Mechanisms of Dissolution from Gibbsite Step Edges Elucidated by Ab Initio Molecular Dynamics with Enhanced Sampling

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ABSTRACT

Many predictive models of geochemical processes (e.g., fate and transport of metals) and industrial utilization of minerals rely upon a detailed understanding of mineral dissolution. Yet atomistic details are rarely known due to the complex mineral/fluid interfacial environment. Here, ab initio molecular dynamics simulations with enhanced sampling has been used to explore the detailed process of the detachment of an aluminate monomer from two types of step edges at the gibbsite aqueous interface. Gibbsite is a primary source of Al in soils and mineral within the industrial processing of aluminum. Surface pit models in conjunction with changes to solution composition that mimic pH effects are employed to create realistic starting points for the simulation. The results indicate two potential pathways for detachment that are differentiated based upon the extent of water hydration. The energy profiles of the elementary bond-breaking events indicate the scission of the first or the second hydroxo bridge is the rate-limiting step for the monomer dissociation. The heights of the energy barriers depend upon the local morphology which influence the number of bridges (quasi-)simultaneously broken (1 or 2) or the Al-O coordination of the neighboring aluminum atoms (5 or 6) at the armchair edge.

1. Introduction

As an interfacially mediated process, mineral dissolution can be studied from the perspective of the mass transport into solution (Perić et al., 1985, Pereira et al., 2009, Addai-Mensah et al., 2000), or alternatively the changes to surface structure - as may be measured from time-resolved surface imaging which can provide estimates of dissolution rates from edge retreat speeds (Peskleway et al., 2003). Surface reactions associated with mineral dissolution include the dissociation of individual crystal building blocks (either as monomers or larger oligomers) and it is the barriers of these reactions that control the mineral dissolution rates (Ruiz-Agudo and Putnis, 2012). Both the mechanism (order of bond breakage, changes to coordination environment, etc) and the barriers can be highly sensitive to cleavage planes, surface termination, defects, and pitting (e.g. the type of exposed step edges) (Trindade Pedrosa et al., 2019, Brandt et al., 2003, Bickmore et al., 2001, Kuwahara, 2011). Consider that prior scanning tunneling microscopy (STM) studies have reported dissolution rates for galena (PbS) that are much faster along the <110> direction instead of the <100> direction on the (001) surface under acidic conditions (Higgins and Hamers, 1996). In contrast, atomic force microscopy (AFM) studies of pit dissolution at the (001) surface of gibbsite does not indicate any preference amongst <110>, <010> and <100> step edges(Peskleway et al., 2003). Yet the solution pH alters the surface termination of cleavage planes and influence barriers for bond breaking, e.g., gibbsite solubility in aqueous solutions highly depends on the pH condition (May et al., 1979).

Surface imaging probes do not often have atomic-level resolution and as such key details of the molecular mechanism are lacking. Subtle variations as a function of surface morphology, protonation state, or other aspects of surface termination are not readily apparent. There is thus a significant need for molecular-level details provided by molecular simulations. These techniques are not without their challenges. Two key criteria should be met: first, the computational methodology should incorporate the necessary physics to accurately describe bond-breaking/formation reactions, and second, the methodology must sample a phase space associated with the rare event that involves going over the reaction barrier. Historically, computational complexity has often necessitated the use of severe
approximations to these requirements, e.g. the use of nonreactive force fields or simplified reaction coordinates like distance. Yet in recent years, there has been a growth of ab initio studies that account for configurational sampling, ab initio molecular dynamics (AIMD) that may be combined with enhanced sampling methodologies to develop a more comprehensive understanding of the mechanisms and the free energy landscape of these important surface reactions (Lee et al., 2015, Klyukin et al., 2018, Schliemann and Churakov, 2021a).

Herein we use AIMD with enhanced sampling to probe the mechanism of the initial dissolution events of the mineral gibbsite (\(\gamma\)-Al(OH)\(_3\)). Gibbsite is an important repository of Al in soils and acts as a strong sorbent of metals and nutrients. Understanding the mechanisms of gibbsite dissolution may help improve models of metal fate and transport in soils (Sposito, 2020). Its precipitation and dissolution also underpin the geochemical modeling of aluminum (oxy-)hydroxide minerals like gibbsite (and boehmite) from alkaline geothermal solutions (predominantly sodium aluminate) and has been the topic of numerous studies (Tagirov, 2001, Bénézeth et al., 2008, Schrödle et al., 2010) The alkaline geochemistry of gibbsite is further leveraged in the refinement of bauxite to produce alumina by the Bayer process as well as in other industrial processing of aluminum. The mechanisms revealed in this study should further be relevant to a broader class of metal oxyhydroxide mineral systems (e.g., kaolinite, layered double hydroxide) with significant relevance to industrial and geochemical cycling (Dietzel and Böhme, 2005, Wang et al., 2020, Liu et al., 2017). We will consider dissolution from surface pits of the gibbsite basal surface (001), which has been reported to initiate dissolution (Brown, 1972, Nagy and Lasaga, 1992, Peskleway et al., 2003). The surface pit defect further has the benefit of allowing us to examine monomer dissolution along two different directions so as to understand subtle variations in barriers that may emerge and lead to directional dissolution preferences. Within industrial applications and processing, gibbsite is often dissolved under alkaline conditions and thus we further consider the role of NaOH\(_{aq}\) upon monomer desorption. The gibbsite crystal consists of a layered structure with each layer comprised of edge-sharing Al-centered octahedral units (Al(OH)\(_6\)) located at pseudo-hexagonal grid points (Fig. 1). Neighboring Al atoms are connected by two Al-OH-Al bridges. Gibbsite layers are held together by hydrogen bonding. These AFM-observed step edges are mainly along the <110>, <010>, and <100> directions which can be categorized into two types; the <110> and <010> are so-called zigzag edges, whereas the <100> is referred to as the armchair edge (blue lines in Fig. 1).

