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Author(s)	Kawano, Jun; Sakuma, Hiroshi; Nagai, Takaya
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RESEARCH ARTICLE

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Incorporation of Mg^{2+} in surface Ca^{2+} sites of aragonite: an *ab initio* study

Jun Kawano^{1,2*}, Hiroshi Sakuma³ and Takaya Nagai²

Abstract

First-principles calculations of Mg^{2+} -containing aragonite surfaces are important because Mg^{2+} can affect the growth of calcium carbonate polymorphs. New calculations that incorporate Mg^{2+} substitution for Ca^{2+} in the aragonite {001} and {110} surfaces clarify the stability of Mg^{2+} near the aragonite surface and the structure of the Mg^{2+} -containing aragonite surface. The results suggest that the Mg^{2+} substitution energy for Ca^{2+} at surface sites is lower than that in the bulk structure and that Mg^{2+} can be easily incorporated into the surface sites; however, when Mg^{2+} is substituted for Ca^{2+} in sites deeper than the second Ca^{2+} layer, the substitution energy approaches the value of the bulk structure. Furthermore, Mg^{2+} at the aragonite surface has a significant effect on the surface structure. In particular, CO_3 groups rotate to achieve six-coordinate geometry when Mg^{2+} is substituted for Ca^{2+} in the top layer of the {001} surface or even in the deeper layers of the {110} surface. The rotation may relax the atomic structure around Mg^{2+} and reduces the substitution energy. The structural rearrangements observed in this study of the aragonite surface induced by Mg^{2+} likely change the stability of aragonite and affect the polymorph selection of CaCO_3 .

Keywords: Aragonite; Impurity; Surface structure; First-principles calculation

Background

The formation of calcium carbonate (CaCO_3) polymorphs, calcite, aragonite, and vaterite has been extensively investigated due to their importance in geological and biological environments. To account for the formation of a particular polymorph, the role of impurities has been proposed as the controlling factors in many studies (e.g., Kitano 1962; Davis et al. 2000); however, the mechanism for the incorporation of impurities during crystal growth is poorly understood. In this study, we focus on the incorporation of Mg^{2+} in the aragonite surface and analyze its behavior using first-principles calculations.

Many researchers have previously reported that alkaline-earth cations other than Ca^{2+} affect the growth kinetics of CaCO_3 (e.g., De Yoreo and Vekilov 2003; Astilleros et al. 2010; Nielsen et al. 2013). In particular, Mg^{2+} has been considered important to the formation of CaCO_3 polymorphs. For example, Kitano (1962)

indicated that the addition of Mg^{2+} to a solution promoted the metastable formation of aragonite. Recently, detailed atomic force microscopy (AFM) observations of the growth surface of calcite suggested that Mg^{2+} inhibits the crystal growth of calcite by blocking the propagation of kink sites (Nielsen et al. 2013) or by increasing the mineral solubility (Davis et al. 2000). To analyze this phenomenon on calcite surfaces at the atomic level, atomistic simulations were also conducted using static lattice energy minimization (Titiloye et al. 1998), molecular dynamics (MD) (de Leeuw and Parker 2001), and electronic structure calculations based on density functional theory (DFT) (Sakuma et al. 2014).

However, there are relatively few studies focusing on the aragonite surface. To discuss the mechanism for the formation of CaCO_3 polymorphs, not only should the atomic behavior on the calcite surface be understood but also that on the aragonite surface. Moreover, the Mg content in coral fossils comprising aragonite has been used to reconstruct the past climatic record (e.g., Mitsuguchi et al. 1996); however, the location of Mg^{2+} in the coral skeleton is strongly debated (Finch and Allison 2008). Therefore, understanding the mechanism for the incorporation of

* Correspondence: j-kawano@mail.sci.hokudai.ac.jp

¹Creative Research Institution (CRIS), Hokkaido University, N21 N10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

²Faculty of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

Full list of author information is available at the end of the article

Mg²⁺ into the aragonite surface is important not only for the mineral and material sciences but also for the biological and environmental sciences.

