orthoclase (62 for K+ ions of orthoclase) coordinated with the lattice oxygen. Ions (Na+, K+, Ca2+, Mg2+, and Cl−) were hydrated in the solution. Then, the hydrated cations (Na+, K+, Ca2+, and Mg2+) were attracted to an oppositely charged orthoclase surface. Here, the cations lost their hydration water and were adsorbed on the orthoclase surface. Cl− ions and adsorbed cations formed an electric double layer at the orthoclase surface (Figures 2 and
3). Meanwhile, about 15 K⁺ ions desorbed from the orthoclase and got hydrated into the solution (Table 2) under the electrostatic force. During the ion exchange process, cations lost their hydration water and K⁺ ions got hydrated. Thus, water molecules were directly involved in the ion exchange process, which is in close agreement with previous simulation results. The remaining ions (about half of cations and most of the anions) were not adsorbed. These ions were distributed uniformly in the diffuse layer (Table 2).

The valence of cations affects the adsorption processes. The stern layer contains both inner-sphere and outer-sphere complexes, but the number of inner-sphere and outer-sphere complexes is different for different cations, as shown in Table 2 and Figure 3. The monovalent cations predominantly are adsorbed inside the stern layer as inner-sphere coordination (~20 for Na⁺ and ~14 for K⁺ in Table 2). In monovalent systems, the charge density profiles of cations consist of two sharp peaks (Figure 2). The first peak shows that the monovalent cations are adsorbed in the cavities (the structures are shown in Figures S1 and S2). The second peak shows that the monovalent cations are adsorbed out of the cavities. However, in divalent systems, there is only one peak (Figure 3). It means the divalent cations are adsorbed predominantly out of the cavities (~10 for Mg²⁺ and ~13 for Ca²⁺ in Table 2, Figures S3 and S4). This is because the charge deficiency of orthoclase is originally compensated by monovalent cations. If the cavities are filled with divalent cations, a large force is required to overcome the excess electrostatic repulsion between the divalent cations and the aluminosilicate framework (Table 2). Thus, only monovalent cations could be adsorbed in the cavities.

The adsorption isotherms of cations are shown in Figure 4. The changes of four curves have a similar tendency. The amount of adsorbed cations increased as the concentration of cations increased. When the concentration is below 0.309 mol/L, over 50% cations are adsorbed at the orthoclase surface. Thus, orthoclase has remarkable potential for removing heavy metal ions from aqueous solutions. The removal efficiency is relatively high at low concentrations.

Most monovalent cations present inner-sphere adsorption (Table 2) because the attraction between cations and negatively charged orthoclase is relatively strong, and the attraction force between cations and water is weak. The shorter radii between monovalent cations and lattice oxygen with substitution (1st max: Na⁺−obts, Na⁺−ohs <Na⁺−OW; K⁺−obts is close to K⁺−OW, K⁺−ohs <K⁺−OW in Table 3) indicate that the monovalent cations prefer to coordinate with lattice oxygen as inner-sphere adsorption rather than water. In comparison to K⁺ ions, Na⁺ ions form shorter bonds with

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**Table 2. Distribution of Ions in Each System**

| species | in surface cavities | out of the cavities | diffuse layer | total |
|---------|---------------------|---------------------|---------------|-------|
| Na⁺     | 6.133               | 13.548              | 5.714         | 24.610 | 50.005 |
| K⁺      | 3.002               | 11.344              | 5.060         | 30.574 | 50.000 |
| Mg²⁺    | 0.000               | 0.000               | 10.696        | 14.303 | 24.999 |
| Ca²⁺    | 0.000               | 13.000              | 0.189         | 11.801 | 24.990 |

K⁺ ions of Orthoclase In Each System

| origin | NaCl | KCl | MgCl₂ | CaCl₂ |
|--------|------|-----|-------|-------|
| 45.000 | 43.045 | 45.141 | 43.016 | 44.832 |
| 17.000 | 2.842  | 2.558  | 4.643  | 3.140  |
| 0.000  | 16.117 | 14.251 | 14.341 | 14.112 |
| 0.000  | 62.004 | 61.950 | 62.000 | 62.084 |
lattice oxygen (1st max: Na+-lattice oxygen < K+-lattice oxygen in Table 3), which means stronger Coulombic interaction between them. Thus, the absorbance of Na+ is relatively large. The first peak of Na+ in Figure 2 has a stronger intensity than that of K+. This result is also supported by the number of cations in the cavities shown in Table 2.