Prior biased classical molecular dynamics simulation by Shen et al. (Shen et al., 2018) indicated that monomer desorption could proceed via kink formation and propagation before the transfer of the monomer into the solution. However, the forcefield used in that study did not allow for charge redistribution—important given the partially covalent character of the Al-O bond—or proton transfer, which could be part of the dissociation mechanism itself (as shown in Fig. 1).

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in this work, *vide infra*). Therefore, a hamiltonian able to handle these aspects is needed, as pointed out in their work. Using a combination of AIMD, metadynamics (metaD), and umbrella sampling (US), we demonstrate two potential pathways for an aluminate monomer to detach from the step edge with a change of the Al coordination number (CN) from 6 to 4. The first or second breaking event out of the four hydroxo bridges that connect the monomer to the edge is the rate-limiting step. Further, the activation energy is greatly reduced from 29.1-33.1 kcal/mol in pure water to 17.2-19.0 kcal/mol in a sodium hydroxide solution. Analysis of bond length distributions as a function of solution conditions implies that basic conditions may weaken key Al-μ$_2$O bonds.

2. Computational Methods & Model Construction

2.1. Surface Pit Models

Two surface pit models within a 2 x 3 cell are employed to independently represent the two types of edges that emerge from cleavage along the <010> and <100> directions of the (001) surface. As shown in Fig. 2a-b, a two-layer gibbsite slab is employed; two rows of (Al(OH)$_3$)$_n$ units along the zigzag <010> or armchair <100> directions are removed from the top layer to create the surface pit (gray areas in Fig. 2). The resulting edge Al atoms have a single terminal -OH and were later saturated through addition of a H$_2$O to recover the bulk 6-fold coordination. We initially presumed this coordination to be the most stable given prior AIMD studies (Liu et al., 2013) that indicate it is favored by 10 kcal/mol with respect to the 5-fold one, however, this was also validated in the current work. To examine the effect of the pH upon monomer detachment, two solutions are considered for the armchair and zigzag edges: pure water and a NaOH solution that represents higher pH. Sixty explicit H$_2$O molecules are added to represent the aqueous phase so that proton transfer and surface reconstruction may occur during equilibration. (Smith et al., 2022) To represent high pH, we transform the edge chemisorbed water molecules into hydroxyl groups and add sodium ions to neutralize the system. In the zigzag edge cell, 2 edge H$_2$O (including one at the target Al site) are replaced by OH$^-$ leaving 58 H$_2$O in the aqueous slab. During equilibration, proton transfer may occur and as such the Al detachment site may not be bound to the newly created OH$^-$. Two Na$^+$ cations are placed close to the opposite surface of the step edge to minimize their potential effect on dissolution energetics. The overall NaOH concentration is ∼ 2 M. The same strategy is applied to the armchair pit surface model.

Figure 2: (a) The side view of the initial (reactant) edge configuration and (b) monomer detached (product) edge configuration. The top view of the zigzag (c) and armchair (d) surface pits. The highlighted polyhedra indicate the target monomer and the blue lines in (c) & (d) indicate the edge outlines. Cyan: detached Al, Teal: Al, Red: O, pink: H.

2.2. Pre-equilibration using Classical Molecular Dynamics

Classical MD (CMD) with the CLAYFF force field (Cygan et al., 2004) is first used to pre-equilibrate the interface prior to AIMD equilibration. A Morse term is added to the Al-O pair to stabilize the edge termination (Shen et al., 2018). Two ns of the NPT ensemble are run at 300K and 1 atm using a 1 fs timestep with the Nosé-Hoover thermostat and barostat (Nosé, 1984, Hoover, 1985). Only the z-direction is allowed to equilibrate so as to remove the artificial extra vacuum between the gibbsite slab and its images introduced by the initial cell construction. An additional 10 ns of simulation is performed in the NVT ensemble under the same conditions. The last configuration of the pre-equilibrium process is then extracted for further AIMD equilibration. The Verlet integration scheme (Verlet, 1967) is applied on all the CMD simulations within the LAMMPS code (Thompson et al., 2022).
2.3. Ab initio Molecular Dynamics Simulations