Divalent cations smaller than Ca²⁺, such as Mg²⁺, do not generally enter the aragonite structure, whereas larger cations, such as Ba²⁺, cannot be incorporated in the calcite structure. However, the structure near a crystal surface differs from the bulk crystal because of its flexibility. Thus, a crystal surface can incorporate ions that are unstable in the bulk structure and play an important role during the formation and subsequent crystal growth of calcium carbonate polymorphs. We investigated the substitution of Mg²⁺ ions at the Ca²⁺ sites of aragonite surfaces. Mg²⁺ is unstable in ninefold coordination in aragonite and does not readily enter into the bulk aragonite structure; however, Mg²⁺ is expected to be substitutable for Ca²⁺ at sites near the surface. Recently, Ruiz-Hernandez et al. (2012) performed MD calculations regarding Mg²⁺ substitution at the aragonite surface. However, they analyzed only the Mg²⁺ substitution into Ca²⁺ sites at the top surface. To discuss the incorporation of an ion into a specific surface, the ion substitution energy for Ca²⁺ sites should be estimated at the top surface and deeper. Furthermore, the substitution of Mg²⁺ for Ca²⁺ may change the surface structure. This could affect the stability relations among polymorphs, as surface energy differences among polymorphs have been proposed to account for their stability field (Navrotsky 2004; Kawano et al. 2009). Hence, an in-depth analysis of these surface structures and their incorporation of ions is important; however, details regarding the surface structural changes when a Mg²⁺ ion is incorporated at the surface are presently lacking. Therefore, in this study, the stability of Mg²⁺ near the aragonite surface and the structure of Mg²⁺-containing aragonite surface were investigated using first-principles calculations, and the effect of Mg²⁺ on the formation of polymorphs was examined.

Methods

The optimized geometries and total energies of the surfaces were obtained using DFT with the Vienna *ab initio* simulation package (VASP) code (Kresse and Hafner 1993, 1994; Kresse and Furthmüller 1996a, b; Kresse and Joubert 1999) and the Perdew-Burke-Ernzerhof version of the generalized gradient approximation (GGA-PBE) (Perdew et al. 1996). The energy cutoff of the plane-wave basis set was 900 eV, which was tested for energy convergence. The valence states for Ca, Mg, C, and O are 3s²3p⁶4s², 2p⁶3s², 2s²2p², and 2s²2p⁴, respectively, following previous DFT calculations for CaCO₃ (Hossain et al. 2009) and MgCO₃ (Hossain et al. 2010).

Prior to calculation of the aragonite surface, the structural parameters of aragonite were simulated. The calculated lattice parameters are $a = 5.022$ Å, $b = 8.042$ Å, and

$c = 5.816$ Å, whereas the experimental values are $a = 4.962$ Å, $b = 7.969$ Å, and $c = 5.743$ Å (Balmain et al. 1999). The calculated C-O bond lengths are 1.291 to 1.301 Å, which are comparable to previous experimentally and theoretically obtained values (Balmain et al. 1999; Akiyama et al. 2011).

Aragonite surfaces were simulated as repeated slabs. The unit supercell contained 80 atoms and 4 or 5 Ca and CO₃ layers of the unit (2 × 1) surface structure with a 15 Å thick vacuum layer. The macroscopic dipole was removed, and the neutrality of the supercell was ensured by the two equivalent surfaces on opposite sides of the slab. To calculate the substitution energy, the total energy of the slab was simulated by relaxing the atoms except those on the bottom layer. In the calculation, the supercell parameters were fixed using the calculated aragonite unit cell parameters, because Mg ions are not supposed to be substituted into the bulk Ca sites but only into surface sites; hence, substitution does not affect the lattice constants. Optimization was performed with a convergence threshold of 5.0×10^{-6} eV/atom for the maximum energy change and 0.05 eV/Å for the maximum force. The atomic structures of the slab were drawn with the VESTA software (Momma and Izumi 2008). CaCO₃ crystals generally grow in an aqueous solution with H₂O molecules just above the surface; however, the presence of the vacuum layer above the surface was considered here. The validity of this setting will be discussed in the next section.

