A computational study of Mg\(^{2+}\) dehydration in aqueous solution in the presence of HS\(^-\) and other monovalent anions – Insights to dolomite formation

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Abstract

Massive sedimentary dolomite formed at near-Earth’s surface temperatures is abundant in the ancient geological rock record compared to modern deposition. Extensive experimental work to synthesize dolomite at low temperature and to reveal the formation mechanism has been attempted previously. Sulfide, the product of bacterial sulfate reduction, has been proposed in the literature to play an active role in promoting dolomite formation by facilitating desolvation of Mg\(^{2+}\) in the bulk solution and, thus, incorporation into the dolomite crystal structure. Chemical intuition, however, does not suggest any particular characteristic of HS\(^-\) that would render it an efficient promoter of Mg\(^{2+}\) desolvation in solution. In order to examine the previously proposed hypothesis, we conduct an \textit{ab initio} reaction path ensemble (RPE) study along a dissociative mechanism to determine the energy penalty of removing a first-shell water molecule around Mg\(^{2+}\) compared to Mg\(^{2+}\) with HS\(^-\) located in the second coordination shell. The solvent effect and specific hydrogen-bond interactions from water beyond the first solvation shell are addressed using large cluster models, where up to the second layer of Mg\(^{2+}\) hydration and the first solvation-shell of HS\(^-\) are included. Within the context of our modeling approach, we find that HS\(^-\) has little, if any, effect on lowering the Mg\(^{2+}\) dehydration barrier in aqueous solution. Alternative mechanisms must then be invoked to explain the apparent promotional effect of HS\(^-\) on Mg\(^{2+}\) dehydration kinetics.

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1. INTRODUCTION

Massive layers of sedimentary dolomite formed at Earth’s surface or near-surface temperatures (\(<\approx 50^\circ\text{C}\)) are found in strata of all ages from the Precambrian to the Cenozoic (Krauskopf and Bird, 1995). Modern dolomite formation is observed only in specific environments, such as highly saline lakes, deep-sea sediments and supersaturated saline lagoons, and only in minor quantities. Extensive attempts to synthesize dolomite have been carried out to reveal the mechanism of dolomite formation (Liebermann, 1967; Katz and Matthews, 1977; Baker and Kastner, 1981). Although dolomite precipitation is obtained under some extreme conditions, e.g., high temperature (Katz and Matthews, 1977;
Baker and Kastner, 1981], increased Mg\(^{2+}\) and Ca\(^{2+}\) concentrations (e.g., dolomite will precipitate directly from solution at a minimum salinity of 4–6 times of normal sea water at pH is 8–9) (Liebermann, 1967), high pH condition with the presence of supporting ions (e.g., NO\(_3^-\)) (Krauskopf and Bird, 1995), synthesis at Earth’s near-surface conditions have been unsuccessful (Land, 1998). The difficulty of low-temperature dolomite formation in modern times compared to the vast abundance in the geological record is referred to as the “dolomite problem”. More generally, the synthesis of mixed cation carbonates ([Fe, Ca, Mg]CO\(_3\)) at Earth’s near-surface temperatures is difficult inorganic (Romanek et al., 2009), although such phases are known geologically as fine-grained early diagenetic phases in sedimentary rocks (Matsumoto and Iijima, 1981; Mozley and Carothers, 1992), as cements in oil reservoir rocks (Thyne and Gwinn, 1994) and in the Martain meteorite ALH84001 (Mittlefeldt, 1994; Romanek et al., 1994). Microbial involvement in the formation of mixed-cation carbonates including dolomites has been proposed previously (Liebermann, 1967; Baker and Kastner, 1981; Patterson and Kinsman, 1982; Hardie, 1987; Vasconcelos et al., 1995; Mortimer and Coleman, 1997; Mortimer et al., 1997; Vasconcelos and McKenzie, 1997; Warthmann et al., 2000; Moreira et al., 2004; Morse et al., 2007). Thus, the occurrence of dolomite or other mixed-cation carbonates may serve as a biosignature on Earth and on other solid worlds such as Mars.

In order to form the dolomite crystal structure, direct Mg\(^{2+}/\text{Ca}^{2+}-\text{CO}_2^-\) interactions need to be established. The dehydration of Mg\(^{2+}\) at temperatures <50 °C has, therefore, been deemed as critical step for dolomite formation (Lippmann, 1973), although the exact mechanism is still unknown. Chemical promotion by organic ligands and inorganic anions such as sulfide by bacterial sulfate reduction has been proposed (Hardie, 1987; Oomori and Kitano, 1987; Buckin et al., 1994; Vasconcelos et al., 1995; Falini et al., 1996; Vasconcelos and McKenzie, 1997; Morse et al., 2007; Hamm et al., 2010). Based on the proposed promoting role of HS\(^-\) in Mg\(^{2+}\) desolvation, high-magnesium calcite and disordered dolomite was successfully synthesized at room temperature (Zhang, 2009; Zhang et al., 2010). The procedure involved mixing NaHCO\(_3\) + Na\(_2\)S (with or without pyrite)/sodium acetate (C\(_2\)H\(_3\)NaO\(_2\)) solution and CaCl\(_2\) + MgCl\(_2\) solution. Dolomite did not form without Na\(_2\)S, and control experiments apparently excluded the effect of pH increase. The authors showed a correlation between MgCO\(_3\) content of the high-magnesium calcite formed with the Na\(_2\)S concentration. The authors, however, did not provide a formation mechanism, and suggested only that the low dielectric constant of aqueous sulfide somehow promoted Mg\(^{2+}\) dehydration in solution.

