

Molecular-level mechanisms of quartz dissolution under neutral and alkaline conditions in the presence of electrolytes

SITING ZHANG and YUN LIU*

State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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The mechanisms of quartz dissolution are affected intricately by pH conditions and electrolyte types. Most previous studies have focused on the mechanisms of quartz dissolution under one specific condition (e.g., temperature, pH, saturation or electrolyte type); however, this study investigates molecular-level mechanisms under combinations of electrolyte and pH conditions, which are more complex but closer to the reality. Under neutral and alkaline pH conditions with Ca^{2+} , Mg^{2+} or Na^+ aqua ions in the solution, the dissolution of Q1 (Si) and Q2 (Si) sites on the quartz surface, which represents the predominant part of the quartz dissolution story, is investigated by first-principles quantum chemistry calculation methods. Our results confirm that quartz dissolution can be enhanced significantly by the presence of electrolytes under neutral pH conditions. However, under alkaline pH conditions, the surface complexes of aquo ions are different, depending on where and how those electrolytes bond onto the quartz surfaces. The energy barriers of all possible hydrolysis reaction pathways are calculated carefully. The activation energies for the reaction between the negatively charged quartz surface and H_2O have never been reported before. Our results of activation energy are closer to experimental values than previous calculations have been, suggesting that the cluster models and theoretical levels used here are more reasonable. Such information provides a molecular-level understanding of the differences of quartz dissolution rates between pure water and ion-containing solutions.

Keywords: quartz dissolution, molecular-level mechanisms, electrolytes, pH conditions, quantum chemistry calculation

INTRODUCTION

Knowledge of silicate mineral-water reaction kinetics is central to understanding many important issues in low-temperature geochemistry; including soil formation, weathering, and CO_2 sequestration processes (Blum and Stillings, 1995; White and Brantley, 2003). One of the major objectives of experimental and theoretical studies on the kinetics of silicate mineral-water reactions is to quantify the important driving forces of mineral dissolution. For a real system, such driving forces are usually numerous and include physical, chemical, and biological factors. Among these driving forces, the most important are pH condition (e.g., Brady and Walther, 1989; Burch *et al.*, 1993; Carroll-Webb and Walther, 1988; Criscenti *et al.*, 2006; Kubicki *et al.*, 1993; Nangia and Garrison, 2008; Pelmeshnikov *et al.*, 2001; Stillings and Brantley, 1995; Xiao and Lasaga, 1994, 1996), ionic strength (e.g., Dove and Crerar, 1990; Dove and Elston, 1992; Dove, 1994, 1999; Dove and Nix, 1997; Dove and Colin, 2005;

Strandh *et al.*, 1997), reactivity of different surface sites (e.g., Blum and Lasaga, 1988, 1991; Blum *et al.*, 1990; Dove, 1994; Furrer and Stumm, 1986; Lasaga, 1992; Pelmeshnikov *et al.*, 2000; Raghavachari and Rohlffing, 1991; Bickmore *et al.*, 2008; Wallace *et al.*, 2010), the extent of undersaturation of the solution (e.g., Dove *et al.*, 2005, 2008; Zhu, 2005; Zhu *et al.*, 2006), and temperature (e.g., Brady and Walther, 1992; Casey and Sposito, 1992; Rimstidt, 1997; Rimstidt and Barnes, 1980). However, the molecular-level mechanisms for many of these driving forces remain elusive.

Quartz is the simplest and an abundant silicate mineral in the earth's crust. The study of its dissolution mechanism was expected to shed light on the dissolution mechanisms of other silicate minerals. However, it has been found that the dissolution mechanism of quartz is very different to that of other silicate minerals in several ways. For instance, the dissolution of most silicate minerals is insensitive in the presence of small amounts of electrolytes (NaCl , CaCl_2). However, experimental data show that at near-neutral pH conditions, quartz will dissolve up to 100 times faster in the presence of small amounts of alkali and alkaline earth electrolytes (e.g., Berger *et al.*, 1994; Dove and Crerar, 1990; Dove and Elston, 1992; Dove, 1994, 1999; Dove and Nix, 1997; Dove and Colin,

*Corresponding author (e-mail: liuyun@vip.gyig.ac.cn)

2005). While the dissolution of most silicate minerals is promoted largely by the H^+ ion, the dissolution of quartz is decreased slightly upon adding H^+ ions until a very acidic condition is attained (i.e., $pH = 2$) (Dove and Elston, 1992; Nangia and Garrison, 2008, 2009). A thin amorphous layer has been found on the surfaces of many silicate minerals that have been in contact with water (e.g., Zhu, 2005; Zhu *et al.*, 2006), whereas this has not been found on the surface of quartz. The discovery of this thin amorphous layer challenges many established theoretical models of mineral dissolution, which are based on the direct interaction between pristine crystalline mineral surfaces, water, and aqueous ions. These “strange” dissolution behaviors of quartz make it a very interesting case for further investigation.

Many researchers have investigated the mechanisms of quartz dissolution in the presence of electrolytes (e.g., Bandstra and Brantley, 2008; Berger *et al.*, 1994; Bickmore *et al.*, 2008; Criscenti and Sverjensky, 2002; Dove, 1999; Dove and Nix, 1997; Dove and Colin, 2005; Gratz and Bird, 1993; House, 1994; Karlsson *et al.*, 2001; Kitamura *et al.*, 1999; Sahai and Sverjensky, 1997; Strandh *et al.*, 1997; Wallace *et al.*, 2010). Their results suggest hydrolysis of the Si–O_{br} bond is affected strongly by the presence of the electrolytes. Dove *et al.* (2005) found that the dissolution mechanisms of quartz were largely different depending on the presence or absence of electrolytes. The hydrolysis of the Si–O_{br} (subscript “br” means the bridging O atom) bond occurs only at the retreating steps or dislocations of the quartz surface in pure water. However, in electrolyte-containing solutions, hydrolysis could occur in the middle of a perfect surface plane, as well as at steps and dislocations, resulting in a significant increase of dissolution. An interesting non-Transition-State-Theory-like behavior of quartz dissolution near equilibrium has also been observed. Dove and Nix (1997) investigated four major electrolytes found in terrestrial and marine environments under neutral pH solutions, and compared their abilities in enhancing quartz dissolution. They found that quartz dissolution rates increased in the order of $MgCl_2 < CaCl_2 \approx LiCl \approx NaCl \approx KCl < BaCl_2$. To explain these results, they studied the surface charge density on silica in alkali and alkaline earth chloride electrolyte solutions (e.g., Dove and Colin, 2005). Their results suggest that IIA cations (Mg^{2+} , Ca^{2+} , Ba^{2+}) have greater ability to increase the negative density on the silica surface than the IA cations do (Li^+ , Na^+ , K^+), i.e., the IIA cations are more easily adsorbed on the quartz surface and exchanged with H^+ than the IA cations. However, the molecular-level information about where and how those cations approach the quartz surface and the consequences to the hydrolysis of Si–O–Si linkages is still not clear.

The role of surface speciation in low temperature dis-

solution of silicate minerals has been studied (Blum and Lasaga, 1988). It was found that the Na^+ adsorbed on the surface of albite could exchange quickly with H^+ , and never be resorbed to the surface under any range of pH (Blum and Lasaga, 1988; Chou and Wollast, 1985). The adsorption of H^+ has a lower energy barrier than the adsorption of Na^+ on the terminal oxygen. Berger *et al.* (1994) suggested that the formation of inner-sphere ion surface complexes was the reason for the increase in the dissolution rate. In a study (Strandh *et al.*, 1997) on the effects of alkali metals in silicate mineral dissolution, it was found that alkali metal cations link with the bridging O_{br} atom under neutral condition. The linkage weakens the Si–O–Si bonding, which makes bond hydrolysis easier and accelerates the dissolution of the silicate mineral.

