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High-temperature molecular dynamics simulation of aragonite

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Abstract

For molecular dynamics simulations using aragonite structure as the initial state, a new phase of space group $P6_322$ (hexagonal aragonite) appeared at temperatures above 510 K at a pressure of 1 atm. It was a first-order phase transition which occurs metastably within the stable region of calcite and the dT/dP slope of the phase boundary between orthorhombic and hexagonal aragonite was about 1.25×10^3 K GPa⁻¹. In the hexagonal aragonite structure, CO₃ groups were rotated by 30° around the c axis and move up and down along the c axis from their position in aragonite, and Ca ions were six-coordinated as they are in calcite. The CaO₆ octahedron of hexagonal aragonite was strongly distorted, whereas in the calcite structure it is an almost ideal octahedron. The transition between hexagonal and orthorhombic aragonite involves only small movements of CO₃ groups. Therefore, it is possible that hexagonal aragonite plays an important part in the metastable formation of aragonite within the stability field of calcite and in the development of sector trilling in aragonite.

1. Introduction

Calcium carbonate, CaCO₃, is important both in earth sciences, as rock-forming minerals, and in chemical technology, as raw material for industrial processes. Furthermore, the occurrence of CaCO₃ in living organisms has received considerable attention for a long time. Consequently, a great number of experimental studies focused on the stability of these CaCO₃ polymorphs, especially the stable relationship between calcite and aragonite, have been carried out [1]. These studies have shown that calcite is the low-pressure phase and aragonite is the high-pressure phase, that the phase boundary between them has a positive dT/dP slope, and that the slope becomes steep at around 400 °C, as summarized by Carlson [2]. However, the transition of calcite to aragonite is still not fully understood. For example, a complete explanation has not yet been found for the metastable nucleation of aragonite in organic or inorganic environments.

Although calcite undergoes various structural phase transitions involving rotation of CO₃ groups or slight differences in the position of Ca²⁺ ions, structural transitions

such as these have not been reported for aragonite. In a molecular dynamics (MD) simulation, Bearchell and Heyes [3] obtained a structure in which CO₃ groups were rotated through an angle of 30° around a threefold axis from their positions in aragonite. However, they did not analyze the structure in detail. To extend this previous work, we used MD simulations to investigate the possible existence of a new polymorph related to aragonite, which could play an important part in the metastable formation of aragonite in the stability field of calcite.

Although there have been many recent simulation studies of calcium carbonate, there have been few of aragonite. Unfortunately, the transition from calcite to aragonite cannot be directly accomplished by MD simulation because of differences in the way the Ca²⁺ and CO₃²⁻ layers are stacked for the two minerals. Our MD simulation of aragonite was carried out using the aragonite structure as the initial state.

2. Method

MD calculations were carried out using the MXDTRICL [4] program with the two-body central force interatomic potential

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Table 1. Parameters used for the interatomic potential function.

Atom	$z(e)$	A (Å)	B (Å)	C (kcal ^{1/2} Å ³ mol ^{-1/2})
O	-0.976	1.8836	0.1658	23.351
C	1.056	0.4638	0.0784	0.0
Ca	1.872	1.4916	0.1042	10.086
Atomic pair	D_1 (kJ mol ⁻¹)	β_2 (Å ⁻¹)	D_2 (kJ mol ⁻¹)	β_2 (Å ⁻¹)
O-C	45 735.0	5.14	-4936.066	2.57
O-Ca	33 171.0	4.0	-814.0	2.0