Chemical intuition, based on considerations of charge density, chemical hardness/softness, or molecular electronic structures, however, does not suggest any particular characteristics of HS\(^-\) that would render it an effective promoter. Yet, this idea of HS\(^-\)—promoted Mg\(^{2+}\) dehydration in solution persists in the literature, and serves as the primary motivation of our work.

We study the mechanism for Mg\(^{2+}\) dehydration without and with HS\(^-\) in the bulk solution. The high charge-density of Mg\(^{2+}\) results in a very stable first hydration shell (Supplementary data Electronic Annex, Section 1). As a first step, we consider a dissociative mechanism where a first-shell water leaves the Mg\(^{2+}\) center before the CO\(_2^-\) can coordinate. We use a combination of computational methods ranging from classical molecular dynamics (MD) simulations to *ab initio* quantum mechanical calculations with model clusters. Alternative solution-phase mechanisms are the associative mechanism where a ligand such as CO\(_2^-\) binds with a hexa-coordinated metal center to form a hepta-coordinated intermediate (Eigen and Wilkins, 1965), and the concerted or interchange mechanism where water leaves and CO\(_2^-\) associates simultaneously with the Mg\(^{2+}\) center (e.g., Bleuzen et al., 1997). The promoting effect of HS\(^-\) may also involve a heterogeneous mechanism at the interface of a solid precursor phase. Our rationale for choosing to examine the dissociative mechanism in bulk solution is explained below briefly, and in detail in Supplementary data Electronic Annex, Section 2.

Previous workers have used computational electronic structure and molecular simulation methods to stay the solvation and water-exchange kinetics around metal ions including Mg\(^{2+}\), Ca\(^{2+}\), Al\(^{3+}\), and Fe\(^{3+}\) (Rustad et al., 1995; Kerisit et al., 2003; Kerisit and Parker, 2004; Stack et al., 2005; Jiao et al., 2006; Piana et al., 2006; Spagnoli et al., 2006; Wang et al., 2007; Criscenti et al., 2008; Evans et al., 2008; Kerisit and Rosso, 2009; Hamm et al., 2010). The structure and dynamics of Mg\(^{2+}\) and Ca\(^{2+}\) hydration are significantly different (see Electronic Annex, Section 1). For example, the water exchange rate around Ca\(^{2+}\) is five orders of magnitude faster than for Mg\(^{2+}\). Due to the significantly different hydration features of Mg\(^{2+}\) versus Ca\(^{2+}\), the formation of the Mg\(^{2+}\)-CO\(_2^-\) versus the Ca\(^{2+}\)-CO\(_2^-\) species proceeds via different mechanisms.

An associative mechanism is found for Ca\(^{2+}\) involving a pentagonal bipyramidal intermediate (Di Tommaso and de Leeuw, 2008), and the energy barrier is also small ~2.0 kcal/mol\(^{-1}\) (Ikedà et al., 2007; Electronic Annex, Section 2). An associative mechanism to form Mg\(^{2+}\)-CO\(_2^-\) interaction is not viable because the seven-fold coordination for Mg\(^{2+}\) is both thermodynamically and kinetically unfavorable, whereas the dissociative mechanism involving a five-fold intermediate is not energetically forbidden (Ikedà et al., 2007; Electronic Annex, Section 2). Once the five-fold coordination is formed, CO\(_2^-\) may, presumably, enter the first-coordination shell and regenerate the six-fold coordination. Hence, we study here the dissociative mechanism combining MD simulations to generate local solvent structures around the solute and Density Functional Theory Reaction Path Energy calculations for the energy profiles (see Electronic Annex, Section 3). The effects of thermal fluctuations are accounted for by using multiple snapshots from the MD simulations to prepare the large cluster models, and statistical results are analyzed.

At the atomistic level, we assume that the pathway involves interactions between the negative charge of HS\(^-\) and the dissociating water that directly interacts with the HS\(^-\), thus lowering the energy barrier for the Mg\(^{2+}\) dehydration process. In principle, HS\(^-\) may facilitate dissociation of the water molecule that does not directly interact
with $\text{HS}^-$, but our small cluster models results suggest that such a pathway is not favorable (see Section 2 and Electronic Annex, Section 4).