Results and discussion

Substitution energy of Mg²⁺ for Ca²⁺ near the aragonite surface

We calculated the surface energies of the aragonite {001}, {010}, and {110} surfaces, which are generally expressed in experimental morphology. On the {001} surface, the CO₃ groups (triangles) are arranged parallel to the surface, whereas these groups are perpendicular to the {010} and {110} surfaces. Recently, Akiyama et al. (2011) determined the stable surface structure of calcite and aragonite via DFT calculations. They reported that the most stable configuration of {001} is a CO₃-terminated surface, wherein the coverage of CO₃ ions is 0.5. In contrast, the most stable configurations for {010} and {110} are Ca-terminated planes, wherein the coverage of Ca²⁺ ions is 0.5. The surface energy of these stable configurations were calculated to be 0.49, 0.57, and 0.49 J/m² for the {001}, {010}, and {110} surfaces, respectively (Table 1). In the calculation, the positions of all the slab atoms were relaxed, and the surface energies E_{surf} were obtained by dividing the difference between the total energy of the slab E_{slab} and that of the bulk crystal E_{bulk} , including the same number of atoms, by the total area of the calculated surface A , which includes the top and bottom surfaces:

Table 1 Estimated surface energies (J/m²) of the aragonite surfaces

Surface		This work	Akiyama et al.	de Leeuw and Parker	
		DFT Pure	DFT Pure	Empirical potential Pure	Empirical potential Hydrated
{001}	$\theta_{\text{CO}_3} = 0.5$	0.49	0.58	0.85	0.90
{010}	$\theta_{\text{Ca}} = 0.5$	0.57	0.73	0.96	0.24
{110}	$\theta_{\text{Ca}} = 0.5$	0.49	0.64	0.88	0.56

$$E_{\text{surf}} = (E_{\text{slab}} - E_{\text{bulk}})/A. \quad (1)$$

The results suggest that the {001} and {110} surfaces are slightly more stable than the {010} surface, which is consistent with previous DFT and empirical potential calculations (Akiyama et al. 2011; De Leeuw and Parker 1998). Therefore, we focused on the {001} and {110} aragonite surfaces and analyzed the substitution energy of Mg^{2+} for Ca^{2+} . The structures considered in this study are shown in Figure 1. In the first Ca layer of the {001} surface, there are two types of Ca sites because the coverage of CO_3 ions is 0.5 in the most stable structure of this surface. The site labeled A in Figure 1 (denoted

as site A hereafter) is the site above which no CO_3 groups are located, whereas the site labeled B in the same figure (site B) is similar to the site in the bulk with respect to the arrangement of surrounding CO_3^{2-} ions, except for the lack of one CO_3^{2-} . In contrast, there are two Ca layers in the {110} surface with different depths between the CO_3 layers.

De Leeuw and Parker (1998) estimated the energies of pure and hydrated surfaces and found that hydration does not stabilize the carbonate-terminated {001} surface and less so the calcium-terminated {110} surface (Table 1). In contrast, the calcium-terminated {010} surface was significantly stabilized by hydration. The surface energies calculated in this study show almost the same trend. Therefore, the substitution energies obtained for nonhydrated and hydrated {001} and {110} surfaces can be considered to have similar features. It is thus reasonable to analyze non-hydrated {001} and {110} surfaces to discuss the exchange energy in aqueous solutions, whereas Nada (2014) recently reported the importance of water layers on the calcite {104} surface.

In an aqueous solution, Mg^{2+} ions are surrounded by H_2O molecules and exist as hydration shells (e.g., Marcus