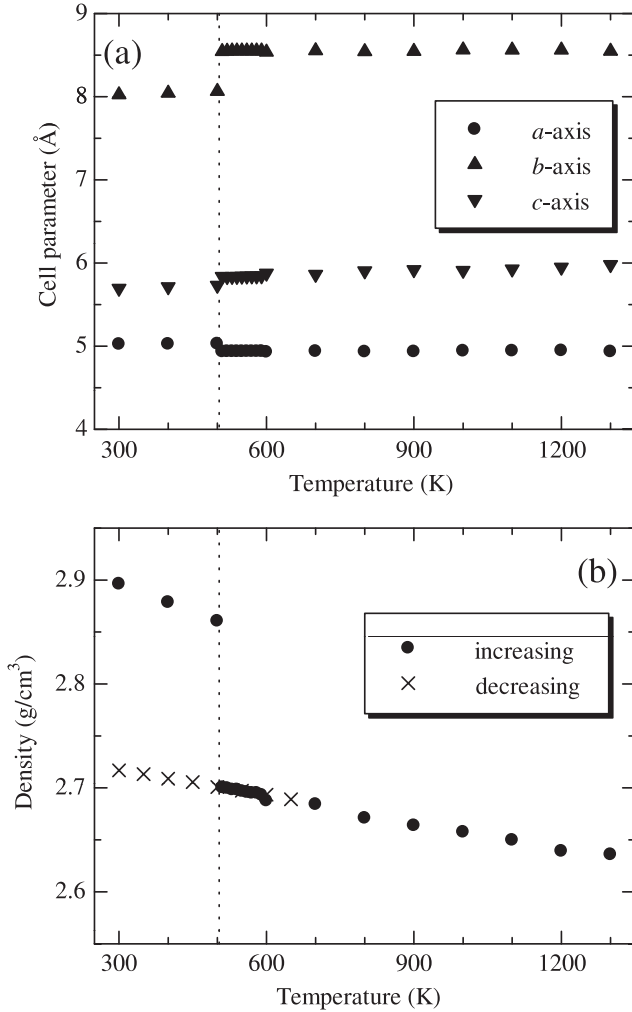


Figure 1. Temperature dependences of (a) cell parameters and (b) density of the MD-simulated structure produced by using an orthorhombic aragonite structure as the initial state. The dashed lines indicate the temperature at which abrupt changes of cell parameters and density were observed. The decreasing temperature dependence of density of the initial structure at 700 K was plotted in (b).

function:

$$\phi_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0 (B_i + B_j) \exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right) - \frac{C_i C_j}{r_{ij}^6} + D_{1ij} \exp(-\beta_{1ij} r_{ij}) + D_{2ij} \exp(-\beta_{2ij} r_{ij}),$$

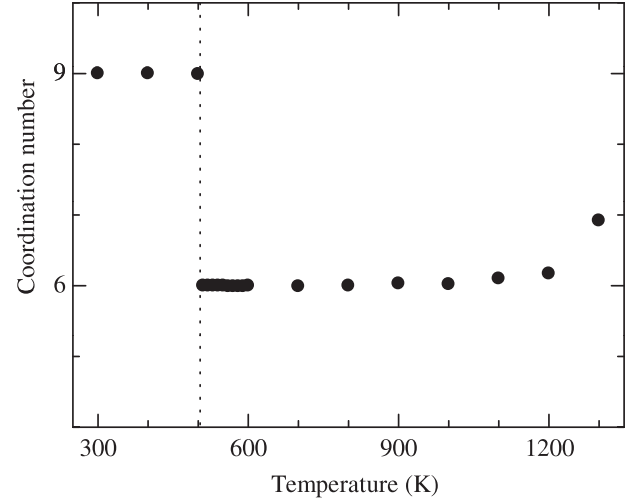


Figure 2. Change of simulated Ca-coordination number with increasing temperature.

which includes terms for the Coulombic interaction between two point charges, short-range repulsion, van der Waals attraction and Morse potential. The parameter r_{ij} is the interatomic distance between atoms i and j ; $f_0 = 6.9511 \times 10^{-11}$ N; e is the electronic charge; z , A , B and C are the parameters for each atomic species; and D_1 , D_2 , β_1 and β_2 are the parameters for each atomic pair. The parameters we used in our MD calculations are listed in table 1. This parameter set was empirically derived to reproduce the aragonite structure at 300 K and 1 atm, which was based on our previous studies [5, 6] for calcite.

We used the Verlet method for integration of equations of atomic motion and the Ewald method for summation of electrostatic interactions. Temperature and pressure were controlled by scaling atomic velocities and simulation of cell parameters, respectively. The time step was 0.5 fs (femtoseconds) throughout our simulations. Periodic boundary conditions for aragonite were imposed with a basic MD cell of 144 crystallographic units ($a_{MD} = 6a$, $b_{MD} = 4a$, $c_{MD} = 6c$) containing 2880 atoms. The diffracted intensity was calculated from the structure factor obtained directly from the MD-simulated atomic positions [7].