2. METHODS

Computational methods are described briefly in this section for the non-specialist. Details are provided below and in the Electronic Annex. Due to the dynamic solution structure, ideally, the water dissociation energy from the ion center should be investigated using the free-energy calculation (e.g., Umbrella Sampling method) with high-level quantum mechanical molecular dynamics simulation techniques, e.g., Car–Parrinello molecular dynamics (CPMD), where both the intrinsic dissociation energy and the solvent effect are addressed. But such calculations are computationally prohibitive (Electronic Annex, Section 3). An alternative choice to overcome this difficulty is to perform the free-energy calculation within a quantum mechanical/molecular mechanical (QM/MM) framework, where the reacting species and the immediate environment are treated with quantum mechanical methods and the rest of the solution system is described with the classical molecular mechanical force field (Warshel and Levitt, 1976; Field et al., 1990). We use large cluster models in order to address the solvent effect and specific hydrogen bond interactions from water beyond the first-solvation shell of Mg$^{2+}$. Up to the second layer of Mg$^{2+}$ hydration and the first solvation-shell of $\text{HS}^-$ are included in these large clusters.

Classical molecular dynamics simulations are employed to study the dynamic solution structure and to prepare snapshots of the initial water structures around the solute for the large cluster models. Statistical results are also analyzed. The MD simulations are performed using CHARMM package (Brooks et al., 1983, 2009). Density functional theory is then used to conduct reaction path ensemble (RPE) studies (Yang et al., 2006). Computational methods are described briefly in this section for the non-specialist. Details are provided below and in the Electronic Annex. Due to the dynamic solution structure, ideally, the water dissociation energy from the ion center should be investigated using the free-energy calculation (e.g., Umbrella Sampling method) with high-level quantum mechanical molecular dynamics simulation techniques, e.g., Car–Parrinello molecular dynamics (CPMD), where both the intrinsic dissociation energy and the solvent effect are addressed. But such calculations are computationally prohibitive (Electronic Annex, Section 3). An alternative choice to overcome this difficulty is to perform the free-energy calculation within a quantum mechanical/molecular mechanical (QM/MM) framework, where the reacting species and the immediate environment are treated with quantum mechanical methods and the rest of the solution system is described with the classical molecular mechanical force field (Warshel and Levitt, 1976; Field et al., 1990). We use large cluster models in order to address the solvent effect and specific hydrogen bond interactions from water beyond the first-solvation shell of Mg$^{2+}$. Up to the second layer of Mg$^{2+}$ hydration and the first solvation-shell of $\text{HS}^-$ are included in these large clusters.

Classical molecular dynamics simulations are employed to study the dynamic solution structure and to prepare snapshots of the initial water structures around the solute for the large cluster models. Statistical results are also analyzed. The MD simulations are performed using CHARMM package (Brooks et al., 1983, 2009). Density functional theory is then used to conduct reaction path ensemble (RPE) studies (Yang and Cui, 2009) with QChem 3.1 packages (Shao et al., 2006). We also use small cluster models, where only first-shell water molecules around Mg$^{2+}$ are taken into account, in order to study the intrinsic promoting ability of $\text{HS}^-$ and other ligands, and to gauge results of our large-cluster REP calculations. If $\text{HS}^-$ bears a special promoting ability for Mg$^{2+}$ dehydration, such a capacity should be observed with the small cluster model calculation, where first-shell water interactions with Mg$^{2+}$ and sulphydryl are maximized because there is no solvent beyond the first shell. For the small cluster model, we perform ab initio minimum energy path (MEP) calculations for hexahydrated Mg$^{2+}$ and for hexahydrated Mg$^{2+}$ with $\text{HS}^-$ or other monovalent ligands in the second coordination shell of Mg$^{2+}$. Results are presented in the Electronic Annex, Section 4.

2.1. Molecular dynamics simulations of Mg$^{2+}$ and Mg$^{2+}$ with $\text{HS}^-$ in aqueous solution

We carry out MD simulations for Mg$^{2+}$-only and Mg$^{2+}$ with $\text{HS}^-$ aqueous solutions up to 2 ns in order (1) to examine dynamic solvent structures around Mg$^{2+}$ within the 2 ns simulation length, and (2) to generate reasonable local solvent structures around Mg$^{2+}$ for large cluster models. We emphasize that the 2 ns MD simulations are not intended to capture the entire water dissociation process which is very around Mg$^{2+}$ ($\sim 6.7 \times 10^5$ s$^{-1}$), corresponding to an order of magnitude of 1 exchange event per microsecond (Bleuzen et al., 1997). The MD simulation is only used to generate local water structure around Mg$^{2+}$. We believe that the 2 ns time scale length is sufficient to sample local Mg$^{2+}$-water interactions in the first two hydration shells, which are the relevant coordination shells for the reaction path explored in our study. Our simulation period is also at the uppermost limit of timescales compared to other related computational studies which had time-scales ranging from $\sim 20$ ps to $\sim 1–2$ ns (Obst and Bradaczek, 1996; Koneshan et al., 1998; Kurnikova et al., 1998; Martinez et al., 1999; Yang and Cui, 2007; Yang and Cui, 2009; Di Tommaso and de Leeuw, 2010; Hamm et al., 2010).