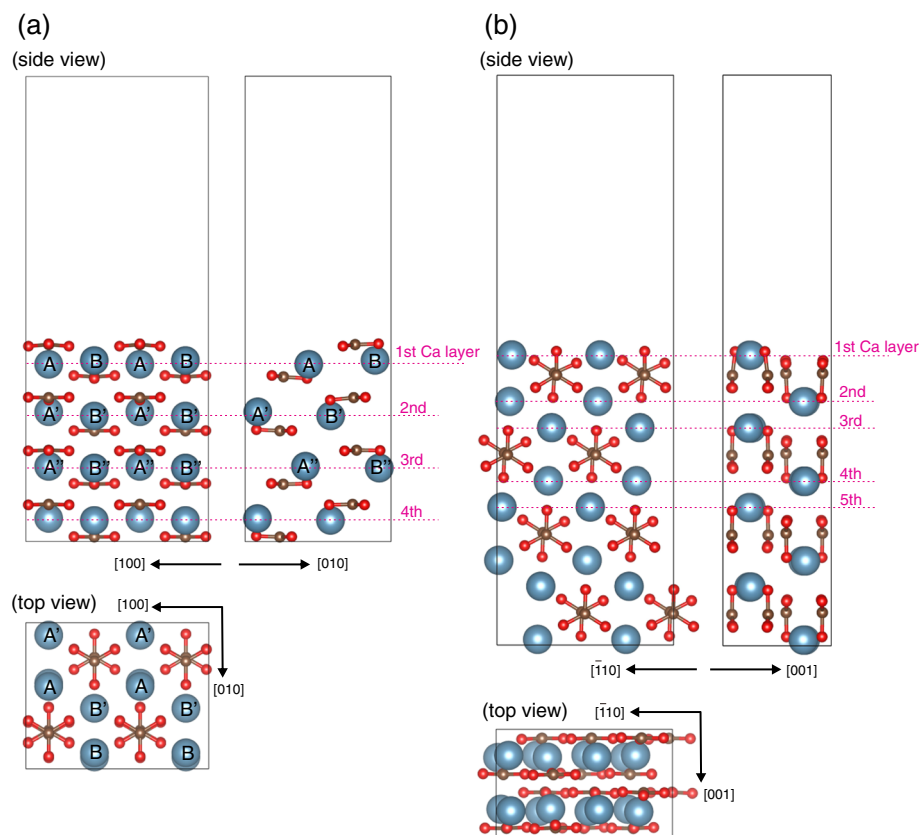
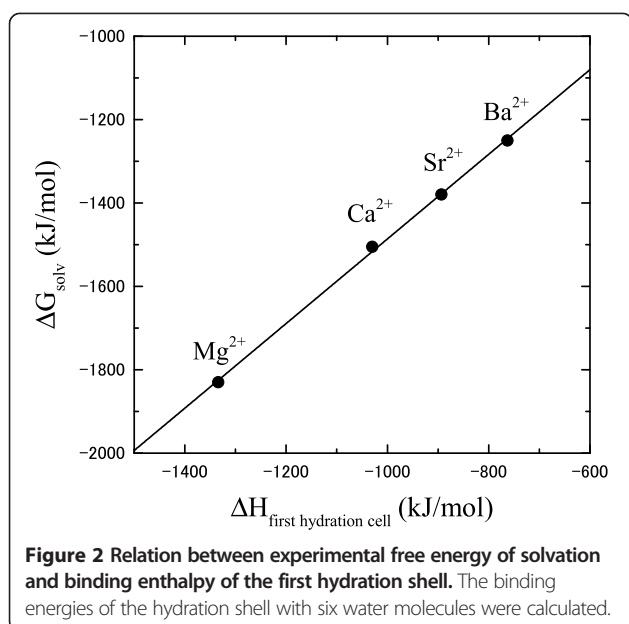


Figure 1 Relaxed atomic arrangement of (a) {001} and (b) {110} surfaces. Red, brown, and blue circles represent O, C, and Ca, respectively. Ca layers are numbered from the top to deeper layers - see text regarding [A] and [B] for the top Ca layer on the {001} surface. In addition, there are two types of sites in the second and third layers of the {001} surface, which are labeled [A'], [B'] and [A''], [B''], respectively.