The aragonite structure determined by Dal Negro and Ungaretti [8] was adopted as the initial state for our MD simulations. After preliminary annealing of the initial structure at 300 K and 1 atm for 5 ps (=10 000 steps), temperature

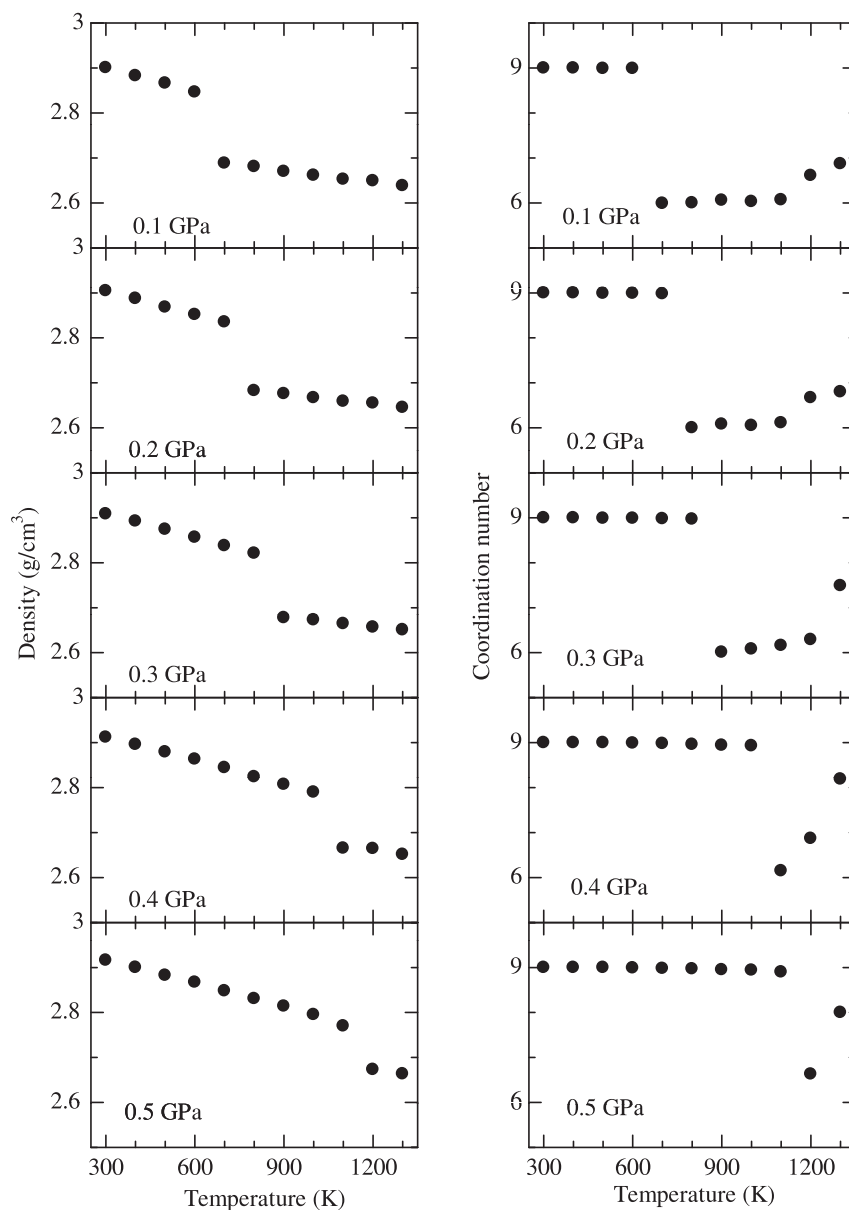


Figure 3. Temperature dependences of the cell parameters and Ca-coordination numbers of the simulated structures for pressures in the range 0.1–0.5 GPa.

was increased from 300 K at a constant pressure of 1 atm. Simulations were run for temperature ranges of 300–1300 K at intervals of 100 K and 500–600 K at intervals of 10 K. Furthermore, temperature was decreased from 650 to 300 K at intervals of 50 K as the initial structure at 700 K and 1 atm.

MD calculations were also carried out at pressures from 0 GPa (1 atm) to 0.5 GPa at intervals of 0.1 GPa. After annealing at 300 K and 1 atm, pressure was increased at a constant temperature of 300 K. All the resulting structures were recognized as aragonite. The temperature was then increased over the range 400–1300 K at constant pressure. For this range, calculations were at 100 K intervals for each pressure. Crystallographic and thermodynamic properties were obtained by calculations over at least 5 ps (=10 000 steps) after annealing for at least 5 ps.