Wallace *et al.* (2010) used first-principles quantum chemistry methods to study the hydrolysis of Si–O–Si linkages in Mg^{2+} - and Ca^{2+} -containing solutions or in pure water under near-neutral pH conditions. They provided molecular-level mechanisms and energy barriers for Si–O_{br} bond breaking estimated by B3LYP (Becke’s three-parameter hybrid functional using the Lee-Yang-Parr (LYP) correlation functional) (e.g., Becke, 1993) or the PBE1PBE (Perdew-Burke-Ernzerhof correlation functional) density functional theory (DFT) method at the 6-31G (d) level. They also compared their results with single-point energy calculations at the 6-311+G (d, p) level to ensure that their results were consistent with those at higher theoretical levels. By comparing the activation energies in Ca^{2+} - and Mg^{2+} -containing solutions and in pure water, they found that the inner-sphere surface complexes of metal ions accelerated the dissolution of quartz, and that the outer-sphere surface complexes had insignificant effects. Because the predominant adsorption surface species are the outer-sphere surface complexes, Wallace *et al.* (2010) suggested that the ion-associated solvent reorganization events are important for the hydrolysis of Si–O–Si linkages. An outer-sphere surface complex needs to lose one coordinated water molecule to form the monodentate inner-sphere surface complex. In addition, the inner-sphere surface complexes can be exchanged into the solution by water or the H^+ ion. These kinetic processes all involve the reorganization of ion-associated solvent molecules. Therefore, the frequency of such reorganization is important for the hydrolysis of Si–O–Si linkages.

To understand the mechanisms of ion-promoted pathways of quartz dissolution, especially under both neutral and alkaline pH conditions, we designed many cluster models of quartz surfaces and evaluated the interactions between electrolytes and active sites of the quartz surfaces. To minimize the size effect, we designed cluster models as large as possible within the limits of the computational cost we could afford. These cluster models are

Table 1. Acid-base quartz surface complex reaction and corresponding surface sites and solution species at 25 °C

Reaction	pH	Surface sites	Solution species
$> \text{SiOH} \leftrightarrow > \text{SiO}^- + \text{H}^+$ pH = 6.8 (Schindler and Kamber, 1968)	pH > 8	Si–O–Si, Si–OH, Si–O [−]	H ₂ O and OH [−]
	5 < pH < 8	Si–O–Si, Si–OH >> Si–O [−]	H ₂ O
	2.3 < pH < 5	Si–O–Si, Si–OH >> Si–O [−]	H ₃ O ⁺ and H ₂ O
$> \text{SiOH} + \text{H}^+ \leftrightarrow > \text{SiOH}_2^+$ pH = 2.3 (Schindler and Stumm, 1987)	pH < 2.3	Si–O–Si, Si–OH ₂ ⁺ and Si–OH	H ₃ O ⁺ and H ₂ O

indeed among the largest that have been used in previous related studies. Our study focused on the Q1 and Q2 Si sites of the quartz surface, because the Q3 Si site can only be broken under extreme conditions (i.e., it needs to overcome an extremely large energy barrier) and thus, it can be considered as a rare event in quartz dissolution. Furthermore, the mechanisms of quartz dissolution under acidic conditions are complex, and after many trial attempts at modeling it, we still do not understand its molecular-level mechanisms.

This study uses several different treatments compared with previous studies. A higher theoretical treatment is used to obtain activation energies that are more accurate. Relaxed cluster models are used to simulate the reactive sites of the quartz surface, instead of the four-membered ring cluster models used in previous studies. In addition to IIA-type aqua ions (i.e., Mg²⁺ and Ca²⁺), the effect of the IA-type aqua ion (i.e., Na⁺) is also investigated, and in addition to near-neutral conditions, the Si–O_{br} bonding hydrolysis reactions under alkaline conditions are also studied.

METHODS

With the change of pH conditions, a variety of charged surface states (or sites), such as neutral (Si–OH), deprotonated (Si–O[−]) or protonated (SiOH₂⁺) states, will be distributed on the quartz surface with different densities (Table 1). Detailed discussions of the mechanisms that develop these sites at the quartz-water interface are presented by Iler (1979) and Kosmulski (2001). The different densities of the charged surface states are believed to control the final reaction mechanisms (e.g., Bickmore *et al.*, 2008; Dove, 1994; Dove and Rimstidt, 1994). In this study, a first-principles quantum chemistry calculation investigation was performed to explore the molecular-level dissolution processes of the Q1 (Si) and Q2 (Si) sites of quartz surfaces in Ca²⁺-, Mg²⁺- or Na⁺-containing solutions or in pure water under neutral and alkaline conditions. The transition state theory was used to study the elementary bond-breaking processes of quartz

dissolution. Similar computational techniques have been used in previous studies on quartz dissolution (Nangia and Garrison, 2008, 2009; Pelmenchikov *et al.*, 2000, 2001; Wallace *et al.*, 2010; Xiao and Lasaga, 1994, 1996). These studies focused on the hydrolysis of Si–O–Si linkages on the quartz surfaces caused by the attack of a single water molecule, because this is believed to be the rate-limiting step of quartz dissolution (Casey *et al.*, 1988). The activation energy barriers E_a for the hydrolysis of Si–O–Si linkages is treated as a function of the connectivity of the Si atoms (Criscenti *et al.*, 2006; Pelmenchikov *et al.*, 2001). The hydrolysis processes of the Si–O–Si bond linkage were studied by following the stationary point geometries along the reaction paths.

The calculations of these hydrolysis reaction paths were performed using the DFT method in the GAUSSIAN03 software package (Frisch *et al.*, 2004). Although the B3LYP DFT method is one of the most popular methods for calculating the quartz-water interface reaction mechanisms and kinetics (e.g., Becke, 1993; Civalleri *et al.*, 1998; Davis *et al.*, 1988; Ribeiro-Claro and Amado, 2000; Sefcik and Goddard, 2001; Teppen *et al.*, 1994; Wallace *et al.*, 2010; Walsh *et al.*, 2000), recent studies have suggested that the B3LYP method may be deficient in the calculation of the energies of intermolecular interactions (e.g., Zhang *et al.*, 2007; Zhao and Truhlar, 2007). Some new DFT methods (e.g., M05 and M06) have been developed specifically for the calculation of the energies of inter-molecular interactions. We choose the M05-2X DFT method (Zhang *et al.*, 2007; Zhao and Truhlar, 2007), which could provide more accurate results of inter-molecular interactions.

Many previous studies have used the 6-31+G (d,p) or 6-31G (d) basis-set in the study of mineral dissolution (e.g., Nangia and Garrison, 2008, 2009; Sefcik and Goddard, 2001). In this study, we used a larger triple-split basis-set (i.e., 6-311+G (d, p)) for energy calculations that are more accurate, especially for calcium-bearing systems. Furthermore, there are some negatively charged species in this study (i.e., under alkaline conditions), for which adding the diffusion function (i.e., “+”) is