For the divalent system, Ca2+ ions prefer to coordinate with oh and obts atoms as inner-sphere adsorption (Table 3). However, Mg2+ ions prefer to be adsorbed as outer-sphere adsorption owing to the strong electrostatic attraction between H2O and Mg2+ ions (Table 3). In other words, the affinity for an adsorbent increases with decreasing ionic potential (IP) for a given valence42 (IP Ca2+ = 20 and IP Mg2+ = 48).

In Table 3, OW (surface) and OW (solution) represent the hydration coordination numbers of cations adsorbed on the surface and those of cations in solution, respectively. Total represents the sum of the coordination numbers in the inner-sphere. In Na+, K+, and Ca2+ systems, the coordination number of OW (solution) is more than that of OW (surface), which reveals that the hydrated cations lose their coordinated water during the inner-sphere adsorption process. In a Mg2+ system, values of OW (solution) and OW (surface) are almost the same, and Mg2+ can only be adsorbed as outer-sphere adsorption. Thus, the adsorption of ions at the interface is not only determined by the surface but also the hydration ability of the cations. The distribution of water is discussed as follows.

**Distribution of Water.** The adsorption of cations on an orthoclase surface is closely related to the behavior of water at the interface. Competitive adsorption between H2O and ions determined the interfacial ion distribution. At the end of the simulations, the interfacial water exhibits similar distribution. Atomic number density of the four systems consists of two peaks at 2.675 and 2.975 nm (Figure 5a). It agrees with the experimental data obtained by Fenter et al.18 Water molecules are adsorbed on the surface through H bonding, resulting in the highest H2O density close to the surface. Then, the density decreases above 2.975 nm until the bulk density is reached.

![Figure 3. Charge density profiles of ions in divalent systems.](image)

![Figure 4. Adsorption isotherms of cations at 300 K.](image)

Table 3. Radial Distribution Functions between the Cations and Five Different Oxygen Types: ob, obts, oh, ohs, and OW

| species | Na+ | K+ | Mg2+ | Ca2+ |
|---------|-----|----|------|------|
|         | 1st max | n     | 1st max | n     | 1st max | n     | 1st max | n     | 1st max | n     |
| ob      | 0.2335  | 0.2587 (inner-sphere) | 0.2945  | 1.9398 (inner-sphere) | 0.4955  | 2.8643 (uncoordinated) | 0.4225  | 1.1482 (uncoordinated) |
| obts    | 0.2265  | 0.9406 (inner-sphere) | 0.2835  | 1.2686 (inner-sphere) | 0.3995  | 0.9995 (outer-sphere) | 0.2505  | 0.5669 (inner-sphere) |
| oh      | 0.2395  | 0.2916 (inner-sphere) | 0.2875  | 0.9523 (inner-sphere) | 0.4405  | 2.0111 (uncoordinated) | 0.4385  | 2.0695 (uncoordinated) |
| ohs     | 0.2285  | 0.7775 (inner-sphere) | 0.2795  | 0.9792 (inner-sphere) | 0.3805  | 0.9962 (outer-sphere) | 0.2375  | 0.9978 (inner-sphere) |
| OW (surface) | 0.2335  | 3.1345 | 5.4029 | 3.7129 | 0.1985  | 5.7631 | 0.2465  | 6.2951 |
| total   | 0.2355  | 5.5739 | 0.2825  | 7.2252 | 0.1975  | 5.7665 | 0.2485  | 7.9473 |

*Shown in the table are the position of the first maximum and the coordination numbers at the first minimum.*
Figure 5b shows the charge density profiles of H$_2$O in each system, which could present the partial charge of different atoms. The orientation of the H$_2$O molecules in the near-surface region ($z < 3.3$ nm) is well-ordered (Figure 5b). Positively charged H of H$_2$O molecules orients toward the surface and their negatively charged O away from the surface. This orientation is because H-bonds between water and the orthoclase surface are stronger than those among the water.