AIMD simulations are carried out to explore the energy profile of bond-breaking events during the gibbsite dissolution using the Vienna Ab initio Simulation Package (VASP) (Kresse and Hafner, 1993, Kresse and Furthmüller, 1996). Electronic structures are calculated on the level of density functional theory (DFT) and the ions’ motion is treated as classical particles (Born-Oppenheimer approximation). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functionals (Perdew et al., 1996) together with the projector-augmented-wave (PAW) method (Kresse and Joubert, 1999) is implemented. The kinetic energy cutoff of the plane wave basis sets is set to 400 eV. The mass of hydron is replaced by tritium (3.0 u), which allows us to use a larger time step and access a longer simulation time (Kamphaus and Balbuena, 2017, Horowitz et al., 2018, Zheng et al., 2019). The Nosé-Hoover thermostat (Nosé, 1984, Hoover, 1985) is applied for the AIMD NVT simulations at 300 K with a time step of 1 fs; more than 5 ps of equilibration is performed until the total energy and temperature converged, i.e., within ±18.2 kcal/mol for the total energy and ±12.3 K for the temperature.

Interestingly, proton transfer is rarely observed during equilibration in the pure water system. At both types of edges, the oxygen of the terminal -OH has the same local connection with the surroundings, i.e. one coordinated Al and one hydrogen bond accepted from a nearby H\textsubscript{2}O. According to the refined MUSIC model (Hiemstra et al., 1996), the association reaction can be expressed as following:

\[ \equiv \text{Al(OH)}^- + \text{H}^+ \rightleftharpoons \equiv \text{AlOH}_2 \] (1)

As such, the same pKa value of 9.9 is predicted for the \( \equiv \text{AlOH}_2 \) site at both edges by the MUSIC model, a value that is consistent with previously reported AIMD values of (9.0–10.0) for similar oxygen sites at the gibbsite (100) edge surface (i.e., a group of <010> edges) (Liu et al., 2013). The rarity of proton transfer from the surface sites to the water molecules belonging to the liquid phase during equilibration is rationalized by this high predicted pKa value.

2.3.1. Enhanced Sampling of Monomer Detachment

Metadynamics (Laio and Parrinello, 2002) (metaD) and umbrella sampling (Torrie and Valleau, 1977) (US) have been employed for biased simulations that explore the detachment of an aluminate monomer, Al(OH)\textsubscript{4}\textsuperscript{−} or Al(OH)\textsubscript{2}(\textsubscript{2}H\textsubscript{2}O), from the different step edges. Direct detachment of the monomer into the solution is considered rather than the kink propagation studied by Shen et al. (Shen et al., 2018), which would involve a much larger structural model (several nm) and much longer simulation time (several ns), intractable using ab initio molecular dynamics. A series of collective variables (CVs) are examined for monomer detachment. The z-distance from the surface of a single Al monomer leaves the monomer free to translate within the basal plane, yet this lateral translation cannot be sampled within typical AIMD timescales. As such, The coordination number (CN) of the target Al to the rest Al atoms on the surface was employed as a collective variable (CV):

\[ CN = \sum_{i=1}^{M} \frac{1 - (q_i/c_i)^n}{1 - (q_i/c_i)^m} \] (2)

In Eqn (2), \( i \) is the index of the atom pair between the studied Al atom and the rest Al atoms, \( M \) is the total number of the atom pairs, \( q_i \) is the distance of the \( i \)-th atom pair, \( c_i \) is the reference distance (chosen as \( c_i = 4.0 \) Å for Al-Al pairs), and \( n = 9 \), \( m = 14 \).

To validate this CV, metadynamics (metaD) simulations of monomer detachment were employed (vide infra) where the CV is compared against the number of hydroxo bridges (inset of Fig. 3(e)) that connect the monomer to the edge. The number of bridges is 4 at most and 0 when completely dissociated (Fig. 3(d) and Fig. 4(d)). As shown in Fig. 3(e) and Fig. 4(e), a general corresponding relationship exists between these two variables. This ensures that the Al-Al CN is able to capture the bond-breaking events during the simulations.

\textbf{Metadynamics}. At the pit edge, four bridging Al-OH-Al bonds connect the monomer to the surface. Within metadynamics (metaD), a series of Gaussian hills are accumulated onto the potential surface in the CV phase space along the simulation trajectory. Here, we set the Gaussian hill size as 2.3 kcal/mol high and with a 0.1 Å width similar size as implemented in prior studies of metal hydroxide dissolution (Klyukin et al., 2018, Schliemann and Churakov, 2021b,a). The Gaussian hills were added every 50 steps, with the simulation being terminated after the four bridging...
bonds are broken. As an automated biasing technique, metaD enables the exploration of edge monomer detachment pathways by flattening free energy landscapes.