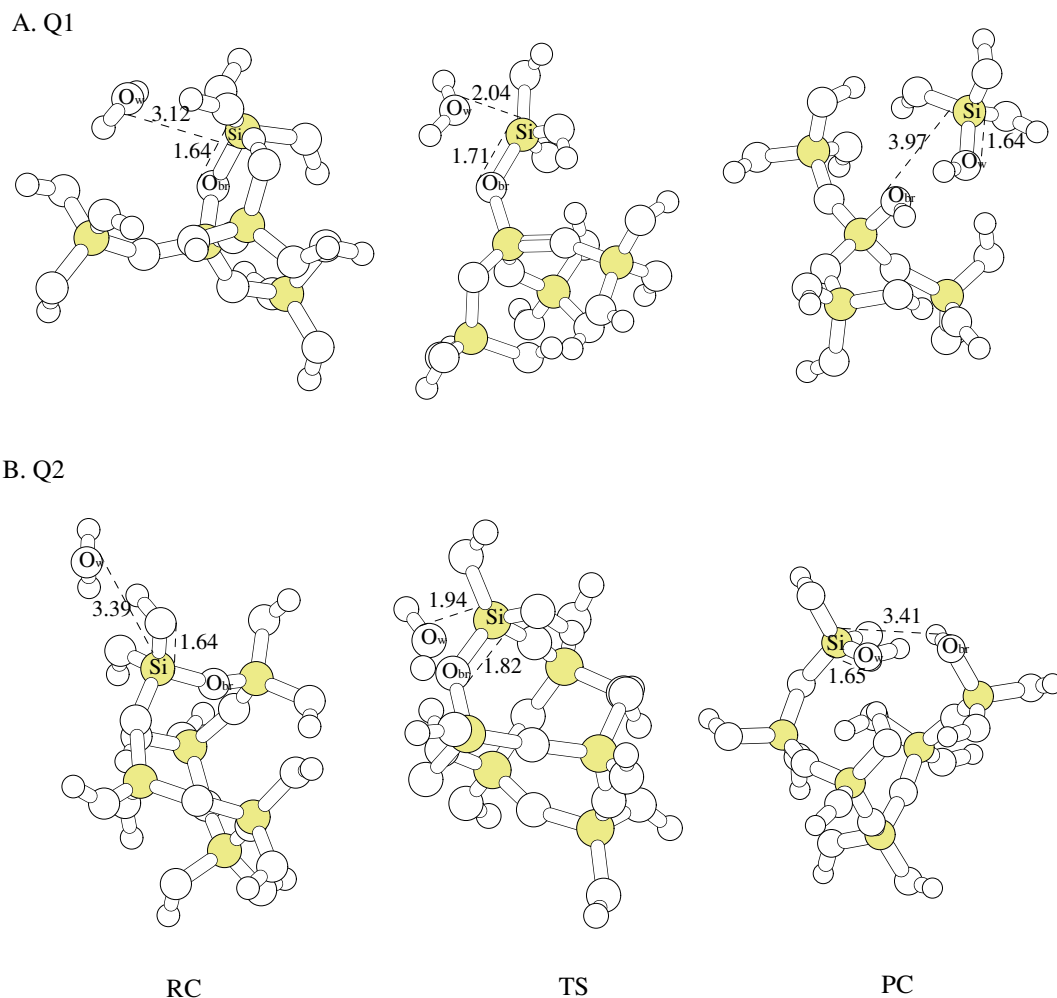


Fig. 1. Stable geometries along the reaction path in pure water under neutral condition. (A) Hydrolysis at Q1 Si site and (B) hydrolysis at Q2 Si site.

into the basis-set is a usual treatment. This triple-split basis-set was also used by Wallace *et al.* (2010) as a standard for checking their results obtained at lower levels. The popular synchronization transition quasi-Newton searching methods (i.e., the QST3 method in Gaussian 03) is also used here (Frisch *et al.*, 2004).

RESULTS

Molecular-level mechanisms of quartz dissolution in pure water

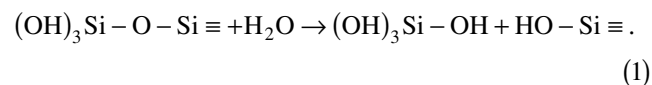
For a better understanding of the different quartz dissolution mechanisms between pure water and electrolyte-containing solutions, we first investigated the simplest case; the hydrolysis reactions of Si–O–Si linkages in pure water under either neutral or alkaline conditions. Several previous studies have investigated the molecular-level mechanisms of quartz dissolution in pure water (Kubicki

et al., 1993; Nangia and Garrison, 2008, 2009; Xiao and Lasaga, 1994, 1996).

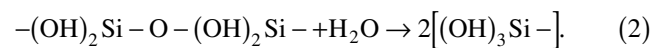
Under neutral conditions

The hydrolysis reactions of the Q1 and Q2 Si sites on neutrally charged surfaces (i.e., terminated by the Si–OH group) are

Q1 Si site:



Q2 Si site:



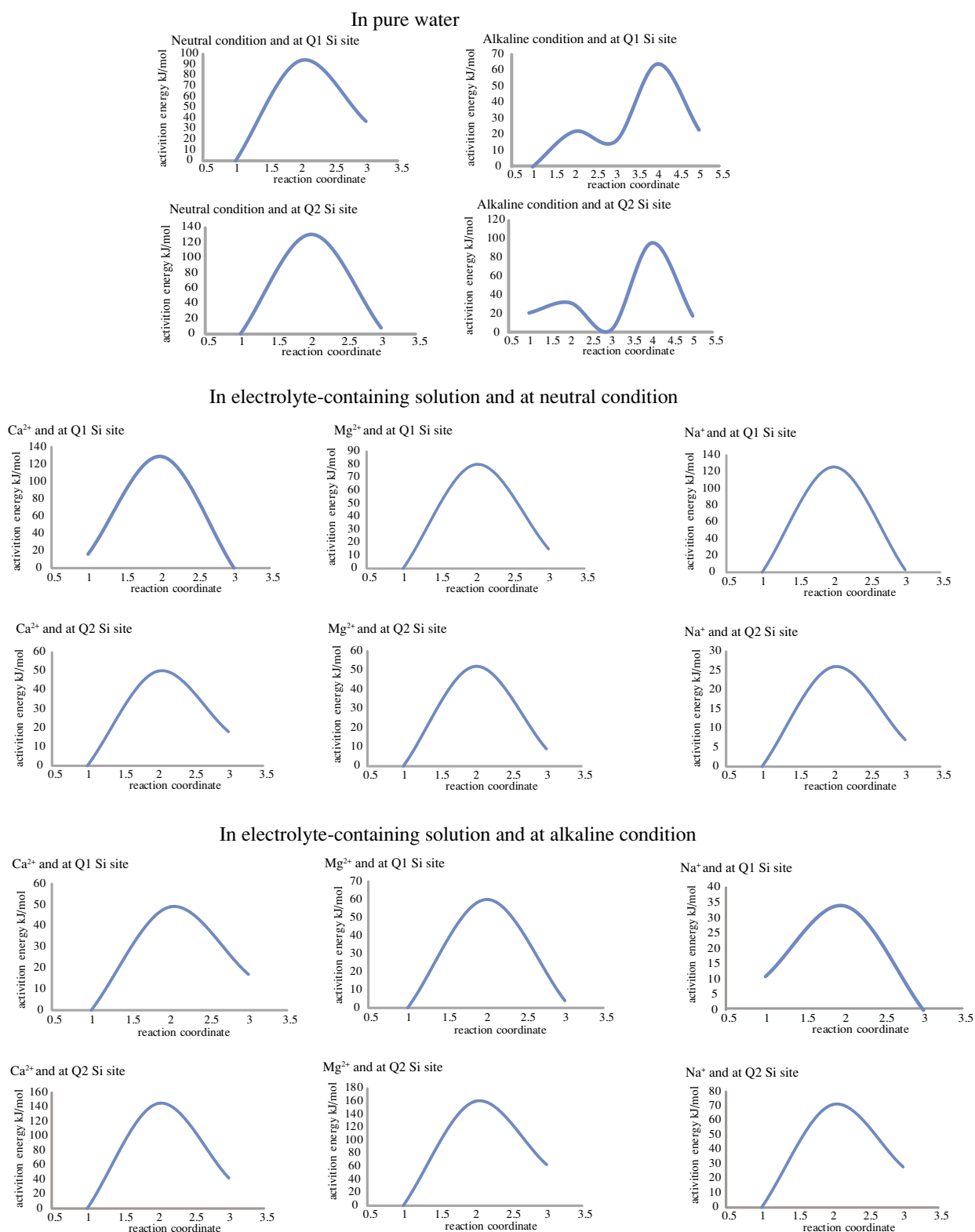


Fig. 2. Reaction energy profiles of Si-O_{br} hydrolysis at Q1 and Q2 Si sites in pure water and in electrolyte-containing solutions.

Table 2. Barrier heights (kJ/mol) and Si–O_{br} bond lengths in Si–O–Si linkage for the dissolution of the Q1 (Si) and Q2 (Si) sites in neutral, alkaline conditions

Metal ion	Calcium		Magnesium		Sodium		Pure water			
	Q1	Q2	Q1	Q2	Q1	Q2	Q1		Q2	
Barrier heights										
Neutral	50	113	52	80	26	126	94		131	
Alkaline	49	145	60	160	23	87	22	48	9	96
Si–O _{br} bond lengths										
Neutral	1.68	1.65	1.69	1.70	1.66	1.65	1.64		1.64	
Alkaline	1.68	1.65	1.67	1.63	1.66	1.66	1.66		1.66	

The optimized geometries of the reactants, transition-state complexes, and products of the Q1 and Q2 sites are illustrated in Fig. 1. Energy profiles along the dissolution reaction pathway are shown in Fig. 2. Hereinafter, the critical bond lengths including both Si–O_w (the subscript “w” means that the O atom is in a water molecule) and Si–O_{br} are used as the reaction coordinates. The profiles of the reaction pathways determined in this study are similar to those found in previous studies (e.g., Morrow *et al.*, 2009; Nangia and Garrison, 2008, 2009; Pelmeshnikov *et al.*, 2000, 2001); however, for some cases, the calculated activation energy values are different.