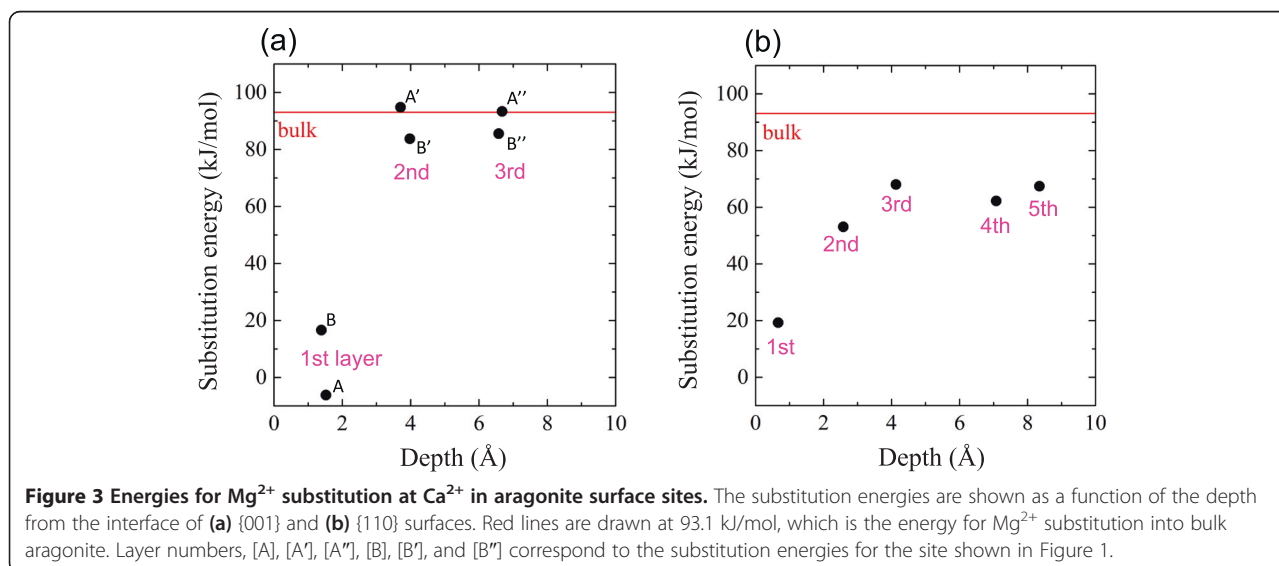
1987; Rodriguez-Cruz et al. 1999; Bock et al. 2006). Therefore, to substitute into a surface Ca^{2+} site, a Mg atom must be released from the hydration shell. In this study, a six-coordinated complex was assumed for the divalent cations in the hydration shells, and the cohesive energies of the primary hydration shells of Ca^{2+} and Mg^{2+} ions were calculated using the DFT method as references. The calculated and experimental Gibbs free energies for hydration (Marcus 1991) have an excellent 1:1 correspondence, as shown in Figure 2. Following the discussion by Sakuma et al. (2014), such correspondence suggests that the relative binding enthalpy of the first hydration shell with six water molecules can describe the relative free energies of divalent cations in water.

Using these results, the energy ΔE of the Mg^{2+} substitution in surface Ca^{2+} sites of aragonite can be expressed as follows:

$$\Delta E = [E_{\text{surface(Mg)}} + E_{\text{hydration shell(Ca)}}] - [E_{\text{surface(Ca)}} + E_{\text{hydration shell(Mg)}}], \quad (2)$$

where $E_{\text{surface(Ca)}}$ and $E_{\text{surface(Mg)}}$ represent the total energies of the aragonite slab with and without Mg, and $E_{\text{hydration shell(Ca)}}$ and $E_{\text{hydration shell(Mg)}}$ are the energies of the hydration shells of Ca^{2+} and Mg^{2+} with $6\text{H}_2\text{O}$, respectively. The calculated cohesive energy of the primary hydration shell of Mg^{2+} with $6\text{H}_2\text{O}$ is approximately -13.8 eV (1,330 kJ/mol) and that for Ca^{2+} is -10.8 eV (1,030 kJ/mol), which indicates that the hydration shell of the smaller cation is more stable than that of the larger cation.

For Mg^{2+} substitution in Ca^{2+} sites of the bulk aragonite structure, the substitution energy obtained from Equation 2 using the energy of the bulk instead of the energy of the slab was calculated as 93.1 kJ/mol. However, the substitution energy for the surface site is much smaller than that for the bulk. Whether Mg ions will actually substitute for Ca depends on the chemical potential difference including entropy, while the entropy of an ion in aqueous solutions is difficult to estimate. Therefore, the negative or positive sign of the substitution energy ΔE does not directly mean that Mg ions enter the crystal or not. However, these energies can provide information regarding the relative stability of Mg in the site around the surface. The results of the present calculations suggest that Mg^{2+} can substitute more easily at surface sites than in the bulk aragonite structure. Figure 3 shows the Mg^{2+} substitution energy ΔE for a Ca^{2+} site as a function of depth for the interface of the {001} and {110} surfaces.



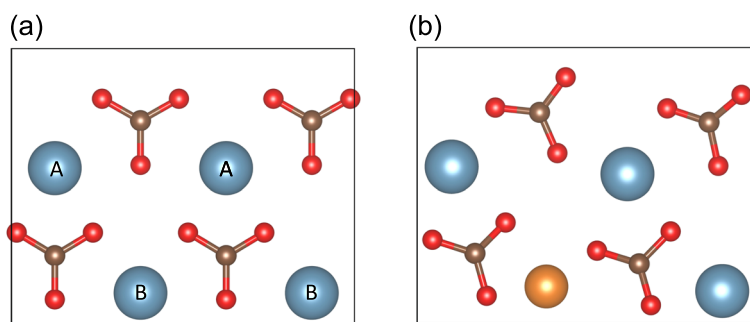


Figure 4 Top view of the relaxed aragonite {001} surface wherein Mg^{2+} substitutes for Ca^{2+} . Comparison of (a) surface structure without Mg^{2+} ions and (b) with Mg^{2+} substituting for Ca^{2+} . Red, brown, blue, and orange circles represent O, C, Ca, and Mg, respectively. [A] and [B] are labeled as in Figure 1.