**Umbrella sampling.** Complementing metaD, we employed umbrella sampling (US) using the same CV to determine the free energy landscape of monomer detachment. In this approach, monomer detachment was divided into 20 windows with an interval of 0.25 in the CV phase space. A harmonic biased potential was added in each window with a spring constant of 140 kcal/mol. Additional complementary windows with much stronger spring constants (416 to 2767 kcal/mol) were performed to ensure sufficient CV sampling overlap among the windows for the calculation of the potential of mean force (PMF). The post-AIMD trajectories were processed by PLUMED (Tribello et al., 2014) to calculate the values of the CVs, and the PMFs were constructed by the weighted histogram analysis method (WHAM) with the code by Grossfield (Grossfield). To get the initial structures of each window, we started from the equilibrium configurations of the complete pit edge in solutions. A harmonic biased potential was applied to the window in which the CV is the closest to the equilibrium value (~4.6 for zigzag edge) and run 500 steps with NVT ensemble. The last step structure was then used as the input of the next window and runs another 500 steps for the pre-equilibrium. This procedure was repeated several times until all the initial structures were set up. In this way, we ensure the edge structure evolves smoothly by avoiding any abrupt changes in the CV value. The simulation was stopped once the PMFs derived from three sequential 2ps-blocks trajectories converged. Production runs were preceded by an equilibration phase of at least 10 ps for each window. Finally, unbiased AIMD simulations were performed to study the properties and stabilities of reactants, intermediates, and product states.

### 3. Results & Discussion

The initial step of gibbsite dissolution (the detachment of an aluminate monomer) was first examined at a pit edge site with termination of $≡$Al(OH)(H$_2$O) in pure water solution using metaD, where it was revealed that two potential pathways existed depending on the extent of hydration at the departing Al-site. Potential of mean force (PMF) simulations were then used to identify the lowest energy state from which to initiate more detailed umbrella

![Figure 3: metaD results for the 6-coordinate pathway. (a) - (d) Select configurations of the detaching monomer unit using the Al-Al CN described in Eqn. 2; image (a) has three Al-O bridges, image (b) has two bridges, while one bridge is observed in (c) and no bridges remain in (d). (e) The relationship between Al-Al CN and number of Al-OH bridging bonds, starting from a 6-coordinated site. The inset shows the initial configuration of the edge monomer as well as the defined bridging hydroxo bridges. The configuration of three (a), two (b), one (c), and zero bridges (d) remaining. Cyan: detached Al, Teal: Al, Red: O, pink: H. The solid teal indicates the edge Al atoms connected to the monomer.](image-url)
sampling studies. The free energy profiles of monomer detachment under pure water and alkaline conditions were finally compared.

### 3.1. Reaction Pathways Identified by Metadynamics

Starting from a 6-coordinated Al monomer, metaD reveals two different pathways for monomer detachment from the zigzag edge; in one reaction pathway the Al monomer is 6-coordinated before any Al-OH bridge bonds are broken and in the second reaction pathway an H₂O leaves the first coordination shell of the Al and the Al monomer detaches as a 5-coordinate species. Similar Al sites have been also reported on gibbsite (100) edge surface of AIMD simulations (Liu et al., 2013). There are thus two initial coordination environments for the Al during the monomer desorption.

#### 3.1.1. 6-coordinate pathway

Monomer detachment from the zigzag edge along the first pathway is illustrated in Fig. 3. A proton transfer occurs between the H₂O attached to the target Al and a neighboring H₂O. The first hydroxo bridge breaks from the monomer side—i.e. via the bond connecting the bridging OH to the departing Al reducing the Al’s CN by 1 as shown in Fig. 3(a), then a second bridge breaks via the surface side—i.e. the bond connecting the bridging OH to the Al remaining on the surface without a change to the target Al’s CN (Fig. 3 (b)).

At this point along the Al-Al CV for monomer detachment, the target Al is five coordinated. It is bound to: one of the original -OH in addition to one -OH that results from the proton transfer from the initially bound H₂O, one terminal -OH that results from bridge breaking, and two bridging Al-OH bonds. During the breaking of the final two bridging Al-O bonds, one of the -OH groups remain bound to the surface such that the monomer becomes 4-coordinate as shown in Fig. 3 (c). Finally, the remaining bridging Al-OH bond breaks from the surface side and the monomer detaches from the step edge, becoming Al(OH)₄⁻ leaving two 5-coordinated Al at the edge—see Fig.3 (d). Note that the fivefold Al sites coexisting with 4- and 6-fold Al sites have been detected by ²⁷Al NMR spectroscopy during gibbsite crystallization (Hu et al., 2017).

#### 3.1.2. 5-coordinate pathway

In the second monomer detachment pathway, the edge H₂O leaves the first coordination shell of the Al before any hydroxo bridge breaks, similar to what has been observed within AIMD simulations of pyrophyllite dissolution (Schliemann and Churakov, 2021b). Mechanistically there are several similarities to the monomer detachment as when the Al is initially 6-coordinate; for example, the first two Al-OH-Al bridge-breaking events yield one hydroxyl that is attached to the monomer and one to the surface. However, after these two breaking events, the target Al is 4-coordinate. It has bound to it one of the original terminal -OH, one terminal -OH that comes from the bridge bond-breaking events and two bridging Al-OH (shown in Fig.4 (b)). As the metaD simulation continues, the last two bridging bonds both break from the surface side which leaves two hydroxyls attached to the monomer such that the dissolved monomer is tetrahedral Al(OH)₄⁻ (Fig.4 (c) and (d)). This pathway leaves one 4-coordinated and one 5-coordinated Al at the edge when the monomer is detached.