3. Results and discussion

3.1. Unit cell parameter variations with temperature

We compared the structural parameters derived from the MD-simulated structure of aragonite at 300 K and 1 atm with those determined by x-ray diffraction (table 2). For our simulation, we employed a parallelepiped MD cell and did not impose rhombohedral or hexagonal symmetry on the MD-simulated crystal. The angles among the crystallographic axes were not fixed in the calculations. The simulated cell parameters at 300 K showed good agreement with those of a real crystal (table 2).

The cell parameters (a , b , c , and density) changed with increasing temperature (figure 1). From 300 to 500 K, each of these parameters gradually increased with temperature.

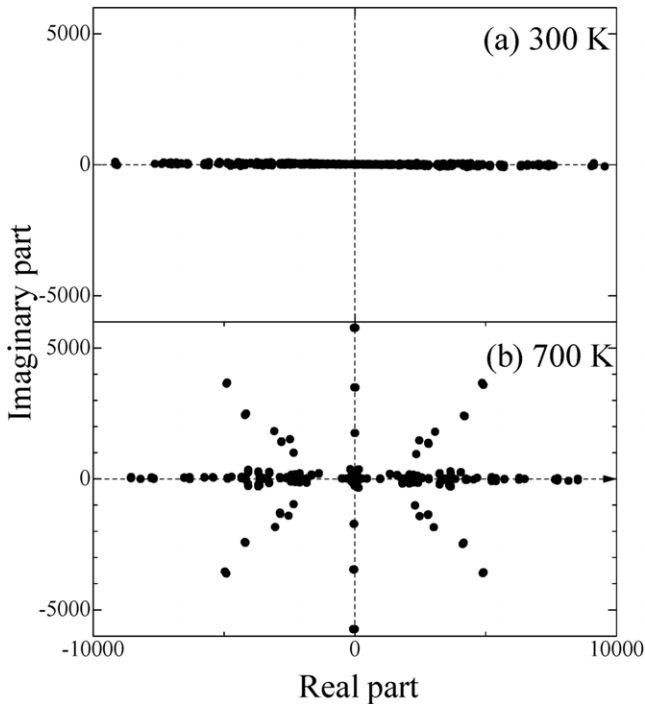


Figure 4. Structure factors for the hexagonal aragonite structure plotted in Gaussian coordinates at (a) 300 K and (b) 700 K.

Table 2. Cell parameters of MD-simulated aragonite at 300 K and 1 atm and those derived experimentally [6].

	a (Å)	b (Å)	c (Å)
MD	5.024	8.024	5.694
Experimental data	4.959	7.968	5.741

Around 510 K, however, a and density decreased, whereas b and c increased. Above 510 K, b was about 1.73 times a . However, the unit cell angles (α , β and γ) did not show significant deviation from 90° . The coordination number changed from 9 to 6 at around 510 K (figure 2). These abrupt changes of unit cell parameters, density and coordination number indicate that a first-order phase transition from aragonite to a high-temperature phase occurred at around 510 K. On the other hand, the phase transition from a high-temperature phase to aragonite did not occur in decreasing temperature simulations (figure 1(b)).

The temperature dependence of unit cell volume at 0.1–0.5 GPa (figure 3) shows that aragonite transforms to the high-temperature phase at about 650 K, 0.1 GPa; 750 K, 0.2 GPa; 850 K, 0.3 GPa; 1050 K, 0.4 GPa, and 1150 K, 0.5 GPa. For each simulated pressure, the coordination number increased to greater than 6 at temperatures above 1100 K (figure 3). We believe that this is because the rotation vibration of the CO_3 group is violent, as was reported for calcite at high temperature by Kawano *et al* [5], or because the structure had broken and melted. We estimated (from figure 3) that the gradient of the phase boundary (dT/dP) was about 1.25×10^3 K GPa^{-1} . Our simulations showed that the high-temperature phase appeared at high temperature and low pressure with a very narrow metastable area.

Table 3. Cell parameters and atomic positions of hexagonal aragonite at 700 K. The space group is $P6_322$ and the unit cell contains 2 CaCO_3 molecules.