For the Mg$^{2+}$ solution, we perform MD simulations with a quantum mechanical/molecular mechanical (QM/MM) potential (Warshel and Levitt, 1976; Gao and Truhlar, 2002; Riccardi et al., 2006b), where the self-consistent-charge density-functional-tight-binding (SCC-DFTB) method (Elstner et al., 1998) and CHARMM force field (MacKerell et al., 1998) serve, respectively, as the QM and MM components. SCC-DFTB is a semi-empirical density functional theory, which, coupled with CHARMM force field, has been widely and successfully applied to study various condensed-phase problems, ranging from chemical reactions in aqueous solution to catalytic processes in heterogeneous enzymatic environments (Cui et al., 2001; Riccardi et al., 2006a,b; Yang and Cui, 2007; Phatak et al., 2008; Yang et al., 2008a).

The Mg$^{2+}$ ion is solvated with a water droplet of 22 Å radius using TIP3P water model (Fig. 1). The CHARMM program, with Miscellaneous Mean Field Potential (MMFP) module is applied. We impose a harmonic restraint on Mg$^{2+}$ with Fig. 1. Solvation of Mg$^{2+}$ with a large water drop (22 Å) used in the molecular dynamics simulation. Mg$^{2+}$ is represented as a green ball, water molecules are rendered in the “surface” mode with white and red colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
around the center of the droplet to keep the ion at the center of the droplet. Mg\(^{2+}\) plus all water molecules within 5 Å from the Mg\(^{2+}\) center (first and second solvation shells) are treated quantum mechanically. A set of locally optimized Hubbard derivatives (Yang et al., 2007; Yang et al., 2008b) are applied to Mg, O and H elements. This approach has given consistent solution structures compared to those from previous CPMD (Car and Parrinello, 1985) simulations (Ikeda et al., 2007). Using the SHAKE algorithm to constrain all bonds involving hydrogen permits us to use an integration time step of 1 fs (Ryckaert et al., 1977). For 300 ps simulations at 298 K, the last 100 ps data in the trajectory are used for analysis.

For the Mg\(^{2+}\) with HS\(^{-}\) solution simulations, we use the classical CHARMM force field, because of the lack of SCC-DFTB parameters for sulfur. The atomic charges for HS\(^{-}\) are computed with the Merz-Singh–Kollman method (Singh and Kollman, 1984; Besler et al., 1990) at B3LYP/6–31+G\(^{*}\) level. A Nuclear Overhauser Effect (NOE) restraint is applied on sulfide with a maximum cutoff distance of 5.5 Å, to ensure that HS\(^{-}\) remains within the second solvation shell of Mg\(^{2+}\). The rest of the simulation setup is similar to the one for the Mg\(^{2+}\)-only solution. Additionally, in order to ensure a consistent comparison of the solvent dynamics and structures for solutions with and without HS\(^{-}\) anion, the Mg\(^{2+}\)-only solution is also simulated with the classical CHARMM force field.

2.2. Reaction Path Ensemble (RPE) study with large cluster models

We adopt large cluster models in order to take into account the effect of water molecules beyond the first solvation shell, where the solvent structures are obtained from the snapshots of the MD simulations. For the Mg\(^{2+}\)-only models, we include water molecules within 5.0 Å from Mg\(^{2+}\). Water molecules within 4.0 Å from HS\(^{-}\) are included for the Mg\(^{2+}\)-HS\(^{-}\) models. In order to explore the impact of thermal fluctuations, 6 snapshots for the Mg\(^{2+}\)-only solution and 4 snapshots for the Mg\(^{2+}\)-HS\(^{-}\) system are randomly selected from the MD simulation.

The number of snapshots chosen is based on both practical and scientific reasons. For the Mg\(^{2+}\) with HS\(^{-}\) system, the MD simulations showed that occasions for HS\(^{-}\) to directly interact with one water molecule in the Mg\(^{2+}\) first solvation shell are dominant, with a probability of ~72%. Encounters between HS\(^{-}\) and two water molecules have a ~20% probability, and chances to interact with more water molecules are negligible. We selected four model clusters in order to reflect this probability distribution. In three of them, HS\(^{-}\) interacts with one water molecule in the first solvation shell of Mg\(^{2+}\), and in the forth, HS\(^{-}\) interacts with two water molecule in the first solvation shell of Mg\(^{2+}\). Thus, the choice of four clusters was based on scientific considerations. For the Mg\(^{2+}\)-only system, the high expense of the simulations even with 8-CPU in parallel, limited the number of snapshots. Taking the model of the Mg\(^{2+}\) with HS\(^{-}\) as an example, each single-point calculation takes about ~80 min CPU time. On average, 120–150 minimization steps are needed to satisfy the optimization threshold for the gradient of root-mean-square (GRMS) of 0.05 kcal (mol Å)\(^{-1}\) with the adopted basis Newton–Raphson method (i.e., ~1440–1800 CPU hours to complete a single energy scan).