Three columns of cluster models are shown in Fig. 1: the first column clusters represent reactant complexes (denoted as RC), the second represent transition-state complexes (denoted as TS), and the third represent product complexes (denoted as PC). As the hydrolysis reaction progresses, one of the silicon tetrahedra is attacked by a water molecule and the O_w–Si distance becomes increasingly short: from 3.12 Å (RC) to 2.04 Å (TS) and from 3.39 Å (RC) to 1.94 Å (TS) for the Q1 and Q2 sites, respectively. Conversely, the Si–O_{br} bond distance increases from 1.64 Å to 1.71 Å and from 1.64 Å to 1.82 Å for the Q1 and Q2 sites, respectively.

There is only one transition state on the hydrolysis reaction pathway for sites of near-neutral charge (Fig. 2). The coordination number of the Si atom is changed from 4 to 5 after the transition-state complex is formed. Then, the Si–O_{br} bond breaks and the attacking water molecule will be dissociated into H⁺ and OH[–]. The H⁺ will bond with the O_{br} atom and the OH[–] will bond with Si to form a neutrally charged Si(OH)₄ tetrahedral, which can be removed (i.e., dissolved) from the quartz surface. This mechanism found here is similar to those found in previous studies (Nangia and Garrison, 2008, 2009; Xiao and Lasaga, 1994, 1996).

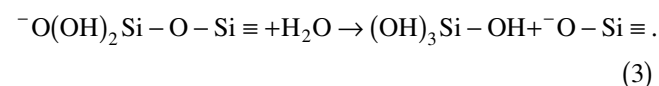
However, the activation energy values in pure water, found here (Table 2), are markedly different to the results of Nangia and Garrison (2008, 2009). The activa-

tion energy for the hydrolysis of the Q1 site, determined in this study, is 94 kJ/mol, whereas it was found to be 152–157 kJ/mol in Nangia and Garrison’s (2008, 2009) studies. The Q1 site is the easiest site to break and therefore, the value of the activation energy of 152–157 kJ/mol appears too large; it is close to those values reported previously for the Q3 sites (Criscenti *et al.*, 2006; Wallace *et al.*, 2010). This difference may be caused by the different sizes of the cluster models and the different theoretical levels used. Larger cluster models and higher theoretical levels are used in this study. Interestingly, our results are close to the results of Xiao and Lasaga (1994, 1996), which were obtained at the MP2/6-31G*-level (including electron correlation corrections), but with smaller cluster models.

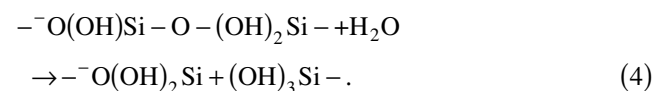
Under alkaline conditions

The hydrolysis reactions of Si–O–Si bonding under alkaline conditions can be written as

Q1 Si site:



Q2 Si site:



Here, we actually assume a hypothetical situation in which, under alkaline conditions of pure water, there are no electrolytes to attack the Q1 and Q2 Si sites. We focus on studying the hydrolysis effects of the water molecules only; however, the effects of the electrolytes will be given later. The optimized geometries of the reactants, transition-state complexes, and products of the Q1 and

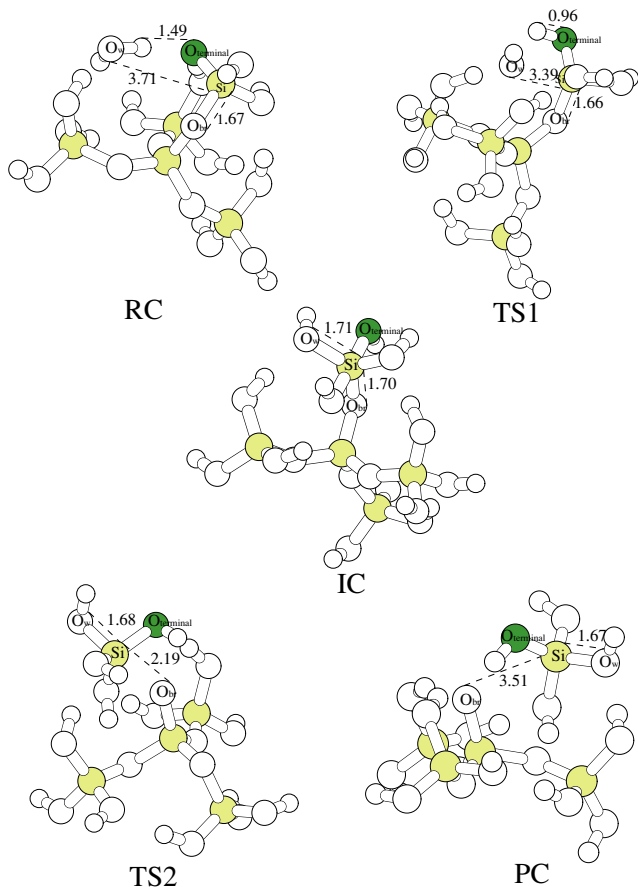


Fig. 3. Stable geometries along the dissolution reaction path of Q1 Si site in pure water under alkaline (deprotonated) conditions.

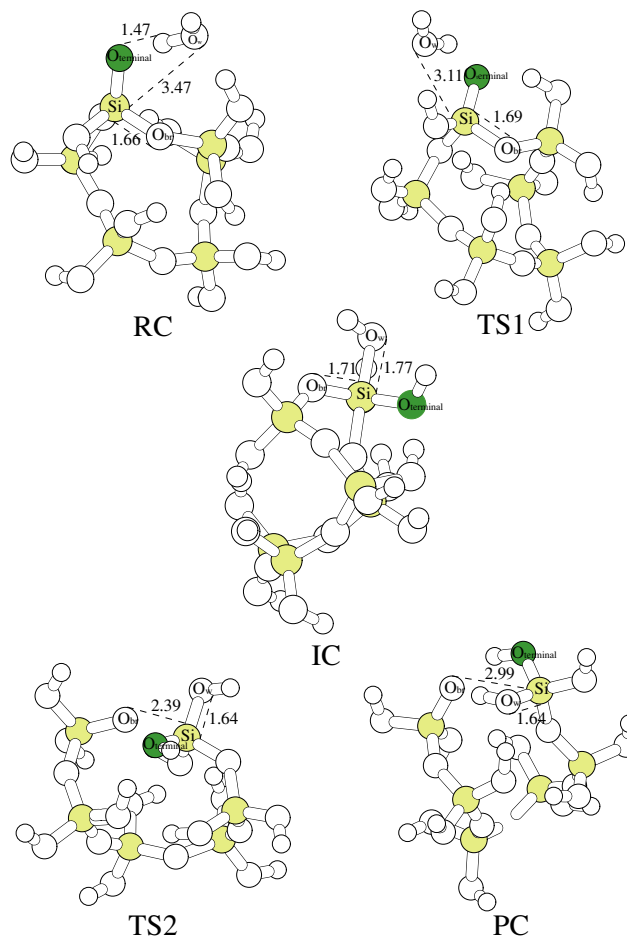


Fig. 4. Stable geometries along the dissolution reaction path of Q2 Si site in pure water under alkaline (deprotonated) conditions.

Q2 Si sites are illustrated in Figs. 3 and 4, respectively. The reaction energy profiles along the demineralization pathway are shown in Fig. 2. In contrast to the neutral condition, there are now two transition states (TS1, TS2) instead of one on the pathway of the hydrolysis reactions, suggesting completely different dissolution mechanisms between the neutral and alkaline conditions. The reaction pathway profiles found here are similar to those of Xiao and Lasaga (1994) and Nangia and Garrison (2009).