Cell parameters:	a	c	
	4.938	5.862	
Atom positions:	x	y	z
Ca	0.333	0.667	0.25
	(1/3)	(2/3)	(1/4)
C	0	0	0
O	0.254	0	0

3.2. Space group of the high-temperature phase

The calculated lengths of the a and b axes at 700 K and 1 atm were 4.938 and 8.555 Å, respectively. The ratio b/a of the new phase in the orthorhombic setting was almost $\sqrt{3}$ (figure 1). Therefore, at 700 K the hexagonal cell may be preferred to the orthorhombic cell, but retaining a common a axis, i.e. unit cell parameters of $a1(\text{hex}) = a(\text{ortho})$, $a2(\text{hex}) = 1/2b(\text{ortho}) - 1/2a(\text{ortho})$, $c(\text{hex}) = c(\text{ortho})$ and $\gamma = 120^\circ$. The structure factors, $F(hkl)$, with indices hkl ($-5 \leq h, k, l \leq 5$) for the simulated high-temperature phase were calculated in reciprocal space for a temperature of 700 K by using the method of Miyake *et al* [7]. The x-ray intensity distribution calculated from the structure factors showed that the Laue group of this structure was $6/mmm$. All the structure factors clearly showed that in Gaussian coordinates the imaginary parts had magnitude at 700 K and could not be neglected (figure 4). Therefore, the simulated structure at 700 K did not have a center of symmetry. The systematic extinction of structure factors $|F(00l)|$ when $l = \text{odd}$ for the hexagonal setting showed a screw axis parallel to the c axis. From these results, the point group and space group of the high-temperature phase were determined uniquely as 622 and $P6_322$, respectively. This new high-temperature phase with hexagonal symmetry can be denoted as ‘hexagonal aragonite’.

3.3. Structure of the high-temperature phase

The atomic coordinates and cell parameters of the hexagonal aragonite simulated at 700 K are shown in table 3. The atomic arrangement of the hexagonal aragonite structure is shown in figure 5. The structures of aragonite and calcite are shown in figures 6 and 7, respectively. The CO_3 groups in hexagonal aragonite have rotated through an angle of 30° around a threefold axis with respect to their positions in aragonite. Consequently, Ca ions in hexagonal aragonite are six-coordinated (figure 5).

The Ca ions in both the calcite and hexagonal aragonite structures are six-coordinated; however, these two structures differ only in the way Ca and CO_3 ions are stacked. If a CO_3 ion is considered to be spherical, the calcite structure is referred to as a cubic close-packing structure of the NaCl type. The Ca layers show an ABCABC sequence along the c axis. Because the Ca layers are separated by CO_3 layers, which have two opposite orientations, the stacking of calcite can be described as $\text{AC}_1\text{BA}_2\text{CB}_1\text{AC}_2\text{BA}_1\text{CB}_2$ (figure 7). Hexagonal aragonite, on the other hand, is related to a hexagonal close-packing