We first discuss the {001} surface (Figure 3a). When Mg^{2+} substitutes into site A in the first Ca layer, above which no CO_3 groups are located, the substitution energy is almost zero and Mg^{2+} is easily incorporated into site A, which agrees with the MD calculations (Ruiz-Hernandez et al. 2012). The substitution energy increases when Mg^{2+} is substituted into the B site but is still much lower than that when it enters the Ca site in the bulk aragonite structure. However, for substitution within the deeper layers, the substitution energies increase significantly and reach almost that of the bulk aragonite structure. Thus, Mg^{2+} readily attaches to the first layer of the {001} surface but less so within the deeper layers.

In the {110} surface, the substitution energy of Mg^{2+} into the first Ca layer is almost the same as that for the B site in the {001} surface, and it rapidly increases with substitution in the deeper layers (Figure 3b). However, for this surface, even the energy for the substitution at Ca sites in the fifth layer is smaller than that for the bulk. This suggests that for {110} faces, a slightly higher energy would be required for Mg^{2+} ions to enter the Ca site of the top layer, whereas Mg^{2+} ions would enter the deeper layers more easily than the {001} face.

Structure of aragonite surfaces with Mg^{2+} ions at the Ca^{2+} sites

The structures of aragonite surfaces that contain Mg^{2+} ions were examined next. In the aragonite {001} surface, the CO_3^{2-} ions are arranged parallel to the surface; therefore, the flexibility of the movement and rotation of ions initially seem higher than those on the other surfaces. Figure 4b shows the relaxed structure of the {001} surface containing Mg^{2+} ions in B sites of the first Ca layer, where Mg^{2+} is surrounded by CO_3 ions. Figure 4 shows that the CO_3 groups move from the original positions and rotate 30° in the same direction. Notably, not only the CO_3^{2-} ions above the Mg^{2+} ions, which exist on the surface, but also the CO_3 groups below Mg^{2+} , which

make up the second CO_3 layer, rotate in the same manner. The arrangement of CO_3 ions around a Mg atom resembles the structure of calcite. To clarify this, the arrangement of the CO_3 groups around the Mg ions is shown in Figure 5. This figure shows that CO_3 groups around a Mg^{2+} ion move and rotate to assume six-coordinate geometry, which is the arrangement of the MgO_6 octahedron in the calcite structure.

Furthermore, the {110} surface seems to have less flexibility than the {001} surface because the CO_3 groups are arranged perpendicular to the {110} surface. However,