In Fig. 3 (RC) and Fig. 4 (RC), the incoming water molecule forms a strong H-bond with the negatively charged oxygen atom on the deprotonated surface. As the hydrolysis reaction progresses, the distance between the O_w and Si becomes increasingly short. Meanwhile, the bond length of Si– O_{br} increases until it breaks. There is a stable 5-coordinated Si intermediate complex formed for both the Q1 and Q2 sites (Fig. 3). To break the Si– O_{br} bond completely, the second energy barrier (TS2) must be overcome. The formation of the 5-coordinated Si intermediate complex (IC) (e.g., Damrauer *et al.*, 1988;

Holmes, 1990; Kubicki and Lasaga, 1990; Kubicki *et al.*, 1993; Kubicki and Sykes, 1993; Kubicki and Heaney, 2003) is a unique step for breaking the Si–O–Si bond in pure water (Figs. 3 and 4).

The activation energies for the hydrolysis of the Q1 Si site are 22 and 48 kJ/mol and for the Q2 Si site, they are 9 and 96 kJ/mol for TS1 and TS2, respectively. Because the slowest step is the rate-determining step, it is much more difficult to break the Q2 sites than the Q1 sites under alkaline conditions without considering the effects of electrolytes. Furthermore, the activation energies calculated in this study are slightly different from those of both Nangia and Garrison (2008, 2009) and Xiao and Lasaga (1996) for alkaline conditions. For example, in our study, the activation energies for the Q1 site are 22 and 48 kJ/mol for TS1 and TS2, respectively. The results of Nangia and Garrison (2008, 2009) had activation energies for the Q1 site of 51–57 and 14–20 kJ/mol for TS1 and TS2, respectively, and Xiao and Lasaga (1996) had

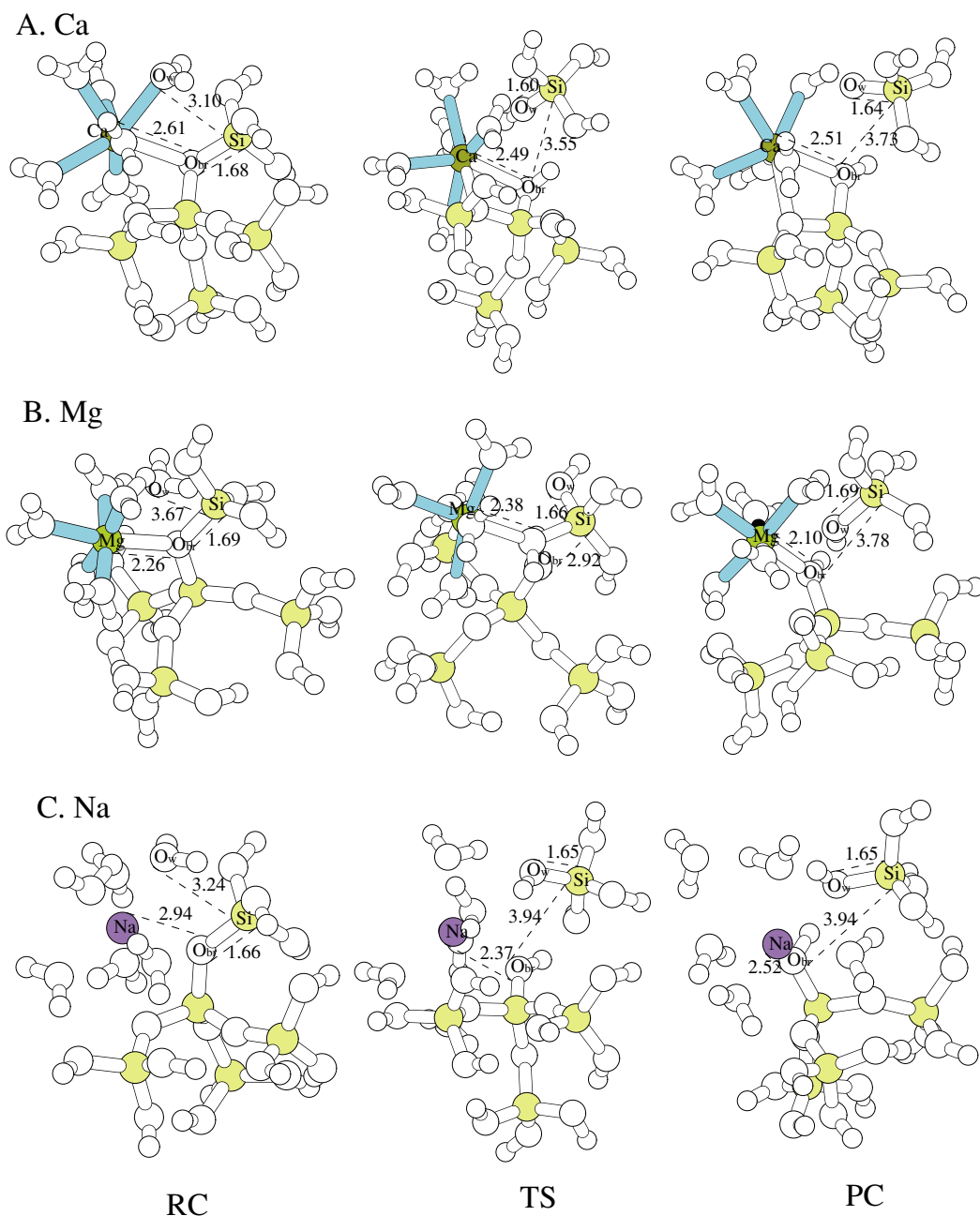


Fig. 5. Stable geometries along the dissolution reaction path of Q1 Si site in electrolyte-containing solutions under neutral conditions. (A) Ca^{2+} -containing solution, (B) Mg^{2+} -containing solution, and (C) Na^+ -containing solution.

79 and 19 kJ/mol for TS1 and TS2, respectively. The barriers estimated in this study are generally smaller than those that are estimated in previous studies.

Molecular-level mechanisms of quartz dissolution in solutions with electrolytes

It has been suggested that electrolytes could affect the dissolution of quartz significantly only if they were adsorbed to the quartz surface via inner-sphere surface

complexes (Wallace *et al.*, 2010). Based on this finding, we studied only the inner-sphere surface complexes of several electrolytes.

Six water molecules are added to surround every electrolyte ion to include an approximation of solvation effects. Of course, this simple treatment is probably only reasonable for comparing the differences of the activation energies either with or without electrolytes.