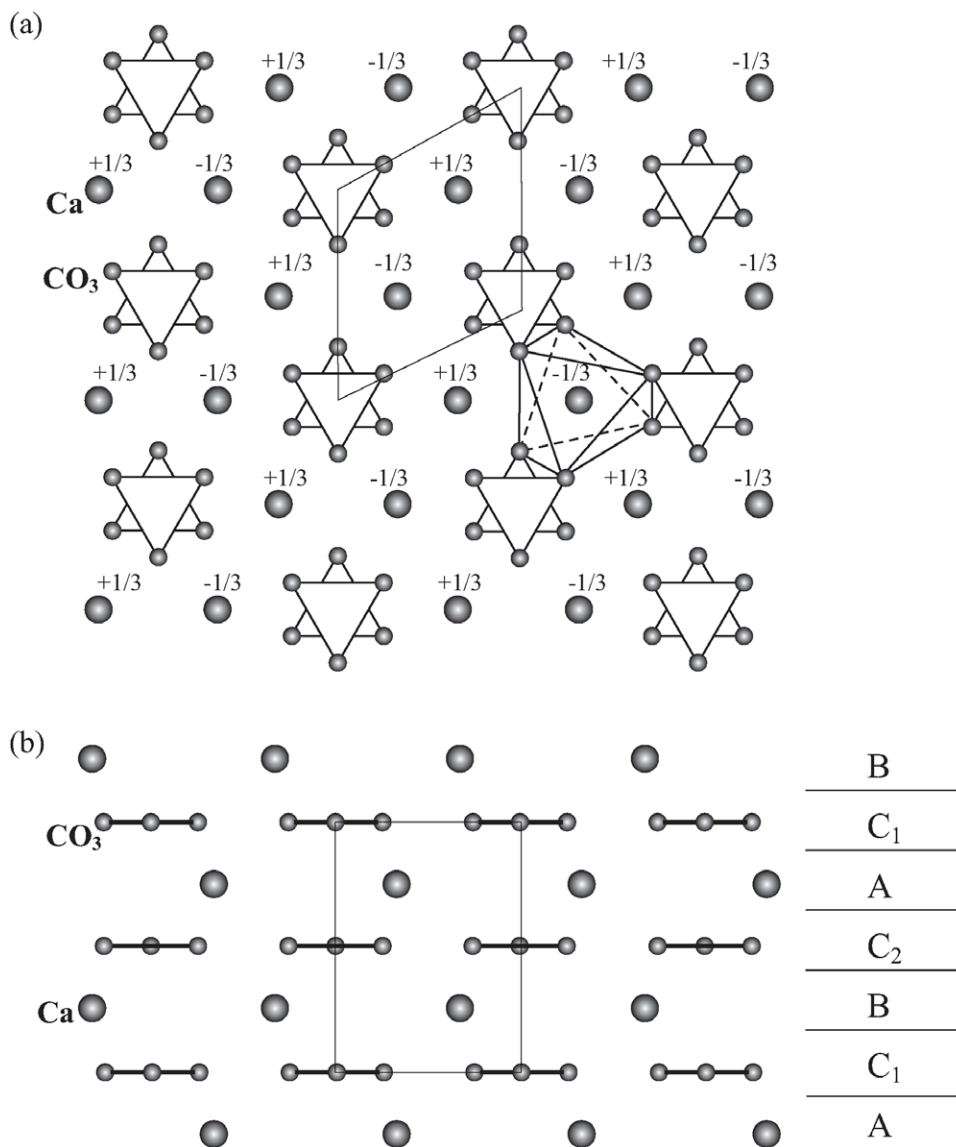


Figure 5. Atomic arrangement of the simulated hexagonal aragonite structure projected along (a) the c axis and (b) the a axis. The unit cell is shown by thin lines. In panel (a) the fractions refer to the elevation of the atoms along the c axis; the CaO_6 octahedron is shown by solid and dashed lines. In panel (b) stacking is shown (A, B, C_1 and C_2).

structure of the NiAs structural type. By assuming replacement of As by Ca and of Ni by CO_3 groups, we obtain the general pattern of the hexagonal aragonite structure. In this structure, Ca layers show an ABAB sequence along the c axis. Because CO_3 groups have two orientations, the stacking of hexagonal aragonite is $\text{AC}_1\text{BC}_2\text{AC}_1\text{BC}_2$ (figure 5). This structure differs from that of calcite, as Ca atoms are aligned only with other Ca atoms along the c axis, and CO_3 groups are aligned only with other CO_3 groups.

Because Ca ions are six-coordinated both in calcite and in hexagonal aragonite, CaO_6 octahedrons are formed in both structures. In the calcite structure, these are almost ideal octahedra (figure 7), but in hexagonal aragonite, the CaO_6 octahedra are strongly distorted (figure 5) because the neighboring CO_3 triangles above and below a particular Ca ion are not rotated 60° with respect to each other. Therefore, we

suggest that the hexagonal aragonite structure is in a higher energy state than calcite and is less stable.

If CO_3 groups are considered as spherules, the stacking of hexagonal aragonite is basically the same as that of orthorhombic aragonite. However, in the hexagonal aragonite structure, all CO_3 groups between two Ca layers are on the same plane and point in the same direction, whereas in the orthorhombic aragonite structure, alternate CO_3 planes have opposite orientations. The transition from hexagonal to orthorhombic aragonite is the result of two displacements: (1) the rows of CO_3 groups parallel to the a axis move up and down along the c axis and (2) CO_3 groups rotate by 30° in opposite directions in alternate planes. For both structures, the stacking of Ca atoms is unchanged. In this transition, the a axes of both phases are the same. Consequently, the transition between hexagonal aragonite and orthorhombic