The model snapshot structures are first optimized at B3LYP/6–31+G\(^{*}\) level. Using the optimized structures, minimum energy path (MEP) calculations are then performed at the same theory level. The Mg\(^{2+}\)-O\(_{\text{water}}\) distance is defined as the reaction coordinate, with a step size of 0.2 Å. For the Mg\(^{2+}\) with HS\(^{-}\) models, we set the first-shell water molecule that directly interacts with HS\(^{-}\) to dissociate from the Mg\(^{2+}\) center (see Electronic Annex, Section 4 for this choice of reaction coordinate). Electronic energy is used to compute the dissociation energy barrier. The large size of the model clusters renders the calculations expensive, even with 8-CPU in parallel.

3. RESULTS AND DISCUSSION

3.1. Solution structures from MD simulations

To have a consistent comparison of solution structures for both solutions (without and with HS\(^{-}\)), up to 2 ns MD simulations with CHARMM force field are performed. Solution structures are analyzed based on the last 1.4 ns production simulations. Radial distribution functions (g(r)) and running coordination number (RCN) of water molecules around the Mg\(^{2+}\) center are computed (Fig. 2a). For Mg\(^{2+}\) only solution, the first peak in g(r) is located at ~2.0 Å, which is consistent with previous experimental and computational results (Neilson and Enderby, 1989; Skipper et al., 1989; Kerisit and Parker, 2004). Along the whole 2 ns simulation, the octahedral structure of the first solvation shell is stable. No water exchange is observed between the first-shell water and water beyond, as reflected by the sharp and narrow first peak in the g(r) plot and by the zero-value region ranging from 2.0 Å to 3.6 Å of the RCN curve. Similar results were observed in an earlier theoretical study of Mg\(^{2+}\) hydration structure (Obst and Bradaczek, 1996).

In order to examine the effect of HS\(^{-}\), the HS\(^{-}\) ion is constrained to move only within 5.5 Å from the Mg\(^{2+}\) center in the simulation, effectively restraining the HS\(^{-}\) within the two solvation shells of Mg\(^{2+}\). The g(r) for Mg–O\(_{\text{water}}\) and RCN are almost identical in the presence of HS\(^{-}\) to the pure Mg\(^{2+}\) system, within 4.0 Å from the Mg\(^{2+}\) center (Fig. 2a). The first peak remains at 2.0 Å, which indicates that HS\(^{-}\) does not weaken the interactions between Mg\(^{2+}\) and first-shell water molecules in the reactant state. This result is consistent with the quantum mechanical calculations on the small model clusters (Electronic Annex, Section 4). The average Mg–S distance is 4.8 Å with a variation of 0.3 Å, and the shortest distance observed is 3.8 Å. Due to the stable first-shell solvation of Mg\(^{2+}\), HS\(^{-}\) constantly occupies the second solvation shell of Mg\(^{2+}\), and cannot penetrate the first water layer to form direct contact with Mg\(^{2+}\). This explains the lack of any significant differences observed between the two solutions beyond 4.0 Å (Fig. 2a).

The radial distribution function and RCN of water molecules around HS\(^{-}\) are also computed, where the S-O\(_{\text{water}}\)
distance is analyzed (Fig. 2b). Based on the g(r), the first solvation shell of HS\(^-\) ends at \(\sim 3.7\) Å, and there are 7.4 water molecules in the first solvation shell. According to the best of our knowledge, there are no previous detailed computational or experimental studies in the literature for HS\(^-\) solution structure for bench-marking our results, so we use studies of Cl\(^-\) solution.

Chloride provides a reasonable comparison with HS\(^-\), because both ions possess the same charge as and similar radii. The two ions also have similar interactions with water. Based on pulsed high-pressure mass spectrometry study, Cl\(^-\) and HS\(^-\) show similar hydrogen-bonding energies (Meot-Ner, 1988). The interaction energy between HS\(^-\) and one water molecule in the gas phase is 14.2 kcal.mol\(^{-1}\), which is very close to that for Cl\(^-\) of 14.8 kcal.mol\(^{-1}\). At infinite dilution and temperature of 25°C, Koneshan et al. (1998) studied Cl\(^-\) in solution using MD simulations with the SPC/E water model (Berendsen et al., 1987). Results showed that 7.2 water molecules occupy the first solvation shell of Cl\(^-\) at a distance of up to 3.8 Å (Koneshan et al., 1998; Chowdhuri and Chandra, 2001), similar to our results for HS\(^-\). Thus, our calculations characterize the local solvent structure around HS\(^-\) reasonably well.

The number of first-shell water molecules around Mg\(^{2+}\) that directly interact with HS\(^-\) is analyzed along the simulation trajectory. The probability distribution is shown in Fig. 3. A high probability of \(\sim 72\%\) exists for occasions where HS\(^-\) directly interact with a single first-shell around the Mg\(^{2+}\). Interactions between HS\(^-\) and two water molecules have a \(\sim 20\%\) probability, and encounters with more water molecules are negligible. In contrast, gas phase results with small model clusters show interactions with three water molecules because the HS\(^-\) has no other choice (See Electronic Annex Fig. S4a). In the large cluster models, HS\(^-\) does not form stable interactions with three water molecules in the first solvation shell of Mg\(^{2+}\) due to the dynamical structure of solution and the full solvation of the anion. Based on these results (Fig. 3), we focus on the situations for HS\(^-\) interacting with one or two water molecules to address the solvent effects beyond the first solvation shell.