Figures 5b and 6 indicate that the majority of H$_2$O molecules in the stern layer are arranged with 2 H atoms pointing toward the surface. In the diffuse layer, they are principally arranged with only one H atom pointing toward the surface. The dipole vector of H$_2$O molecules in the stern later mostly is perpendicular to the surface, and the dipole vector of H$_2$O molecules in the diffuse layer is mostly parallel to the surface. This is consistent with the charge density profiles of H$_2$O and previous studies of clay minerals.\textsuperscript{31–36} Because of the H-bond interaction and electrostatic attraction, the interfacial H$_2$O molecules formed two compact layers. Therefore, the diffusion of water molecules along the surface is slowed down compared to those in the solution, which is in reasonable agreement with the simulation results.\textsuperscript{4}

The different lattice oxygen–water radial distribution functions (RDF) obtained from the NaCl system are shown in Figure 7. Because the number of water molecules on the surface is far more than that of ions, the influence of ions on water distribution is negligible. The RDFs of each system are identical. Thus, only a NaCl system is discussed here. The bridging oxygen (ob)–water hydrogen (HW) RDF shows a flat peak at 0.18 nm. The value of the bridging oxygen (ob)–water oxygen (OW) at 0.27 nm is 0 (Figure 7a), which is different from others. In addition, the coordination numbers of ob–HW/OW is smaller than others, as shown in Table 4. This result indicates that the interaction between water and ob is weak, and ob atoms can barely attract the water to the surface.

The first sharp peak is at 0.165 nm and the second one is at 0.325 nm in bridging oxygen with substitution (obts)–HW RDF (Figure 7b). The distance between the two peaks is 0.16 nm, which is almost equal to the distance between two hydrogens in an SPC/E model (about 0.163 nm). The first peak in obts–HW is at 0.165 nm and the first peak in obts–OW is at 0.265 nm. The distance between the two peaks is 0.1 nm, which is equal to the bond length of the SPC/E model (0.1 nm). It reveals that water molecules are arranged with one H atom pointing to obts and the other one away from obts. As shown in Table 4, the coordination numbers of HW/OW–obts give the same value. It means that the H$_2$O molecules preferred to donate $\sim 1$ H-bond to obts, as shown in Figure 7b.\textsuperscript{47}

The first peak at 0.275 nm of hydroxyl oxygen (oh)–OW RDF is about three times as tall as that of hydroxyl oxygen (oh)–HW RDF (Figure 7c). The coordination number of oh–OW is about three times that of oh–HW (Table 4). The first oh–OW peak is at 0.275 nm under the maximum donor–acceptor distance of the H-bond (0.35 nm). It suggests that most of the silanol group could donate $\sim 1$ H-bond to water. Only a few oh could accept the H-bond from H$_2$O. The first peak of hydroxyl oxygen with substitution (ohs)–OW RDF is a little higher than that of hydroxyl oxygen with substitution (ohs)–HW RDF (Figure 7d). The coordination number of ohs–OW is more than that of ohs–HW (Table 4). It indicates that the water molecules around the ohs are both acceptors and donors.

According to the coordination numbers in Table 4, the majority of H$_2$O molecules are still a donor, which suggests that the electrostatic attraction of ohs is stronger than any other oxygen atoms in an orthoclase slab. Finally, the intensity of the first peak of each oxygen–HW RDF in Figure 7...
confirmed that the electrostatic attraction is in following order: ohs > oh > obts > ob. The H-bond numbers and lifetimes are shown in Table 5. A geometrical criterion of a H-bond is with a maximum donor−acceptor (lattice oxygen−OW) distance of 0.35 nm and a donor−hydrogen−acceptor angle of 30°. Because water molecules in the solution are surrounded by other water molecules, the H-bond number of water is more than that of lattice oxygen. The H-bond lifetimes reveal the H-bond stability in the following order: obts > ohs > oh > water > ob. However, the H-bond number of oh and ohs is more than that of obts. Because of steric hindrance from the surface functional groups, only a minority of water molecules can form H-bonds with obts. Most of interfacial water prefer to form a H-bond with oh and ohs. Each ohs atom forms the most H-bonds (2.156 H-bonds on average). Thus, ohs is most favorable for adsorption of cations. The value of the H-bond number and lifetime of ob is the smallest, which indicates that the H-bond of ob−water is the weakest.

In summary, the dipole moment of H2O is induced by a charged surface, which also forms an energy barrier. In the case of inner-sphere coordination, the hydrated cations should lose one or two water and the H-bond between water and orthoclase must be broken; otherwise, the cations will be adsorbed as outer-sphere coordination.