#### 3.1.3. Comparison between the two pathways

The primary differences between the two detachment pathways lie in the edge water behavior and the origin of the final monomer charge of -1. In the 6-coordinate pathway, the edge water site (≡Al-H₂O) transfers a proton to another ≡AlOH site through a transfer chain of ≡Al-H₂O ==> ≡Al-OH...H ==> H₂O...H ==> H...HO-Al≡ and the -1 charge of the final detached monomer originates from this proton transfer event. In the 5-coordinate pathway, the whole water molecule desorbs from the edge and the monomer gains the -1 charge directly from the gibbsite surface through bond-breaking events.

Both pathways that have been identified for the zigzag edge pit also exist at the armchair edge. Given the potential competition of the 6- and 5-coordinate pathways, it is important to assess their relative likelihood through a more detailed understanding of the energetics for H₂O dissociation from the first coordination shell of the Al. Toward this end, umbrella sampling was performed using the distance between the target Al and the water oxygen (O_w) as a CV (Fig. 5). Large uncertainties were obtained for r > 3.8 Å when the water molecule reaches the solution and/or the opposite surface of the pit, thus the PMF is cut off at 3.8 Å. In the case of the zigzag edge, an energy barrier of ~ 11.92 kcal/mol needs to be overcome for H₂O to leave the first shell while only a 3.72 kcal/mol barrier is observed for the armchair edge, but in both cases the 6-coordinate form is more stable.
Figure 4: metaD results for the 5-coordinate pathway. (a) - (d) Select configurations of the detaching monomer unit using the Al-Al CN described in Eqn. 2; image (a) is the initial state with four Al-O bridges, image (b) has two bridges, one bridge is observed in (c) and no bridges remain in (d). (e) The relationship between Al-Al CN and the number of Al-OH bridging bonds. The inset shows the initial edge water is desorbed before the bridging hydroxo breaking. Color codes are the same as Fig.5.

The barrier difference between the two edges could be related to different hydrogen bonding formed by the terminal H$_2$O groups. As demonstrated by the snapshots in Fig. 5’s insets and the ensemble-averaged g(r) in Fig. S1, 3 hydrogen bonds are formed at the zigzag edge when the Al is 6-coordinated (within the d $\sim$ 2.0 Å window): 1 donated to and 1 accepted from free water and 1 donated to another surface hydroxyl of length 1.63 Å and only 2 hydrogen bonds are donated to the surrounding water at the armchair edge (insets of Fig. 5 and Fig. S1). The extra short hydrogen bond connects the H$_2$O to the zigzag edge, elongated in the d $\sim$ 2.6 Å window (Fig. S2), explains the increase in the PMF when water is desorbed from the zigzag edge by 8.20 kcal/mol compared to the armchair edge. The barrier difference may be generalizable: the topologies of the armchair and zigzag edges are such that the probability to form hydrogen bonds between surface groups of the same layer is lower at the armchair edge. The order of the values of the barriers is consistent with those reported previously, with an activation energy of $\sim$ 13 kcal/mol at gibbsite zigzag type edge surface (Liu et al., 2013) and $\sim$ 6.5 kcal/mol from the Al$_6$(OH)$_{18}$(H$_2$O)$_6$ cluster similar to and armchair edge(Qian et al., 2009).

3.2. Free Energy Landscapes Determined by Umbrella Sampling
3.2.1. Detachment in water

Umbrella sampling is then performed to elucidate the free energy landscapes for monomer detachment, starting from the 6-coordinate Al site in pure water. The resulting PMFs are shown in Fig. 6, where the shaded area along the PMF corresponds to the standard deviation of the PMF derived from the three 2ps-blocks of production trajectories. By examining the edge configurations and the corresponding Al-Al CN values in each window (Fig. S3 & S4), the bond-breaking events are identified and labeled accordingly. In the case of the zigzag edge (Fig. 6a), the first hydroxo bridge breaks at CV $\sim$3.94 needing an energy of 27.5 kcal/mol and the second bridge breaks at CV $\sim$3.67 with an additional 5.6 kcal/mol. Supplementary unbiased MD performed starting from the structure corresponding to CV = 3.79 shows that the structure corresponding to a single bridge broken is converted back to the initial structure with the 4 bridges present within the first 0.7 ps. This indicates the first and second scissions can be considered quasi-simultaneous. Thus, the overall free energy needed to break these 2 bridges is 33.1 kcal/mol. Breaking of the 3$^\text{rd}$ and 4$^\text{th}$ bridging bonds occurs with barriers of 7.5 kcal/mol, and 8.2 kcal/mol, respectively. In comparison, at the armchair edge (Fig. 6b), the rate-limiting step is the breaking of the first hydroxo bridge with a barrier of 28.5 kcal/mol. Notably, the breaking of
the 2nd bridge requires an additional 21.7 kcal/mol as a result of the asymmetric connection to the armchair edge when removing the monomer. The 3rd bridge breaks spontaneously without any barrier and the 4th bridge breaks with an energy barrier of 6.7 kcal/mol.