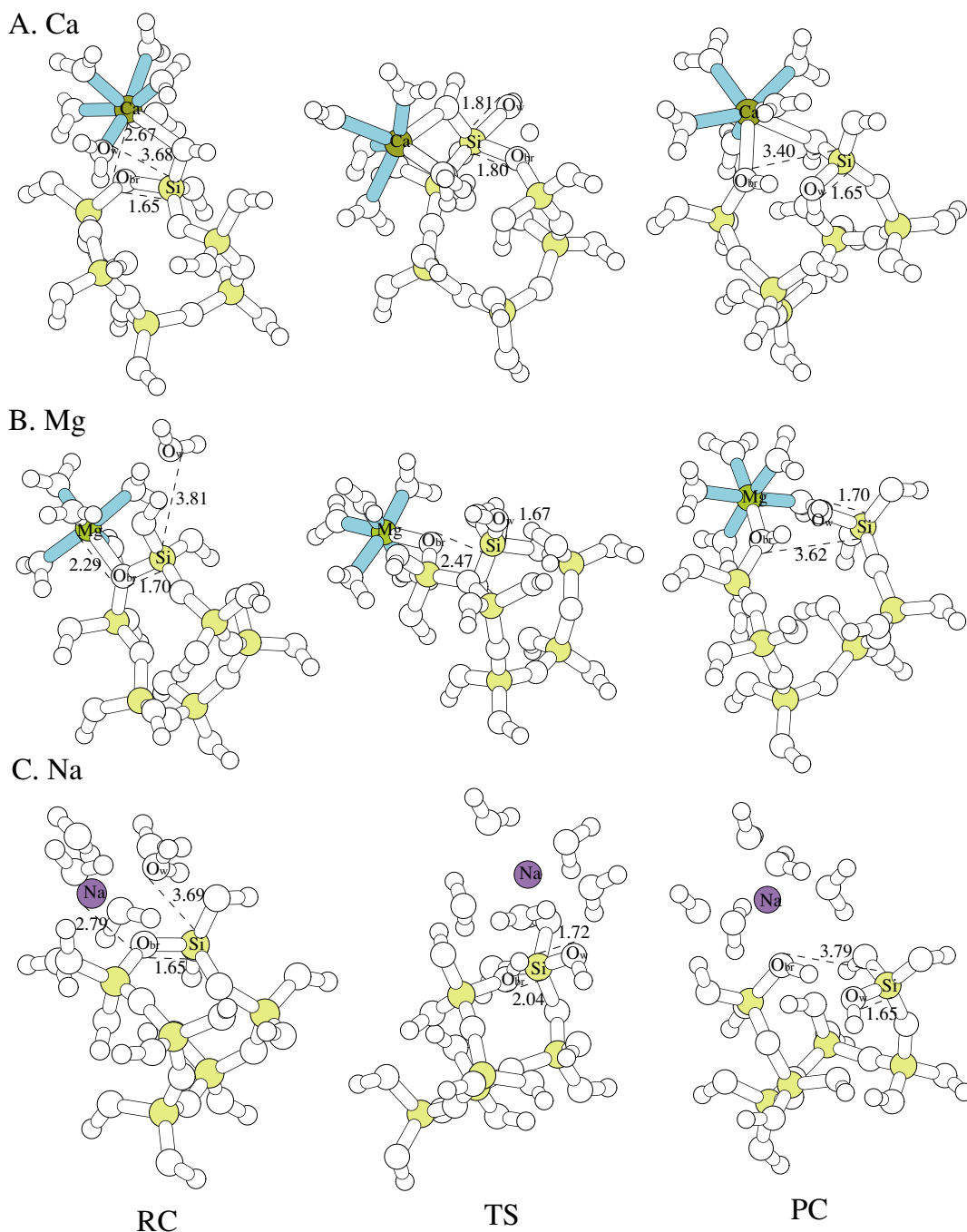


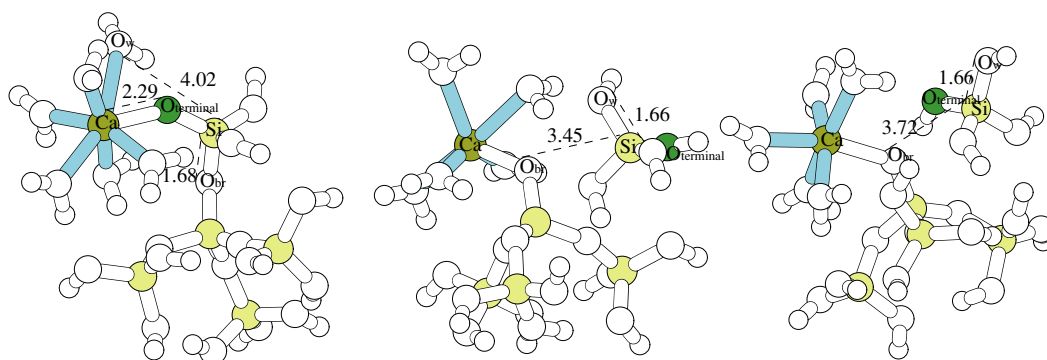
Fig. 6. Stable geometries along the dissolution reaction path of Q2 Si site in electrolyte-containing solutions under neutral conditions. (A) Ca^{2+} -containing solution, (B) Mg^{2+} -containing solution, and (C) Na^+ -containing solution.

Under neutral conditions and with electrolytes

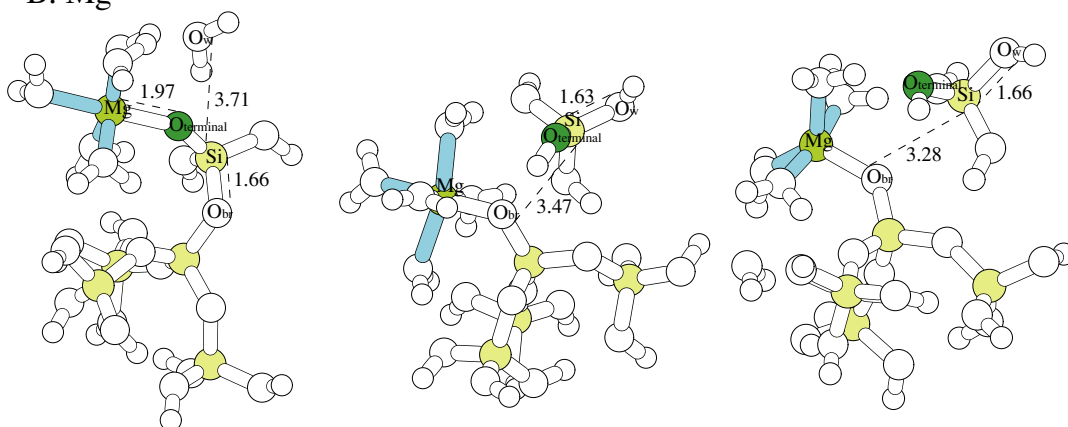
The calculated geometries of the reactants, transition-state complexes, and products of the Q1 and Q2 Si sites are illustrated in Figs. 5 and 6, respectively. The optimized RC geometries in Figs. 5 and 6 show that Ca^{2+} , Mg^{2+} or Na^+ will bond directly to the bridging oxygen atoms on the quartz surface. However, their inner-sphere adsorp-

tion surface complexes are different: Ca^{2+} is 7-coordinated, Mg^{2+} is 6-coordinated, and Na^+ is 5- or 6-coordinated. The lone pair of electrons on the bridging oxygen atom is important in stabilizing the Si–O–Si linkage (Gibbs *et al.*, 2009). Therefore, the attachment of Ca^{2+} , Mg^{2+} or Na^+ on the bridging oxygen atom will weaken the Si–O–Si linkage, because some electrons on

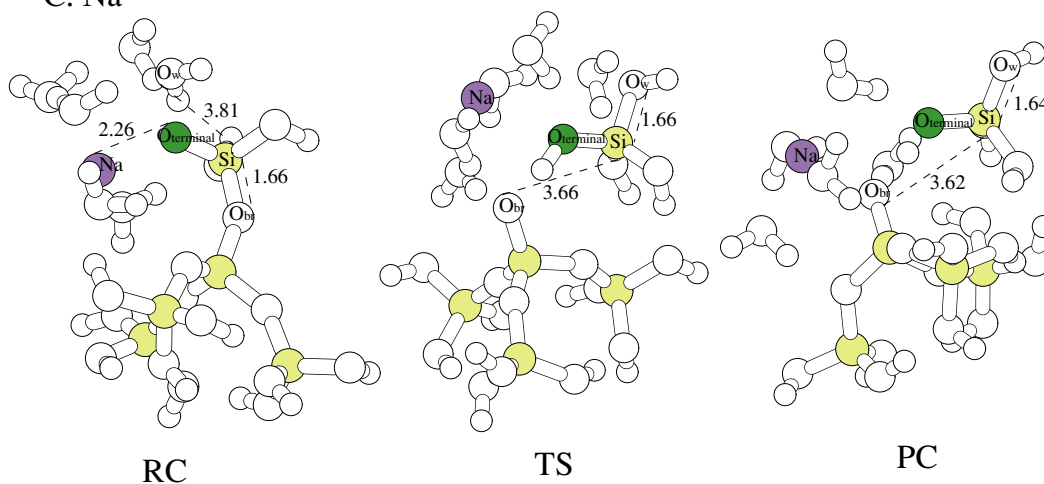
A. Ca



B. Mg



C. Na



RC

TS

PC

Fig. 7. Stable geometries along the Q1 Si site dissolution reaction path in electrolyte-containing solutions under alkaline conditions. (A) Ca^{2+} -containing solution, (B) Mg^{2+} -containing solution, and (C) Na^+ -containing solution.

the bridging oxygen atom will be transferred to the attached cation. The data of Si–O_{br} bond length (Table 2) show the effects during the approach of those cations. All of the Si–O_{br} bond lengths increase following the approach of the cations, which results in an easier approach

to the Q1 or Q2 Si sites for a water molecule. Consequently, a water molecule will be dissociated into a hydroxyl and an H⁺ ion. The hydroxyl will become part of an isolated Si(OH)₄ and will be removed from the surface. The H⁺ ion is linked to the broken bridging oxygen

respectively. For the hydrolysis of the Q2 Si site, the activation energies are 113, 80, and 126 kJ/mol for Ca^{2+} , Mg^{2+} , and Na^+ , respectively. Wallace *et al.* (2010) studied the Q3 Si site hydrolysis under neutral conditions in the presence of Ca^{2+} and Mg^{2+} . Their results showed that the activation energies of the Q3 Si site are much larger than the Q2 Si site (i.e., about 142 kJ/mol for Mg^{2+} and 158.5 kJ/mol for Ca^{2+}).