**Interaction between H2O−Ion−Orthoclase.** The adsorption of cations on an orthoclase surface mainly depends on the Coulombic interaction because ions, orthoclase, and water are charged or polar molecules. Previous analysis indicated that the electrostatic attraction force between the cations and lattice oxygen is favorable to the adsorption of cations on the orthoclase surface. Meanwhile, the electrostatic repulsion between cations and the Si/Al atoms of the surface inhibits the adsorption process.

![Figure 7](https://doi.org/10.1021/acsomega.1c00826)
As shown in Figure 8, the interaction energy of a cation–aluminosilicate framework is negative and decreases. It indicates that the driving force of cation adsorption is the Coulombic attraction between cations and the aluminosilicate framework. The interaction energy of water–cation is negative and increases slightly. It indicates that the resistance of cation adsorption is the Coulombic attraction between water and cations.

Na\(^+,\) K\(^+,\) and Ca\(^+2\) ions diffused to the orthoclase surface and were all adsorbed as inner-sphere adsorption. Thus, the interaction energy of a Na/K\(^+\)/Ca\(^+2\)–aluminosilicate framework decreases apparently. Na\(^+,\) K\(^+,\) and Ca\(^+2\) ions lost 1–3 hydration water during the adsorption process (Na\(^+\)–OW in solution: 5.5739, Na\(^+\)–OW at the interface: 3.1345, K\(^+\)–OW in solution: 7.2252, K\(^+\)–OW at the interface 3.7129, Ca\(^+2\)–OW in solution: 7.9473, and Ca\(^+2\)–OW at the interface 6.2951 in Table 3). Thus, the interaction energy of Na/K\(^+\)/Ca\(^+2\)–water increases slightly.

Mg\(^+2\) ions diffused to the orthoclase surface and were only adsorbed as outer-sphere adsorption. The distance between Mg–orthoclase is longer than that between Na/K\(^+\)/Ca\(^+2\)–orthoclase. Thus, the interaction energy of a Mg–aluminosilicate framework decreases slightly. During the adsorption process, the hydration number of Mg\(^+2\) is barely changed. Therefore, the interaction energy of Mg–water remains the same.

The interaction energy of cation–surface hydroxyl group is also important. Monovalent cations are adsorbed in the cavities. The interaction energy of monovalent cation–surface hydroxyl group (Na/K\(^+\)/Al/SiOH) is positive (Figure 9). There is a Coulombic repulsion between monovalent cations and Al or Si atoms of a surface hydroxyl group. The interaction energy of Na/K\(^+\)/Al/SiOH is lower than that of Na/K\(^+\)/SiOH, which shows that electrostatic repulsion from SiOH is stronger than that from AlOH. Thus, aluminol groups are the main adsorption site for monovalent cations.

The interaction energy of Na/K\(^+\)/Al/SiOH is less than 1 × 10\(^3\) kJ/mol (Figure 9), and that of a Na/K\(^+\)/aluminosilicate framework is greater than −2.5 × 10\(^3\) kJ/mol (Figure 8). Their sum is negative, which indicates that the driving force between the Na/K\(^+\)/aluminosilicate framework is stronger than the resistance between Na/K/Al/Si of the surface hydroxyl group.

Divalent cations are adsorbed out of the cavities. The interaction energy of divalent cation–surface hydroxyl group (Mg/Ca/Al/SiOH) is negative (Figure 9). It implies that there is a Coulombic attraction between divalent cations and oxygen atoms of the surface hydroxyl group (oh and ohs). The interaction energy of Mg/Ca/AlOH is lower than that of Mg/Ca/SiOH, which reveals that electrostatic attraction from ohs is stronger than that from oh. Thus, aluminol groups are main adsorption sites for divalent cations as well. It is also confirmed by the fact that the 1st max distance derived from RDF between ohs and ions (Table 3) is shorter than others.

The changes of the cation–Al/SiOH energy are different because the strength of resistance is different. The Coulombic attraction between Ca/AlOH is stronger than the Coulombic attraction between Ca–water (the first max value of Ca–ohs: 0.2375 is smaller than that of Ca–OW: 0.2465 in Table 3). Thus, Ca\(^+2\) ions can be adsorbed as inner-sphere adsorption. The monovalent cations are adsorbed in the cavities near the Si/Al atoms. The energy between monovalent cations and Si/AlOH is positive (Figure 9), which reveals the Coulombic repulsion between Si/Al and monovalent cations. Ca\(^+2\) ions are adsorbed out of the cavities. They coordinate with the negatively charged ohs atoms. Thus, the Coulombic energy of Ca/AlOH is negative (Figure 9). The Coulombic repulsion between Ca–Al/Si is larger than that between monovalent cations and Al/Si because the divalent cations possess more positive charge. The adsorption of Ca\(^+2\) into the cavities is inhibited by the electrostatic repulsion between Ca–Si/Al. Thus, Ca\(^+2\) can only be adsorbed out of the cavities away from Si/Al and coordinate with ohs, resulting in the negative Coulombic energy between Ca–AlOH.