Comparing the PMF between the zigzag and armchair edges, the largest difference in the free energy landscape and mechanism is associated with the manner in which the second Al-OH-Al bridge is broken. At the armchair edge, this event requires an extra 21.7 kcal/mol after the first bridge breaking and only 5.6 kcal/mol at the zigzag edge. For both edge types, the final thermodynamic state should be characterized by the Al(OH)\textsuperscript{4−} solvated in bulk water and with complete water saturation at the detachment site. Due to the restricted simulation time and the size of the water slab employed in the PMF (to keep computational costs reasonable), there is no guarantee that the site of detachment reaches full equilibrium with surface water, and further that the Al(OH)\textsuperscript{4−} achieves a bulk solvation environment. To address this potential limitation, unbiased AIMD equilibration (with production trajectories of at least 5 ps) was first performed with the newly exposed edge sites manually saturated by water molecules, this altered Δ\textit{U}\textsubscript{r} to 19.5 and 11.5 kcal/mol for the zigzag and armchair edge pit, respectively (Table 1). To evaluate the impact of bulk water solvation of Al(OH)\textsubscript{4−}, a thicker water slab (> 15 Å) was then employed and re-equilibrated, which further reduced the Δ\textit{U}\textsubscript{r} from 19.5 to 14.9 kcal/mol for the zigzag step-edge system. Due to the significant computational cost, this latter calculation was only performed for the zigzag step-edge, however it is likely that a similar stabilization of the anion would occur for the anion detached from the armchair edge. Further effects that could result in a reduction of the Δ\textit{F}_\text{r} difference and that are not accounted for here include: a larger number of water layers, a larger pit width eliminating the potential confinement effects, the stabilization of Al(OH)\textsubscript{4−} by ion-pairing with Na\textsuperscript{+}, and the stabilizing entropy of the detached monomer in the solution.

3.2.2. Detachment in NaOH(aq)

In comparison to the pure water case, the energetic landscape for monomer detachment is significantly altered when sodium hydroxide is added into the solution. Within the zigzag edge pit, the barrier for breaking the first bridge is decreased from 27.5 kcal/mol to 19.0 kcal/mol; the scission of the second bridge increase to 15.7 kcal/mol. The rupture of the 3rd bridge costs 18.6 kcal/mol, and that of the last bridge has a relatively small energy of 3.7 kcal/mol. The order of the bridge-breaking events is maintained for the armchair edge irrespective if the surface is in contact with water or NaOH\textsubscript{(aq)}, but the barrier for bond breaking is reduced. The first bond breaking is reduced from 29.1 kcal/mol to 15.3 kcal/mol. The remaining three bonds are broken sequentially with energy barriers of 17.2 kcal/mol, 10.4 kcal/mol, and 6.3 kcal/mol, respectively. Unbiased AIMD results show a Δ\textit{U}\textsubscript{r} of 13.8 kcal/mol in the zigzag:NaOH\textsubscript{(aq)} model which is smaller than that in zigzag:H\textsubscript{2}O model (19.5 kcal/mol). Similar to the zigzag model, the Δ\textit{U}_\text{r} of the overall reaction for the armchair:NaOH\textsubscript{(aq)} model (0.4 kcal/mol) is less than that of the armchair:H\textsubscript{2}O model (11.5 kcal/mol).
Figure 6: Potential of mean force of the detachment of an aluminate monomer from the zigzag and armchair step edges in pure water. The $n^{th}$ bond breaking events are labelled as 1$^{st}$, 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ along with the respective energy barriers.

These differences in $\Delta U_f$ are probably related to a stabilizing release of OH$^-$ into the solution during the detachment in NaOH$_{\text{aq}}$ which is absent in the water system, deriving from the larger slab net charge gain in NaOH$_{\text{aq}}$ (2.8 and 2.5 for zigzag and armchair, respectively) than in water (1.0 and 1.3, respectively) (Table 1).

Figure 7: Potential of mean force of the detachment of an aluminate monomer from the zigzag and armchair step edges in NaOH$_{\text{aq}}$. The $n^{th}$ bond breaking events are labelled as 1$^{st}$, 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ along with the respective energy barriers.