Under alkaline conditions and with electrolytes

Under alkaline conditions, there are more deprotonated Si–O sites on the quartz surfaces. The optimized geometries of the reactants, transition-state complexes, and products of the Q1 and Q2 Si sites are shown in Figs. 7 and 8, respectively. The energy profiles along the hydrolysis reaction pathway of the Q1 and Q2 Si sites are shown in Fig. 2.

By comparing the energy profiles in Fig. 2, we find that the reaction mechanisms in electrolyte solutions are completely different from those in pure water. There is only one transition state for the hydrolysis reactions in electrolyte-bearing solutions. However, there are two transition states (TS1, TS2) and a stable 5-coordinated intermediate (I) for the reactions in pure water under alkaline conditions.

The RC geometries illustrated in Figs. 7 and 8 show that the IIA-type cations (i.e., Ca^{2+} and Mg^{2+}) will bond with the deprotonated terminal oxygen atoms on the quartz surface. They can even compete with water molecules that can form strong H-bonds on the deprotonated terminal oxygen atoms (denoted as O_{term}^-). A water molecule will approach and attack the Si atom with the deprotonated terminal oxygen atom. The IIA-type cations affect the hydrolysis reactions under alkaline conditions indirectly by changing the bonding of $\text{Si}-\text{O}_{\text{term}}^-$. For the Q1 Si site (Fig. 7), the Si atom will be dissolved into solution in the form of $\text{Si}(\text{OH})_4$ and this allows another Si atom on the quartz surface with a deprotonated terminal oxygen atom to bond with the IIA cation. For the Q2 Si site (Fig. 8), the approaching water molecule will break the Si–O–Si linkage to produce two Q1 Si sites, one of which has a deprotonated terminal oxygen atom.

However, those IA cations (i.e., Na^+) will not bond with the deprotonated oxygen atom because of the stronger H-bond formed between the O_{term}^- and a nearby water molecule, which expels Na^+ . The Na^+ can form only outer-sphere surface complexes in this situation, exhibiting a completely different dissolving mechanism compared with the IIA-type cations. The H-bonding also causes the bonded water molecule to be easily dissociated; the length of the $\text{O}_{\text{w}}-\text{H}$ bond in that water molecule increases from 0.96 to 0.99 Å for the Q1 Si site and from 0.96 to 1.04 Å for the Q2 Si site after the H-bond is formed. The dissociated water molecule will produce a

hydroxyl, and this will also bond with Si to form a 5-coordinated Si complex and finally, break the Si–O–Si linkage (Figs. 7 and 8).

There are no previous energy barriers data regarding quartz dissolution under alkaline conditions in the presence of electrolytes. From the bond length data listed in Table 2, we can estimate the influence of the electrolyte ions on the Si–O–Si linkages of the Q1 and Q2 Si sites. Under neutral conditions, all the $\text{Si}-\text{O}_{\text{br}}$ bond lengths in the Si–O–Si linkages of the Q1 and Q2 Si sites will increase in the presence of electrolytes. However, under alkaline conditions, the influence of the electrolytes for the Q1 and Q2 Si sites is different. The $\text{Si}-\text{O}_{\text{br}}$ bond lengths in the Si–O–Si linkages of the Q1 Si sites increase slightly, whereas they decrease or remain unchanged for the Q2 Si sites. Consequently, the hydrolysis activation energies for the Q1 Si site are 49, 60, or 23 kJ/mol if with Ca^{2+} , Mg^{2+} , or Na^+ , respectively, and for the Q2 Si site, they become 145, 160, or 87 kJ/mol if with Ca^{2+} , Mg^{2+} , or Na^+ , respectively.

DISCUSSION

The molecular-level mechanisms of quartz dissolution with electrolytes under neutral conditions

Many experimental data (Dove and Crerar, 1990; Dove *et al.*, 2005, 2008) have indicated that the “salt effect” has strong influence on quartz dissolution. The dissolution rate of quartz is increased by up to almost 100 times in the presence of electrolyte ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) in natural water. However, the mechanisms of the “salt effect” are complex and the molecular-level mechanisms are not fully understood.

Under neutral conditions, when comparing the activation energies of quartz hydrolysis in ion-free and ion-induced situations, the barriers for breaking the Si–O–Si linkages are reduced significantly in the latter case, indicating that the adsorption of metal ions must have some effect on the hydrolysis processes. Wallace *et al.* (2010) showed that if only forming outer-sphere surface complexes, these cations exert no influence on the hydrolysis reaction of the Si–O–Si linkages. They suggested, and confirmed in this study, that inner-sphere surface complexes could change the activation energies significantly for such hydrolysis reactions. For example, according to the activation energies provided in this study, the activation energy of the hydrolysis reactions at the Q1 sites in pure water is 94 kJ/mol; however, in the presence of Ca^{2+} , Mg^{2+} , or Na^+ , this energy barrier is reduced to 50, 52, or 26 kJ/mol, respectively. The situations for the hydrolysis of the Q2 and Q3 sites are similar. Therefore, a reasonable estimate is that the formation of inner-sphere surface complexes of cations is the cause of the increase in the dissolution rate. This was exactly what Berger *et al.*

(1994) proposed; however, the observed dissolution rates did not change as much as suggested by the activation energy results. This is probably because the formation of inner-sphere surface complexes is a rare event on the pathway of Si–O–Si hydrolysis. It can only accelerate the net dissolution to some extent, depending on how often and for how long these inner-sphere surface complexes are formed.

It is worth noting that the activation energy data provided here are different from previous experimental data (Dove and Crerar, 1990; Dove, 1994, 1999). Dove and Crerar (1990) provided the “apparent activation energies” of quartz dissolution in pure water and ion-associated solutions. They suggested that the apparent activation energies were all very close to each other, both with or without electrolytes. Dove (1994, 1999) suggested the observed differences in the dissolution rate are caused by something that contributes to the pre-exponential factor “A” in the Arrhenius rate equation, but which is not the activation energies. However, the activation energy term used by Dove and coworkers is different from that used here. They employed a commonly used one-step Arrhenius rate equation to fit the bulk experimental dissolution rates and obtain their “apparent activation energies”. The Arrhenius rate equation is very similar to the rate equation based on transition-state theory. However, the latter is designed for a well-defined single-step reaction. In the case of quartz dissolution, there are various different reactive sites on the quartz surfaces and thus, numerous different reactions occur simultaneously. In fitting the net dissolution data into a single-step rate equation, we do not know the meaning of apparent activation energies such as these. Seemingly, these apparent activation energies are significantly different from those for elementary single-step processes and thus, they should not be compared directly.

Therefore, a “composite rate equation” that includes reasonably important elementary steps is highly desirable, even though it will be a little more complicated than those previously suggested (Bickmore *et al.*, 2008; Davis *et al.*, 2011). In such a composite rate equation, there are many different parallel reaction pathways involving different reaction sites (i.e., different activation energies). These activation energies are for elementary steps and can be estimated by carefully designed quantum chemistry calculation. If we analyze the accumulated experimental data by using such a composite rate equation and the estimated activation energies, we may be able to obtain greater insight into the pre-exponential factors of each elementary step in that equation.

Under neutral conditions, our activation energies results suggest that the ability of electrolytes to enhance quartz dissolution increases in the order of $\text{H}_2\text{O} < \text{Mg}^{2+} \approx \text{Ca}^{2+} < \text{Na}^+$ for the Q1 (Si) site, and it is $\text{H}_2\text{O} < \text{Na}^+ <$

$\text{Ca}^{2+} < \text{Mg}^{2+}$ for the Q2 (Si) site. Wallace *et al.* (2010) calculated the influence of the Mg^{2+} and Ca^{2+} cations on the hydrolysis of the Q3 (Si) sites and our results agree with theirs, suggesting that Mg^{2+} significantly promotes quartz dissolution for the Q2 (Si) site. However, such results are inconsistent with experimental results (Dove, 1994; Dove and Nix, 1997). The experimental data suggest that the rate-promoting ability increases in the order of $\text{H}_2\text{O} < \text{Mg}^{2+} < \text{Ca}^{2+} \approx \text{Na}^+$. Such a discrepancy could be the result of the distribution density of cations on the quartz surfaces, which actually is the most important part of the pre-exponential factor in a rate equation. Mg^{2+} has a larger energy barrier of solvent reorganization than Ca^{2+} . This higher barrier means that Mg^{2+} has less chance than Ca^{2+} to extract a coordinated water molecule and form inner-sphere adsorption surface complexes. Consequently, Ca^{2+} has greater surface density in inner-sphere adsorption complexes. Thus, the experimental results show that the “net” dissolution rate is increased more by Ca^{2+} than it is by Mg^{2+} (Wallace *et al.*, 2010).