The sum of Coulombic attraction between Mg–AlOH and the Coulombic attraction between a Mg–aluminosilicate framework is weaker than the Coulombic attraction between Mg–water (the first max value of Mg–OW is the smallest in Table 3). Thus, Mg\(^+2\) ions cannot lose their hydration water, and they can only be adsorbed as outer-sphere adsorption. The tendency of interaction energy of water–K and K–orthoclase in each system is similar, as shown in Figure 10. The interaction energy of water–K decreases, which reveals that the driving force of K desorption is the hydration effect. The interaction energy of K–orthoclase increases, which reveals...
that the resistance of K⁺ desorption is the Coulombic attraction between K⁺ and orthoclase. The change of interaction energy of water⁻⁻K and K⁻⁻orthoclase in a Na⁺ system is larger than that in other systems. It indicates that more K⁺ ions are exchanged into the solution by Na⁺. It is consistent with the data shown in Table 2. Consequently, the interaction energy analyses are further proof of the simulation results. First, the divalent cations cannot be adsorbed in the cavities because of the strong electrostatic repulsion between the divalent cations and the Si/Al. Second, water molecules are directly involved in the ion exchange process and have a significant effect on the process.

**CONCLUSIONS**

In summary, the simulations provided insights into the microscopic surface effects on a H₂O⁻⁻ion⁻⁻orthoclase system. The results demonstrated that the adsorption type and site of different ions are influenced by the valence, ionic radius, hydration stability, the component, and the structure of the surface.

The adsorption isotherms showed that orthoclase has a remarkable efficiency in the removal of cations from wastewater with low ion concentration. The high valence and small ionic radius result in a strong interaction between cations and the surface and a more stable hydration layer. When the attraction between cations (such as Mg²⁺) and H₂O is stronger than that between cations and lattice oxygen, the cations are adsorbed as outer-sphere coordination. Otherwise, it would be inner-sphere coordination (such as Na⁺, K⁺, and Ca²⁺). Only monovalent cations could be adsorbed in the cavities. The preferential adsorption site is determined by the composition and the structure. Aluminol groups are the main adsorption sites by virtue of higher negative charges. Furthermore, the competitive adsorption between H₂O and ions affects the interfacial ionic distribution. The main factors and interaction mechanism of ion adsorption and ligand exchange on orthoclase were revealed in this work. These results provide theoretical guidance for water treatment, the removal of heavy metals, and uranium remediation.

**COMPUTATIONAL METHODS**

**Structure of Orthoclase.** Orthoclase is a potassium end-member of alkali feldspar, a framework silicate. AIO₄ and SiO₄ tetrahedra form a three-dimensional lattice in which K⁺ ions fill cavities to charge compensate for Al substitution of Si with Al. The lattice parameters of orthoclase in this work were derived from the experimental data by Kimata et al., which are a = 0.8600 nm, b = 1.3005 nm, c = 0.7193 nm, α = 90°, β = 116.03°, and γ = 90°. Previous research reported that the (0 0 1) and (0 1 0) surfaces showed similarities in the extent of H₂O ordering at the interface, the activation energies for H₂O and K⁺ desorption, and adsorption localization of interfacial species. In this work, an orthoclase unit cell was cleaved along the (0 0 1) surface. The final (0 0 1) slab area was 5.16 × 5.202 nm² and the thickness was approximately 2.5 nm. The
nonbridging oxygens of the mineral slab were saturated as hydroxyl groups. The number of silanol and aluminol groups is equal on the surface. The net charge of the structure was balanced by adding 288 K⁺ ions. The system was first minimized using the steepest descent method. Then, MD simulation under canonical ensemble was carried out for 10 ns. Periodic boundary conditions were applied in the x, y, and z directions. Figure 11 shows the equilibrium structure of orthoclase.