3.2.3. Origins of the differences in the free energy profiles

Bond-breaking events are the elementary steps of solid dissolution, and apriori the progress of dissolution is limited by the highest energy barrier for an individual bridging bond broken (provided the barriers for the backward reaction are sufficiently high). Comparing the monomer detachment PMFs from the zigzag and armchair edges in water and NaOH$_{\text{aq}}$, we predict that breaking the first bridging bond requires the most energy except in the case of the armchair edge in NaOH$_{\text{aq}}$, where the second bridge requires slightly more energy. Here we analyze the origins of the most
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Table 1
Edge termination, net charges (e), Al-$\mu$-O distances (Å) and reaction internal energies ($\Delta U_r$, kcal/mol) for the zigzag armchair pits in water and NaOH$_{(aq)}$. Data are collected from 5 ps unbiased AIMD production trajectories and the net charge is averaged by assigning a formal charge of 0 to the site for an $\equiv$Al(OH)($OH_2^-$) form and -1 for $\equiv$Al(OH)$_2^-$. Italics: large cell; all values are averages except $d$(Al-$\mu$-O)$_{max}$.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Zigzag NaOH$_{(aq)}$</th>
<th>Armchair NaOH$_{(aq)}$</th>
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</thead>
<tbody>
<tr>
<td>$\Delta U_r$</td>
<td>19.5</td>
<td>14.9</td>
<td>13.8</td>
</tr>
<tr>
<td>Initial target site net charge</td>
<td>-0.996</td>
<td>-0.226</td>
<td>0.000</td>
</tr>
<tr>
<td>Initial slab net charge</td>
<td>0.110</td>
<td>-1.810</td>
<td>0.066</td>
</tr>
<tr>
<td>Final slab net charge</td>
<td>1.158</td>
<td>1.045</td>
<td>1.370</td>
</tr>
<tr>
<td>$&lt;d$(Al-$\mu$-O)$&gt;$ all bonds</td>
<td>1.941</td>
<td>1.946</td>
<td>1.922</td>
</tr>
<tr>
<td>$&lt;d$(Al-$\mu$-O)$&gt;$ longest bond</td>
<td>2.029</td>
<td>2.021</td>
<td>1.964</td>
</tr>
<tr>
<td>$d$(Al-$\mu$-O)$_{max}$ all bonds</td>
<td>2.381</td>
<td>2.483</td>
<td>2.235</td>
</tr>
</tbody>
</table>

important differences between the PMFs. Additional AIMD simulations were performed without bias for the initial, intermediate structures and final state. The properties of the target site were averaged from a 5 ps production trajectory, including the net charges and the Al-$\mu$-O bond lengths, which are listed in Table 1.

The first intermediate for detachment at the zigzag:water interface is very short-lived, while the others exist for at least 6 ps within the simulation. The energy barriers of the zigzag and armchair edge dissolution should be 33.1 (the first two bridges) and 29.1 kcal/mol or 19.0 and 17.2 kcal/mol respectively based on solution condition, i.e., water or NaOH$_{(aq)}$. Yet the kinetic stability of the first intermediates in the armchair:H$_2$O and zigzag:NaOH$_{(aq)}$ systems does not align with the PMFs that do not have a corresponding minima and no preceding transition state. Since overlaps between consecutive CV distributions are sufficient, this deviation is likely due to slow degrees of freedom that are insufficiently sampled over the course of the 6 ps production MD runs in every window. As such, the uncertainties are larger than the statistical uncertainties given in the PMFs, which supports the idea that only the largest differences between barriers (more than 5-10 kcal/mol) should be considered here. Note that the experimentally determined activation energy of gibbsite dissolution of particles in alkaline solutions from the Arrhenius equation is in the range 17.3-26.3 kcal/mol based on 0.1-8 M NaOH solutions (Perić et al., 1985, Pereira et al., 2009, Addai-Mensah et al., 2000, Grenman et al., 2010). The nature of the surfaces subject to dissolution in these studies is unknown, but the simulation values are within the range of the experimental ones (17.2-19.0 kcal/mol) in alkaline conditions and higher values (29.1-33.1 kcal/mol) are obtained in pure water. This is consistent with the experimental data and the simulations in this work provide a potential explanation as the monomer detachment could be the elementary step of the gibbsite dissolution.

The strong decrease of the first energy barrier for the zigzag edge between the water and the NaOH$_{(aq)}$ system (33.1 to 19.0 kcal/mol) may be understood by the fact that a single bridge is broken in the latter compared to the quasi-simultaneous breaking of 2 bridges in the water system. However, in the armchair model, a single bridge is broken in both water and NaOH$_{(aq)}$ and therefore cannot explain the decrease (29.1 to 15.3 kcal/mol). By inspecting the armchair edge structures around the transition state (CV $\sim$ 3.70 in water and CV $\sim$ 3.94 in NaOH$_{(aq)}$) (Fig. S5), we observe that in NaOH$_{(aq)}$ one of the Als bridged to the target Al is terminated by a single group and the other one by two groups, while both neighboring Als are terminated by two groups in the water system. The lower barrier of the former case may result in a weakening of the Al-$\mu$-O bonds at the target Al site.

Since the decrease of the barriers correlates with the change in concentration, one may rationalize that the decrease of the charge of the terminal groups expected at high pH impacts the mechanisms and the barriers mentioned previously. However at the zigzag edge in pure water, the Al site is terminated by two -OHs ($\equiv$Al(OH)$_2^-$) and thus carries $\sim$ -1 net charge; this is compared to the termination of $\equiv$ Al(OH)($H_2$O) in NaOH$_{(aq)}$ where the site has a less negative (-0.226) net charge. Thus, the local Al site termination does not relate to the overall pH value as the net charges of Al sites are supposed to be lower on average at higher pH. Given that alkaline solutions result in higher dissolution rates, thus lower expected barriers, the decrease in barriers observed here from pure water to NaOH$_{(aq)}$ systems cannot be explained by the difference in local site termination. This further holds true for the armchair edge, as the initial target...
Figure 8: Box plots of the Al-$\mu_2$O length of the target site on the zigzag edge and armchair edge in water and NaOH\(_{aq}\) before dissociation. The ratio of the number of outliers above the upper whisker and the total number of points are 2.20, 2.02, 1.11 and 1.50 % for the box plots from left to right.