![Fig. 2. Radial distribution function (g(r), solid curves) and running coordination number (RCN, dashed curves) of water around (a) Mg\(^{2+}\) for solutions with and without HS\(^-\) and (b) of water around HS\(^-\).](image)

![Fig. 3. The probability distribution of the number of water molecules which are located on the first solvation shell of Mg\(^{2+}\) and directly interact with HS\(^-\).](image)

3.2. Reaction path ensemble study with large cluster models

3.2.1. Mg\(^{2+}\)-only system

Six snapshots of large model clusters of the Mg\(^{2+}\)-only system without HS\(^-\) are obtained from MD simulations. The interactions between Mg\(^{2+}\) and first-shell water molecules of the optimized structures for the reactant state are consistent with results from the small model cluster. In detail, six water molecules form an octahedral geometry surrounding the Mg\(^{2+}\) ion, with an average Mg–Ow distance of 2.12 Å (36 Mg–Ow distances from all of the six large clusters are taken into account, and a variation 0.05 Å). One interesting observation is that the first-shell water molecules around Mg\(^{2+}\) coordinate asymmetrically to Mg\(^{2+}\) through one of the oxygen lone pair orbitals (Fig. 4). The asymmetric coordination was also obtained in a CPMD study to of Mg\(^{2+}\) hydration (Lightstone et al., 2001). Each first-shell water molecule forms \(~2–3\) hydrogen bonds with the water molecules in the second solvation shell, which makes the observed asymmetric water orientations possible. In contrast, the first-shell waters in the small cluster model,
coordinate symmetrically to Mg2+ by bisecting the two oxygen lone pair orbitals (Electronic Annex Fig. S3).

We next compute the energetics for dissociation of a first-shell water molecule around Mg2+. The MD simulations of Mg2+ in aqueous solution show that the first shell ends at Mg–Ow ~ 3.5 Å. Therefore, we define the Mg–Ow distance as the reaction coordinate and set 3.7 Å as the upper limit for the energy scans to ensure that the dissociating water escapes from the first solvation shell. As stated above, we assume that the transition from a six-fold hydration of Mg2+ to a five-fold geometry involves two elementary steps (Ikeda et al., 2007). The first step involves removing one water molecule from the first solvation shell. Subsequently, the remaining first-shell water molecules relax structurally into a trigonal bipyramidal geometry due to thermal fluctuations that would overcome the hydrogen bonding interactions between the first and second water shells. The first step is an energy-increase process, and the subsequent structural relaxation for the five water molecules is an energetically down-hill process. If both steps are captured in the simulation, then an energy barrier will be obtained. If the water molecules are unable to relax then a monotonically increasing profile will be seen. The energy increases with increasing Mg–Ow distance for all six scans, but in only one of the scans, does the energy decrease resulting in an energy barrier of 9.9 kcal mol−1 (Fig. 5a).

The decrease in energy occurs because the five remaining first-shell water molecules relax and form a trigonal bipyramidal geometry at Mg–Ow ~ 3.5 Å. For five out of six large model clusters, the energy scans show a monotonic energy increase with the Mg–Ow distance going up to 3.7 Å, no local energy minima or energy barriers are obtained (Fig. 5a). The lack of an energy barrier is ascribed to the fact that the five remaining first-shell water molecules do not form a trigonal bipyramidal geometry at the end point of the energy scan, even though the dissociating water has escaped. Instead, small contractions are observed for the two axial ZO – Mg – O angles from ∼180° in the reactant state to 163° at the scan end point, with a variation of 6.8° (see a representative structure in Fig. 5b). The limited relaxation of the water molecules in the first solvation shell occurs due to hydrogen bond interactions with second-shell water molecules. A similar result has been obtained previously (Evans et al., 2008).

Despite the lack of an energy barrier for five of the six scans, we believe that our computational approach is relevant, because the average value for the difference in energy between the end point of the scan and the reactant state (ΔE(Mg–Ow = 3.7 Å – ΔE(Mg–Ow = 2.1 Å)) is 10.4 kcal mol−1, with a variation of 2.9 kcal mol−1. The average energy difference is similar to the Gibbs free energy barrier of 10.5 kcal mol−1 obtained for water dissociation using the small cluster model with PCM solvation (see Electronic Annex Fig. S1). The average energy difference is also similar to the single scan that did show an energy barrier of 9.9 kcal mol−1. A direct comparison of our calculated energies to experimental values is not easy (e.g., potential energy versus free energy), but we report here a value of 9.5 kcal mol−1 for water exchange on Mg(H2O)62+ at 300 K from 18O NMR experiment (Bleuzen et al., 1997). Our calculated values for both, the average of the six scans as well as the single scan which did show an energy barrier, are in fair agreement with the experimental value. A similar barrier height of ∼9 kcal mol−1 was obtained using the molecular mechanics-based potential of mean force calculations (Kerisit and Parker, 2004). These considerations suggest that our RPE calculations are meaningful.