Construction of Simulation Systems. To simulate the properties and the structure of an electrolyte solution on a surface and in bulk, 5000 H₂O molecules were added above the orthoclase surface. The solution slab was about 5 nm in thickness. Four systems containing different cations were investigated in this work. A total of 50 Cl⁻ ions were added to the four systems. The net charge of each system was balanced by adding 50 Na⁺ ions, 50 K⁺ ions, 25 Mg²⁺ ions, and 25 Ca²⁺ ions, respectively. The concentration of monovalent ions and divalent ions was 0.618 and 0.309 mol/L, respectively.

The simulations were initialized by minimizing the energies of the initial configurations with the steepest descent method. After that, all of the molecular dynamics simulations were performed for 50 ns in the canonical ensemble at 300 K. A time step of 1 fs was used to integrate the equations of motion. In the simulation, a GROMACS free software package (version 2019.3) was employed. All parameters were set the same as previously reported by Kerisit et al., which showed good agreement with the experimental data of Fenter and co-workers. The extended simple point charge (SPC/E) model was adopted for all H₂O molecules, and the interatomic interactions for an orthoclase slab and a Mg²⁺ ion were calculated using the CLAYFF force field and the INTERFACE force field that is well-tested in molecular simulations of clay minerals and related materials. The schematic plot of the molecular dynamics simulations workflow is shown in Figure 12.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00826.

Conformation snapshots of various adsorption types and the hydration shell of Na⁺, conformation snapshots of various adsorption types and the hydration shell of K⁺, conformation snapshots of various adsorption types and the hydration shell of Ca²⁺, and conformation snapshots of various adsorption types and the hydration shell of Mg²⁺ (PDF)
Notes
The authors declare no competing financial interest.
The data that support the findings of this study are available
within the article and its supporting material.