The ratio of the number of outliers above the upper whisker and the total number of points are 2.20, 2.02, 1.11 and 1.50 % for the box plots from left to right.

328 site is neutral both for the water and the NaOH\(_{aq}\) models. The mean and maximum bridging bond lengths among the
329 8 Al-$\mu_2$O bonds display little difference in water and NaOH (being 1.941 and 2.029 Å in water vs 1.946 and 2.021 Å in
330 NaOH, respectively). However a large number of jumps to higher values (beyond normal bond stretching) are observed in
331 the gibbsite:NaOH\(_{aq}\) system compared to the gibbsite:water system, shown in Fig. 8. The individual Al-$\mu_2$O bond
332 length distributions are plotted in Fig. S6 - S7, which clearly show that one of the Al-$\mu_2$O bonds is severely stretched in
333 NaOH\(_{aq}\) compared to the other Al-$\mu_2$O bonds or those in water. The same trend for the overall and individual bond
334 length distributions can be found in the armchair pit model (Fig. 8 and Figs. S8 - S9). Overall, smaller barriers may be
335 related to a larger propensity for the bond lengths to explore large values. Of course, we cannot omit the possibility that
336 this observation is purely stochastic: biasing the Al-Al coordination number without applying other constraints may
337 leave enough degrees of freedom for the monomer to dissociate in different ways. To create a more robust simulation
338 framework in studies of monomer detachment in mineral dissolution we recommend strict study of how different CVs
339 that control individual bond breakage events influence the detachment energetics.

3.3. Geochemical Significance

Over the past century, significant attention has been devoted to studying aqueous aluminum species in alkaline
340 conditions, this includes the precipitation and dissolution processes of aluminum (oxy-)hydroxide minerals like gibbsite
341 (and boehmite) from alkaline geothermal solutions as well as in the Bayer process for alumina refinement.(Tagirov,
342 2001, Bénézet et al., 2008, Schrödle et al., 2010) The atomistic details of the interfacial reactions of aluminum (oxy-
343 hydroxide minerals have only begun to be understood, led by high-resolution microscopic techniques (STM, AFM,
344 TEM, et al.) and atomistic simulation methods (MD & DFT). Gibbsite, a primary form of bauxite ore and a major
345 source of aluminum in the Earth’s crust, is of particular interest. The initial stages of gibbsite dissolution is essential to
346 advancing existing geochemical models and in the development of new predictive models for weathering and aluminum
347 transport in hydrothermal and orthomagmatic fluids, as well as in the industrial Bayer process. The work presented
348 here is the first reported AIMD-derived free energy landscape and mechanistic analysis of the initial stages of gibbsite
349 dissolution from a defect-laden surface in the presence of different solution conditions (pure water versus alkaline).
350 The barriers for monomer detachment, specifically the rate-limiting step, are highly dependent on the neighboring Al
351 site’s Al-O coordination number or the number of Al-O bonds broken during that step. This suggests that mineral
352 morphology and defects will significantly impact observed dissolution rates. Additionally, changes to pH significantly
353 alter the rate-limiting step. This work provides motivation for more detailed studies exploring the role of complex

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surface morphologies and sorbate configurations in the initial stages of gibbsite dissolution, filling in the missing pieces of earlier macro-level studies.

4. Conclusions

In the current work, we have explored two gibbsite surface pit models (having zigzag edges and armchair edges) in both pure water and NaOH solution by AIMD simulations. Metadynamics simulations have demonstrated two possible pathways for an edge monomer detachment that are delineated by the extent of hydration at the detaching site. Potentials of mean force derived from umbrella sampling simulations show that the rate-limiting step of the monomer detachment is the first or second bridge-breaking event for the studied cases. The largest energy barrier decreases from 29.1 - 33.1 kcal/mol when the surface is in contact with pure water to 17.2 - 19.0 kcal/mol when in contact with NaOH\(_{\text{aq}}\)—this decrease is related to either a lower number of bridges involved in the breakage event at the zigzag edge or to a decrease of the Al-O coordination number of the neighboring Al at the armchair edge. In the initial state, the Al-\(\mu_2\)O bond lengths exhibit larger fluctuations which are consistent with the lower barriers observed for detachment in the presence of NaOH\(_{\text{aq}}\). Although beyond the scope of the current work, a more precise link between the NaOH concentration and the dissolution energy profile could involve biased simulations of the nucleophilic attack of OH\(^-\) on Al sites(Schliemann and Churakov, 2021a) and/or the examination of the role of inner-sphere(Shen et al., 2017, Liu et al., 2022) alkali cation binding upon the reaction intermediates which has been shown in previous work to alter the energy profile of aluminate dimerization(Pouvreau et al., 2020).
5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Acknowledgements

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7. Appendix A. Supplementary material

The supplementary material contains: (1) Hydrogen bonding of the desorbing water: radial distribution functions; (2) Distribution of the number of Al-OH-Al bridges in different CN(AI-Al) umbrella sampling windows; (3) Structures of the first transition state for the armchair edge; (4) Boxplots of the Al-$\mu$$_2$O bond distributions; (5) Research data for the plots in this article.

References