3.2.2. Mg2+ with HS− system

From the four optimized reactant state structures, we see that HS− does not perturb the interactions between Mg2+ and the first-shell water molecules, which is consistent with our small cluster model results (see Electronic Annex Figs. S3a and S4a). In detail, the average Mg–Ow distance is 2.12 Å with a variation of 0.03 Å. As observed in the Mg2+z-only system, the first-shell water molecules coordinate asymmetrically to Mg2+ through one of the oxygen lone pair orbitals. This result is ascribed to preferred interactions with water molecules in the second solvation shell.

In three of the large model clusters, HS− interacts with a single first-shell water molecule around Mg2+. The average S–Hwater distance obtained is 2.34 Å, where “Hwater” refers to the hydrogen atom of the water molecule that directly interacts with HS−. For the fourth large model cluster, HS− interacts with two first-shell water molecules around Mg2+, with S–Hwater distances of 2.24 Å and 2.36 Å. In all four cases, HS− remains in the second solvation shell of Mg2+ with an average Mg–S distance of ∼4.8 Å.

The energy scan is set up similar to the Mg2+z-only case. We set the Mg–Ow distance as the reaction coordinate with 3.7 Å as the upper limit for the energy scan to ensure that the dissociating water escapes from the first solvation shell of Mg2+. Based on results of the small cluster study (see
The water molecule which interacts directly with HS\(^{-}\) is defined to dissociate from the Mg\(^{2+}\) center. All four energy scans show monotonically increasing profiles as the Mg–O\(_w\) distance increases, similar to the Mg\(^{2+}\)-only large cluster model (Fig. 6a). Interestingly, the average energy difference between the end point of the scan and the reactant state (\(E_{\text{Mg–O}} = 3.7\) Å−\(E_{\text{Mg–O}}\) Ow = 2.1 Å) from the four scans is 14.3 kcal mol\(^{-1}\). This average energy difference value is much higher than the dissociation barrier of 7.9 kcal mol\(^{-1}\) for the small cluster model in the solution phase (see Electronic Annex Table EA1), and than the energy difference of 10.4 kcal mol\(^{-1}\) for the large cluster Mg\(^{2+}\)-only system. Similar to the Mg\(^{2+}\)-only system, for all of the four scans, the five remaining first-shell water molecules do not gradually form a trigonal bipyramidal geometry along the water dissociation pathway. The two axial \(\angle O = \text{Mg} – O\) angles contract from \(\sim 180^\circ\) in the reactant state to \(161^\circ\) at the end of scans (Fig. 6b).

The results of the present computational approach indicate a large energy barrier for Mg\(^{2+}\) dehydration in the presence of HS\(^{-}\) (Fig. 6a), suggesting that HS\(^{-}\) did not facilitate water dissociation. The lack of structural relaxation of first-shell water molecules can be understood by comparing the large cluster and the small cluster results.

The \textit{ab initio} small cluster calculations using the Natural Bond Orbital (NBO) method (Foster and Weinhold, 1980; Glendening et al., 2001) capture the intrinsic interactions of ligands with first-shell water molecules around Mg\(^{2+}\) without effects of solvation beyond the first shell (see Electronic Annex Section 4.3). Those results show that the major lowering of the energy barrier (i.e., energy stabilization) for water dissociation by HS\(^{-}\) comes from the interactions between HS\(^{-}\) and the remaining first-shell water molecules around Mg\(^{2+}\).

In three out of four large cluster models, HS\(^{-}\) interacts only with one water molecule and when that molecule departs, there are no direct interactions between HS\(^{-}\) and the remaining first-shell water molecules. Consequently, the resulting penta-hydrated complex of Mg\(^{2+}\) cannot be stabilized effectively by HS\(^{-}\). For the fourth large cluster model, HS\(^{-}\) directly interacts with two water molecules in the first solvation shell of the reactant state. As one water molecule leaves, the interaction between HS\(^{-}\) and the second water molecule becomes stronger, with the S–H\(_\text{water}\) distance decreasing from 2.36 Å in the reactant state to 2.28 Å in the penta-hydrated complex. Even here, though, the HS\(^{-}\)-water stabilization is still much weaker than for the small model cluster, where two HS\(^{-}\)-water interactions exist and each S–H\(_\text{water}\) distance is shorter than 2.00 Å. In the small cluster model, the remaining first-shell water molecules have no choice but to interact with HS\(^{-}\), whereas those in the large cluster model have the ability to interact with HS\(^{-}\) as well as with second-shell water molecules. Furthermore, we note that the remaining first-shell water molecules are relatively far away from the HS\(^{-}\) ligand (the minimum S–O\(_\text{water}\) distance is over 5 Å). It is then reasonable to assume that HS\(^{-}\) may not directly affect the structural rearrangement for the five remaining first-shell water molecules.