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■ REFERENCES
(1) Gaied, M. E.; Gallala, W. Beneficiation of feldspar ore
for application in the ceramic industry: Influence of composition on the
physical characteristics. Arabian J. Chem. 2015, 8, 186–190.
(2) Kerisit, S.; Liu, C.; Iton, E. S. Molecular dynamics simulations of the
orthoclase (001) and (010)-water interfaces. Geochim. Cosmochim. Acta
2008, 72, 1481–1497.
(3) Kerisit, S.; Liu, C. Molecular Simulations of Water and Ion
Diffusion in Nanosized Mineral Fractures. Environ. Sci. Technol. 2009,
43, 777–782.
(4) Al-Anber, M. A. Adsorption of ferric ions onto natural feldspar:
kinetic modeling and adsorption isotherm. Int. J. Environ. Sci. Technol.
2015, 12, 139–150.
(5) Kerisit, S.; Liu, C. Diffusion and Adsorption of Uryanl Carbonate
Species in Nanosized Minerat Fractures. Environ. Sci. Technol. 2012,
46, 1652–1640.
(6) Yu, S.; Zhang, C.; Ma, L.; Fang, Q.; Chen, G. Experimental and
DFT studies on the characteristics of PbO/PbCl2 adsorption by Si/
Al-based sorbents in the simulated flue gas. J. Hazard. Mater. 2020,
407, No. 124742.
(7) Yazdani, M.; Tuttijärvi, T.; Bhatnagar, A.; Vahala, R. Adsorptive
removal of arsenic(V) from aqueous phase by feldspars: Kinetics,
mechanism, and thermodynamic aspects of adsorption. J. Mol. Liq.
2016, 214, 149–156.
(8) Fraga, C. G. Relevance, essentiality and toxicity of trace elements
in human health. Mol Aspects Med 2005, 26, 235–244.
(9) Liu, L. H.; Tang, C. W.; Peng, Y. L.; Pan, F.; Lin, H.; Zhang, X. H.;
Chhuon, K. Modification of bentonite by Al/Mg-impregnated hydroxy for Cu2+,Cd2+, and Pb2+ removal from aqueous solutions. Desalin. Water Treat. 2019, 147, 243–254.
(10) Aşıçi, Y.; Nurbas, M.; Sağ Açikel, Y. A comparative study for
the sorption of Cd(II) by K-feldspar and sepiolite as soil components, and
the recovery of Cd(II) using rhamnolipid biosurfactant. J. Environ.
Manage. 2008, 88, 383–392.
(11) Sun, Z. M.; Qu, X. S.; Wang, G. F.; Zheng, S. L.; Frost, R. L.
Removal characteristics of ammonium nitrogen from wastewater by modified Ca-bentonites. Appl. Clay Sci. 2015, 107, 46–51.
(12) Liu, C. X.; Zachara, J. M.; Qafoku, O.; McKinley, J. P.; Heald, S. M.;
Wang, Z. M. Dissolution of uranil microprecipitates in subsurface sediments at Hanford site, USA. Geochim. Cosmochim. Acta 2004,
68, 4519–4537.
(13) McKinley, J. P.; Zachara, J. M.; Liu, C. X.; Heald, S. C.;
Prenitzer, B. I.; Kempshall, B. W. Microscale controls on the fate of
contaminant uranium in the vadose zone, Hanford Site, Washington.
Geochim. Cosmochim. Acta 2006, 70, 1873–1887.
(14) Kerisit, S.; Parker, S. C. Free energy of adsorption of water and
metal ions on the (1014) calcite surface. J. Am. Chem. Soc. 2004, 126,
10152–10161.
(15) Fenter, P.; Geissbuhler, P.; DiMasi, E.; Srajer, G.; Sorensen, L. B.;
Sturchio, N. C. Surface speciation of calcite observed in situ by high-
resolution X-ray reflectivity. Geochim. Cosmochim. Acta 2000, 64,
1221–1228.
(16) Israelachvili, J.; Wennerstrom, H. Role of hydration and water
structure in biological and colloidal interactions. Nature 1996, 379,
219–225.
(17) Park, C.; Fenter, P. A.; Nagy, K. L.; Sturchio, N. C. Hydration and
distribution of ions at the mica-water interface. Phys. Rev. Lett. 2006,
97, No. 016101.
(18) Fenter, P.; Cheng, L.; Park, C.; Zhang, Z.; Sturchio, N. C.
Structure of the orthoclase (001)- and (010)-water interfaces by high-
resolution X-ray reflectivity. Geochim. Cosmochim. Acta 2003, 67,
4267–4275.
(19) Fenter, P.; Park, C.; Cheng, L.; Zhang, Z.; Krekeler, M. P. S.;
Sturchio, N. C. Orthoclase dissolution kinetics probed by in situ X-ray
reflectivity: Effects of temperature, pH, and crystal orientation.
Geochim. Cosmochim. Acta 2003, 67, 197–211.
(20) Rotenberg, B.; Marry, V.; Malikova, N.; Turq, P. Molecular
simulation of aqueous solutions at clay surfaces. J. Phys.: Condens.
Matter 2010, 22, No. 284114.
(21) Ngouana, W. B. F.; Kalinichev, A. G. Structural Arrangements
of Isomorphic Substitutions in Smeectites: Molecular Simulation of the
Swelling Properties, Inter layer Structure, and Dynamics of Hydrated
Cs-Montmorillonite Revisited with New Clay Models. J. Phys. Chem.
C 2014, 118, 12758–12773.
(22) Liu, X.; Lu, X.; Wang, R.; Zhou, H. Effects of layer-charge
distribution on the thermodynamic and microscopic properties of Cs-
smectite. Geochim. Cosmochim. Acta 2008, 72, 1837–1847.
(23) Morrow, C. P.; Yazaydin, A. Ö.; Krishnan, M.; Bowers, G. M.;
Kalinichev, A. G.; Kirkpatrick, R. J. Structure, Energetics, and
Dynamics of Smeectite Clay Interlayer Hydration: Molecular Dynamics
and Metadynamics Investigation of Na-Hectorite. J. Phys.
Chem. C 2013, 117, 5172–5187.
(24) Sutton, R.; Sposito, G. Animated molecular dynamics simulations
of hydrated caesium-smectite interlayers. Geochem. Trans. 2002,
3, No. 73.
(25) Sutton, R.; Sposito, G. Molecular Simulation of Interlayer Structure
and Dynamics in 12.4 A Cs-Smectite Hydrates. J. Colloid Interface Sci.
2001, 237, 174–184.
(26) Kosakowski, G.; Churakov, S. V.; Thoenen, T. Diffusion of Na
and Cs in montmorillonite. Clays Clay Miner. 2004, 52, 90–206.
(27) Holmboe, M.; Bourg, I. C. Molecular Dynamic Simulations of Water and Sodium Diffusion in Smectite Interlayer Nanopores as a
Function of Pore Size and Temperature. J. Phys. Chem. C 2014, 118,
1001–1013.
(28) Bourg, I. C.; Sposito, G. Connecting the Molecular Scale to the
Continuum Scale for Diffusion Processes in Smeectite-Rich Porous Media. Environ. Sci. Technol. 2010, 44, 2085–2091.
(29) Loganathan, N.; Yazaydin, A. Ö.; Bowers, G. M.; Kalinichev, A. G.;
Kirkpatrick, R. J. Structure, Energetics, and Dynamics of Cs+ and
H2O in Hectorite: Molecular Dynamics Simulations with an
Unconstrained Substrate Surface. J. Phys. Chem. C 2016, 120, 10298–10310.
(30) Kerisit, S.; Liu, C. Molecular dynamics simulations of uranyl
and uranyl carbonate adsorption at aluminosilicate surfaces. Environ.
Sci. Technol. 2014, 48, 3899–3907.
(31) Lee, S. S.; Fenter, P.; Nagy, K. L.; Sturchio, N. C. Monovalent
Ion Adsorption at the Muscovite (001)–Solution Interface: Relations-
ships among Ion Coverage and Speciation, Interfacial Water
Structure, and Substrate Relaxation. Langmuir 2012, 28, 8637–8650.
(32) Wang, J. W.; Kalinichev, A. G.; Kirkpatrick, R. J.; Cygan, R. T.
Structure, energetics, and dynamics of water adsorbed on the
muscovite (001) surface: A molecular dynamics simulation. J. Phys.
Chem. B 2005, 109, 15893–15905.
(33) Marry, V.; Rotenberg, B.; Turq, P. Structure and dynamics of
water at a clay surface from molecular dynamics simulation. Phys.
Chem. Chem. Phys. 2008, 10, 4802–4813.
(34) Whitely, H. D.; Smith, D. E. Free energy, energy, and entropy
of swelling in Cs-, Na-, and Sr-montmorillonite clays. J. Phys.
Chem. 2004, 120, 5387–5395.
(35) Xu, J.; Camara, M.; Liu, J.; Peng, L.; Zhang, R.; Ding, T.
Molecular dynamics study of the swelling patterns of Na/Cs-, Na/
Mg- montmorillonites and hydration of interlayer cations. Mol. Simul.
2017, 43, 575–589.
(36) Marry, V.; Turq, P. Microscopic Simulations of Interlayer Structure and Dynamics in Bihydrated Heteroionic Montmorillonites. *J. Phys. Chem. B* 2003, 107, 1832−1839.