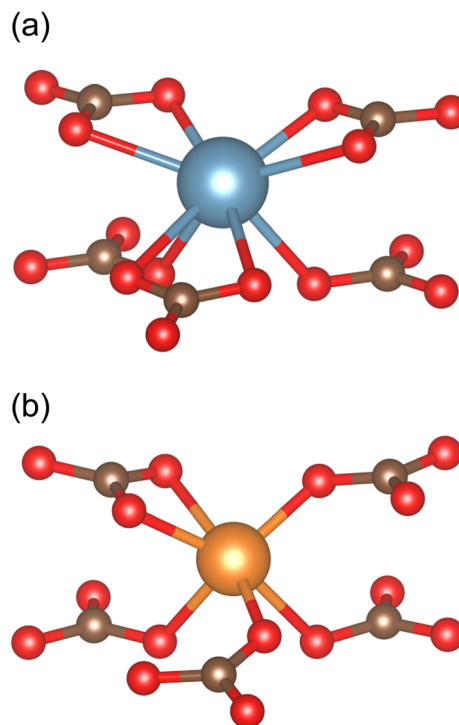
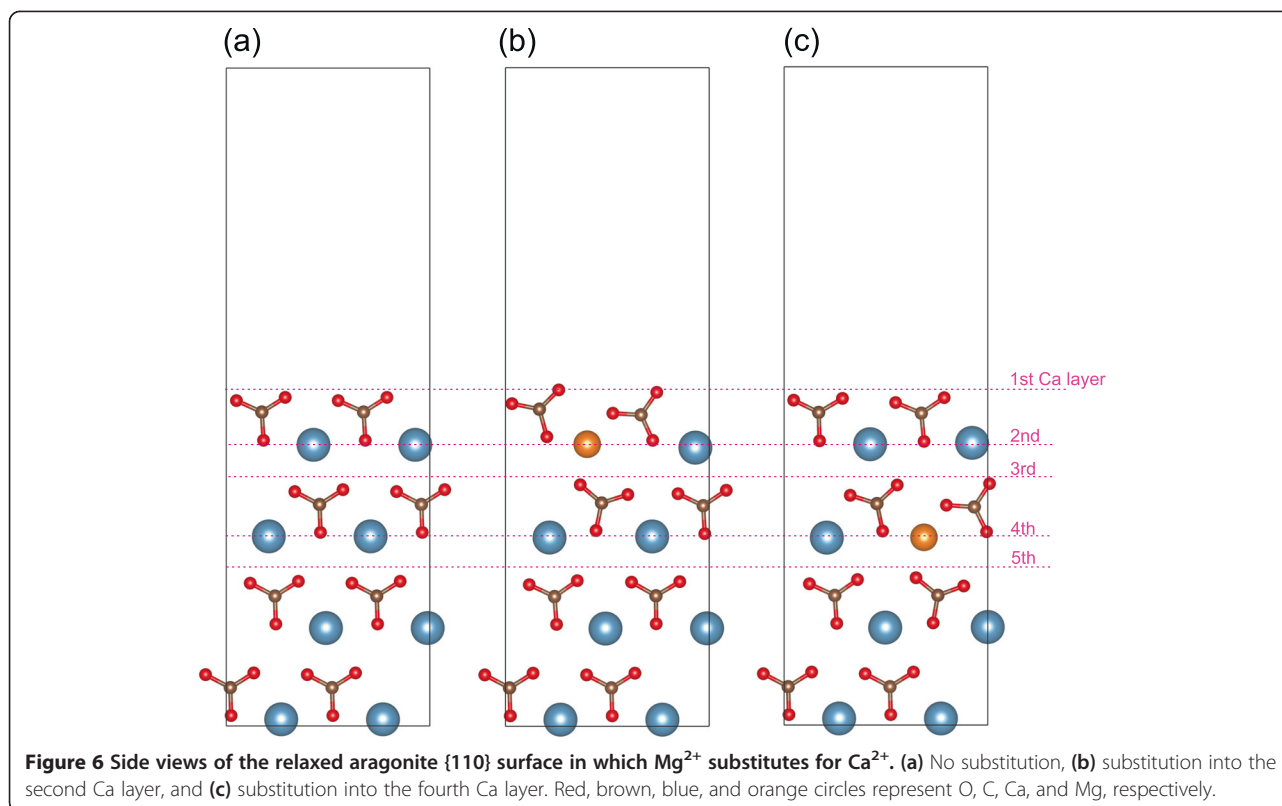


Figure 5 Details of the arrangement of CO_3 groups around the cation on the top {001} surface. (a) Ca and (b) Mg in the B site on the top layer of the {001} surface. Mg presumably prefers six-coordinate (octahedral) geometry as in the calcite structure.