This is why the importance of solvent reorganization events on the quartz surface are emphasized (Wallace *et al.*, 2010). Such events can change the activities of the reactants significantly. However, studying the solvent reorganization events and the activities of inner-sphere surface adsorption complexes of electrolytes is very difficult and beyond the scope of this study. Pico-second-level molecular dynamic simulations of these processes may be too short to obtain the entire picture of Si–O–Si hydrolysis at low temperatures. This type of molecular dynamic simulation is limited by computing power, especially for slow processes such as quartz dissolution. Therefore, for now, static quantum chemistry computation on reaction barriers for some well-identified single-step events of quartz dissolution is still the practical method.

Molecular-level mechanisms of quartz dissolution in pure water under alkaline conditions

The energy barriers of Si–O_{br} bond breaking are 49 kJ/mol for the Q1 (Si) surface site and 96 kJ/mol for the Q2 (Si) site in ion-free water under alkaline conditions; these results have never been reported before. The predicted activation energies are in line with experimental results, which suggest quartz dissolution increases if conditions change from neutral to alkaline (Table 2).

The optimized geometries (Figs. 3 and 4) of the reaction complexes with deprotonated surface Q1 (Si) and Q2 (Si) sites illustrate that the deprotonated oxygen atom is the reason for the change of geometries and the increase of dissolution rates. The extra electrons on the deprotonated oxygen atom result in a stronger Si–O_{term}[−] bond. The Si–O_{term}[−] bond length is much shorter than a common Si–O (H) bond (i.e., 1.64 Å); it is 1.59 Å for the

Q1 (Si) site or 1.56 Å for the Q2 (Si) site (Table 2). The short Si–O_{term}⁻ bond allows more Si electrons to migrate to it from the Si–O_{br} bond, resulting in a longer (or weakened) Si–O_{br} bond. For example, the bond length of Si–O_{br} changes from 1.64 about 1.67 Å (Table 2). This permits an easier hydrolysis reaction than for a neutral surface. Furthermore, one of the water molecules forms a strong hydrogen bond with the deprotonated oxygen atom. The O_w–H bond length is elongated from 0.96 to 0.99 or 1.04 Å for the Q1 (Si) or Q2 (Si) site, respectively. The consequence is that the dissociation of that water molecule also becomes easier. Therefore, the formation of the 5-coordinated Si transition-state complex is easy with a dissociated hydroxyl nearby. All of the above processes promote hydrolysis reactions.

Molecular-level mechanisms of quartz dissolution in electrolyte-containing solutions and under alkaline conditions

Although it is well known through experimental studies that at near-neutral conditions electrolytes promote quartz dissolution significantly, there are no computational studies for alkaline conditions with electrolytes (Davis *et al.*, 2011; Gratz and Bird, 1993; Strandh *et al.*, 1997). Experiments have shown that the Mg²⁺ and Ca²⁺ cations slow the dissolution rate under alkaline conditions (Strandh *et al.*, 1997). Calculations suggest that the adsorption of alkali metals results in changes in both the geometry and the Si–O bond strength (Gratz and Bird, 1993). The adsorption of alkali metal ions (e.g., Na⁺) weakens the Si–O bond. In this study, we provide the barrier heights of hydrolysis at the Q1 (Si) and Q2 (Si) sites of quartz surfaces in the presence of Na⁺, Mg²⁺, and Ca²⁺ under alkaline conditions. Our results show that Na⁺ decreases the barrier height and therefore, it increases the hydrolysis reaction of the Si–O_{br} bond. However, the influence of the IIA-type electrolytes (e.g., Mg²⁺, Ca²⁺) on the dissolution of quartz under alkaline conditions is completely different. The predicted bond-breaking barrier heights of Si–O_{br} are higher than in pure water. Furthermore, the formation of the Si–O–M²⁺ (M = Mg²⁺ or Ca²⁺) linkage inhibits the formation of H-bonding between the incoming water molecules and the deprotonated oxygen atom. The possibility of the dissociation of the incoming water molecule becomes smaller than in pure water. Therefore, the presence of Mg²⁺ or Ca²⁺ slows the hydrolysis reaction of the Si–O_{br} bond under alkaline conditions. This finding is consistent with earlier experiments by Strandh *et al.* (1997).

Na⁺ has weaker electronegativity than Mg²⁺ or Ca²⁺. It can form only weaker bonds with the O_{term}⁻ atom and cannot compete with nearby water molecules, which form stronger H-bonds with the O_{term}⁻. Therefore, Na⁺ has much less chance to form the Si–O–M²⁺ linkage than Mg²⁺ or

Ca²⁺ do. In addition, the forming of H-bonds between the incoming water molecule and the deprotonated terminal oxygen atom increases the possibility of the dissociation of that water molecule. The produced hydroxyl (OH⁻) will attack one adjacent Si tetrahedral and enhances the dissolution of quartz significantly.

CONCLUSION

Previous experimental studies have suggested that electrolytes affect quartz dissolution significantly, especially under near-neutral conditions. In this static first-principles DFT study, the M05-2X/6-311+(d,p)-level method is used for geometry optimization and transition-state searching to elucidate the molecular-level mechanisms of quartz dissolution under neutral and alkaline conditions, both with or without electrolytes. We find that electrolytes can enhance the hydrolysis reaction of the Si–O_{br} bond greatly under neutral conditions, but have different influences under alkaline conditions. The IIA-type electrolytes link to the bridging oxygen atoms under neutral conditions, but link to negatively charged terminal oxygen atoms under alkaline conditions. Although both neutral and alkaline conditions result in inner-sphere M–O linkages (i.e., M^{z+}–O_{br} or M^{z+}–O⁻), the consequences on the hydrolysis of adjacent Si–O–Si linkages via attack by another water molecule are different. The linking of M^{z+} (M = Ca²⁺ or Mg²⁺) to the bridging oxygen atom under neutral conditions weakens the Si–O–Si linkage and makes it easier for the hydrolysis reaction to occur. However, the formation of M^{z+}–O_{term}⁻ (M = Ca²⁺ and Mg²⁺) under alkaline conditions slows the hydrolysis reaction of quartz, because the electrons transferred to M^{z+} will shorten the adjacent Si–O–Si linkage. Owing to the weaker electronegativity, IA-type electrolytes (e.g., Na⁺) cannot bond directly to the deprotonated terminal O⁻ atom under alkaline conditions; a water molecule will form a stronger H-bond with that terminal O⁻ atom instead. Such H-bonding will allow that water molecule to become easily dissociated and thus, it results in an increase of dissolution. Therefore, under alkaline conditions, Ca²⁺ and Mg²⁺ will slow the hydrolysis reaction of the Si–O_{br} bond, but Na⁺ will accelerate it.

By comparing the energy profiles of many hydrolysis pathways, we have detailed information about the molecular-level mechanisms of those reactions. The dissolution mechanisms are quite different between pure water and electrolyte-containing solutions. Not only are the activation energies quite different, but also the numbers of transition states are different. There are two transition states (TS1, TS2) and a stable 5-coordinated intermediate (I) on the hydrolysis reaction pathways in pure water under alkaline condition; however, there is only one transition state along the reaction pathway in electrolyte-

containing solutions.

The important salt effect on the energetics of the breaking of the Si–O–Si bond under different pH environments is investigated carefully in this study. The main characteristics of such hydrolysis reactions have been captured and elucidated. The results of this study can be used to explain the differences in the experimental dissolution rate of crystalline or amorphous silica, which are affected by the combination of pH and electrolyte conditions.

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