(37) Teng, H. H.; Fenter, P.; Cheng, L. W.; Sturchio, N. C. Resolving orthoclase dissolution processes with atomic force microscopy and X-ray reflectivity. *Geochim. Cosmochim. Acta* 2001, 65, 3459−3474.

(38) Kubicki, J. D.; Blake, G. A.; Aptiz, S. E. Ab initio calculations on aluminosilicate Q3 species: Implications for atomic. *Am. Mineral.* 1996, 81, 789−799.

(39) Criscenti, L. J.; Brantley, S. L.; Mueller, K. T.; Tsomaia, N.; Kubicki, J. D. Theoretical and Al-27 CPMAS NMR investigation of aluminum coordination changes during aluminosilicate dissolution. *Geochim. Cosmochim. Acta* 2005, 69, 2205−2220.

(40) Kimata, M.; Saito, S.; Shimizu, M.; Iida, I.; Matsui, T. Low-temperature crystal structures of orthoclase and sanidine. *Neues Jahrh. Mineral., Abh.* 1996, 171, 199−213.

(41) Brantley, S. *Kinetics of Mineral Dissolution. Kinetics of Water-Rock Interaction*; Springer: New York, 2008; p 109.

(42) Thompson, A.; Goyne, K. W. Introduction to the sorption of chemical constituents in soils. *Nat. Educ. Knowledge* 2012, 4, No. 3447.

(43) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W.; Hermans, J. Interaction models for water in relation to protein hydration. *Intermolecular Forces*; 1981; pp 331−342.

(44) Cygan, R.; Liang, J.; Kalinichev, A. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J. Phys. Chem. B* 2004, 108, 1255−1266.

(45) Heinz, H.; Lin, T. J.; Mishra, R. K.; Emami, F. S. Thermodynamically Consistent Force Fields for the Assembly of Inorganic, Organic, and Biological Nanostructures: The INTERFACE Force Field. *Langmuir* 2013, 29, 1754−1765.

(46) Hess, B.; et al. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *J. Chem. Theory Comput.* 2008, 4, 435−447.