In summary, the limited interactions between the remaining water molecules in the first solvation shell and HS\(^{-}\) provide inadequate stabilization of the transition state, which is mainly responsible for the large and monotonically increasing energy profiles in the presence of HS\(^{-}\) (Fig. 6a). The current computational result showing an apparent lack of any HS\(^{-}\) effect is consistent with our chemical intuition, and is supported by the small cluster studies showing no correlation between the intrinsic chemical properties of HS\(^{-}\) or other inorganic ligands and their ability to lower the Mg\(^{2+}\) dehydration behavior.

3.3. Implications for dolomite formation

The elementary step of water leaving from the Mg\(^{2+}\) center in the solution phase has previously been widely
accepted as the most critical step towards dolomite formation. According to our current study, and consistent with our chemical intuition, it is unlikely that HS<sup>-</sup> has a specific ability to promote Mg<sup>2+</sup> dehydration in aqueous solution via a dissociative mechanism. It is entirely possible, however, that HS<sup>-</sup> may facilitate dolomite formation via other pathways. For instance, a concerted (interchange) mechanism is conceivable, where a water molecule leaves the Mg<sup>2+</sup> solvation shell and CO<sub>3</sub><sup>2-</sup> attacks the Mg<sup>2+</sup> center simultaneously. Such a mechanism will be explored in future work. Alternatively, HS<sup>-</sup> may promote cation desolvation at the interface of a solid precursor phase or seed crystal.

The difficulty of dehydrating Mg<sup>2+</sup> is supported by empirical observations that magnesite (MgCO<sub>3</sub>) is difficult to synthesize directly at low temperature and a number of hydrated MgCO<sub>3</sub> solid precursor phases are formed instead (Marschke, 1969; Fischbec and Muller, 1971; Garvie, 2003; Romanek et al., 2009). A hydrated, amorphous CaCO<sub>3</sub> solid precursor to calcite has also been reported in recent biominalization literature and depending on solution conditions (Weiss et al., 2002; Politi et al., 2004; Politi et al., 2006; Politi et al., 2008). Static lattice energy minimization calculations have shown that a solid phase 50/50 mixture of (Ca/Mg) CO<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> is thermodynamically more stable than ikaite (CaCO<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> (de Leeuw and Parker, 2001). Since ikaite is a potential precursor of calcite (Ito, 1998), de Leeuw et al. proposed that the solid 50/50 mixture of (Ca/Mg) CO<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub> may be a precursor to low-temperature dolomite. Although our computational approach does not indicate a promoting effect of HS<sup>-</sup> on Mg<sup>2+</sup> dehydration in bulk solution, Zhang et al. (2010) apparently did synthesize dolomite in the presence of HS<sup>-</sup>.

We speculate, then, that HS<sup>-</sup> or some organic ligands may promote Mg<sup>2+</sup> dehydration at the surface of a solid precursor phase resulting in (proto)dolomite. If no promoter anion is present, then it follows logically that a CaCO<sub>3</sub> solid precursor will form first and hydrated Mg<sup>2+</sup> will be adsorbed to the precursor surface. Since direct Mg<sup>2+</sup>-CO<sub>3</sub><sup>2-</sup> ion interactions cannot be established, the proto-dolomite precursor will not be formed. Instead, separate phases consisting of a calcium carbonate kernel and a hydrated magnesium carbonate outer shell would be produced. Results of preliminary experiments in our laboratories support these speculations, though detailed work remains to be done (Chakraborty and C. S. Romanek, unpublished results). An anion-promoted interfacial mechanism has also been proposed for barite formation, where Ba<sup>2+</sup> desolvation was assisted by anions (inorganic ligands like SO<sub>4</sub><sup>2-</sup> or biological ligands like aspartic acid) adsorbed on the crystal surface (Piana et al., 2006, 2007). We have previously reported the formation of an amorphous, hydrated, mixed anion phase at room temperature (Sahai et al., 2007).

While dolomite synthesis at Earth’s near-surface conditions has been a fascinating challenge for geochemists over decades, the question remains as to whether any laboratory experiments can capture the true geological process. As noted in Hardie’s (1987) excellent and provocative review, massive sedimentary dolomitization occurs over ~100,000 time periods, so it is entirely plausible that completely different mechanisms operate over geologic time and space, and that given enough time, dolomitization may not be a “problem”.

4. CONCLUSIONS

The “dolomite problem” has puzzled geochemists and sedimentologists for a long time. The difficulty of Mg<sup>2+</sup> dehydration is deemed as the biggest hurdle toward dolomite formation. Sulfide was proposed to play an active role in promoting dolomite formation. Using our current computational approach, HS<sup>-</sup> does not seem to have any specific ability to promote Mg<sup>2+</sup> dehydration in aqueous solution via simple hydrogen-bond-like interactions. It is entirely possible, however, that HS<sup>-</sup> may facilitate dolomite formation by some other mechanism(s). We propose that Mg(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> associates with the surface of a calcium carbonate solid precursor phase (potentially amorphous and
hydrated), and HS\(^{-}\) promotes dehydration of Mg\(\text{H}_2\text{O}\)\(^{2+}\) at the solution–solid interface resulting in a “protodolomite” precursor that eventually transforms to dolomite.

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**APPENDIX A. SUPPLEMENTARY DATA**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.03.018.

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