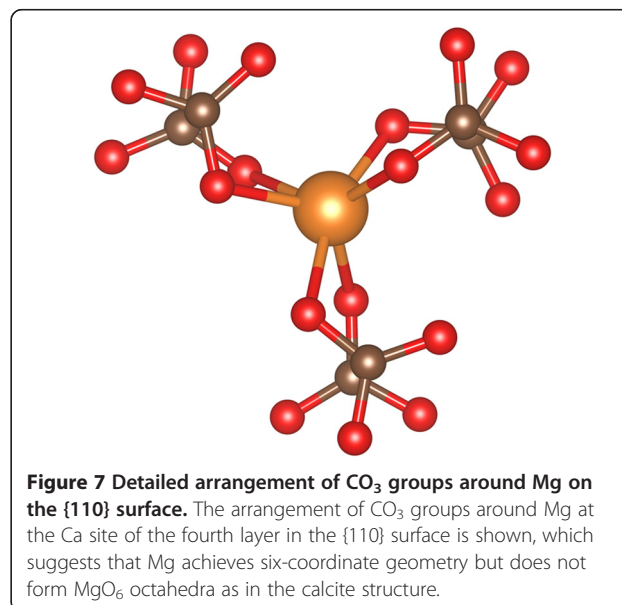


even in this case, the CO_3 groups move and rotate to achieve six-coordinate geometry, as shown in Figure 6. Moreover, for the {110} surface, when Mg^{2+} substitutes at a Ca site, not only in the first but also in the fifth Ca layer, the CO_3 groups also rotate to achieve six-coordinate geometry but do not form MgO_6 octahedra (Figure 7). This is opposite to the {001} surface, wherein the CO_3 groups do not move to accommodate the Mg substitution into the Ca sites near the {001} surface, except in the top layer. This is probably because atoms can move easily perpendicular to the surface, but less easily when parallel to it because the size of the surface is fixed, even though the layer thickness is not fixed. Therefore, contrary to the first expectation, it is easier for CO_3 groups to rotate in the {110} surface where atoms easily move parallel to the CO_3 groups. In contrast, in the {001} surface, atoms do not readily move in the long direction parallel to the CO_3 groups, because the size of this plane is fixed.

The differences between the {001} and {110} surfaces lead to differences in the substitution energies; when Mg^{2+} ions substitute in the deeper Ca layers, the atomic arrangement near the {110} surface is more relaxed than that near the {001} surface. Hence, the substitution energies for {110} are lower than those for the {001} surface. The energy gained by the rotation of CO_3 is estimated to be around 20 eV, by comparison of the substitution energy for the deep layers of the {110} surface and the value for

the substitution in the bulk where CO_3 groups are not rotated.

The results suggest that the CO_3 groups near the surface easily move and rotate relative to their original positions. Moreover, Mg^{2+} ions strongly prefer six-coordinate geometry. Therefore, the presence of Mg^{2+} affects the surface stability of aragonite, and it may further affect the



structure of the small clusters that appear during the early formation of CaCO_3 , which has more flexibility than the surface, both of which affect the polymorph selection of CaCO_3 .

Conclusions

First-principles calculations were performed for Mg^{2+} -containing aragonite surfaces. The results suggest that the substitution energy of Mg^{2+} for Ca^{2+} at the surface is lower than the substitution energy of Mg^{2+} for Ca^{2+} in the bulk structure. However, for the {001} surface, when Mg^{2+} substitutes for Ca^{2+} deeper than the second Ca layer, the substitution energy is almost the same as that for substitution in the bulk aragonite structure. In contrast, for the {110} surface, even when Mg^{2+} ion substitutes into deeper layers, the substitution energy is still lower than the substitution energy in the bulk aragonite structure. Thus, Mg^{2+} ions easily attach onto the {001} surface with lower energy; however, it should be difficult for these ions to move to deeper layers. In contrast, for the {110} surface, a relatively higher energy is required for Mg^{2+} ions to substitute for Ca^{2+} at the top surface sites, whereas they enter more easily to deeper layers than the {001} face. This is probably because the atomic structure of this surface is more relaxed, and the CO_3 groups move and rotate from their original positions even when Mg^{2+} ions are in deeper layers. In contrast, for the {001} surface, the CO_3 groups do not move when Mg^{2+} substitutes for Ca^{2+} , except in the top layer sites where CO_3 groups easily move and rotate to achieve six-coordinate geometry, such as CaO_6 octahedra in the calcite structure. Mg^{2+} generally assumes a preferential six-coordinate geometry, even at the aragonite surface, indicating that it changes the surface stability of aragonite, which may affect the formation of CaCO_3 polymorphs.

Abbreviations

AFM: atomic force microscopy; DFT: density functional theory; GGA-PBE: generalized gradient approximation-Perdew-Burke-Ernzerhof; MD: molecular dynamics; VASP: Vienna *ab initio* simulation package.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

JK proposed the topic, designed the study, conducted the simulations, and interpreted the results. HS contributed to the simulations and data interpretation. TN contributed to the discussions with the corresponding author throughout the study. All authors read and approved the final manuscript.

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Author details

¹Creative Research Institution (CRIS), Hokkaido University, N21 N10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan. ²Faculty of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan. ³Environment and Energy Materials Division, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

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