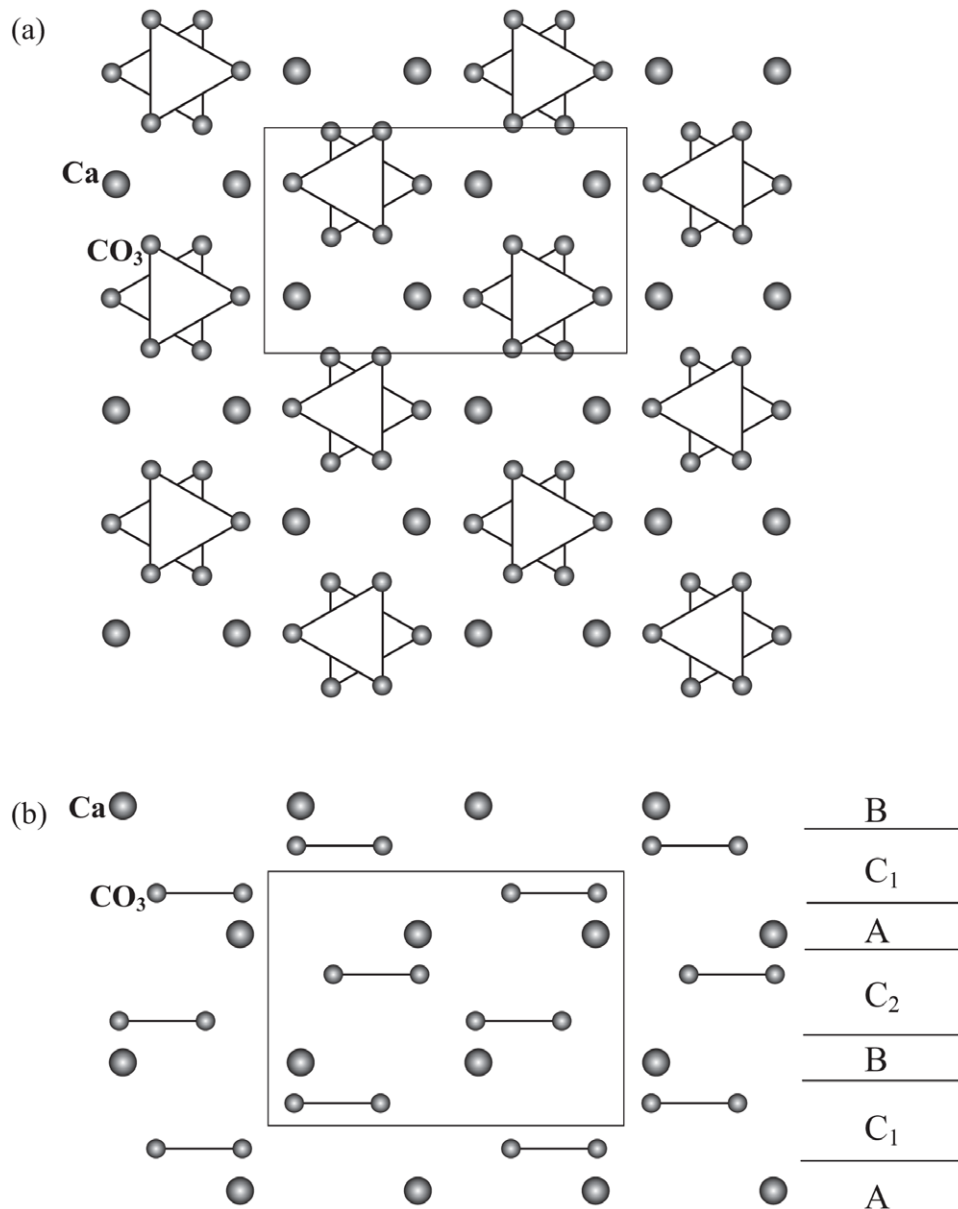


Figure 6. Atomic arrangement of the orthorhombic aragonite structure from Dal Negro and Ungaretti [6] projected along (a) the c axis and (b) the a axis. The unit cell is shown by thin lines. In panel (b) stacking is shown (A, B, C_1 and C_2).

aragonite occurs with the displacement of only CO_3 groups, without further reconstruction, while the transition between calcite and hexagonal aragonite requires reconstruction of the stacking of Ca and CO_3 .

3.4. Possibility of natural existence of hexagonal aragonite

The simulated hexagonal aragonite had a very simple structure. However, this structure has not been reported in nature. This may be because the CaO_6 octahedra in this structure were strongly distorted, creating a higher energy state than that of calcite. Therefore, the phase boundary between orthorhombic and hexagonal aragonite would be in the stable region of calcite, and hexagonal aragonite would be metastable with respect to calcite. As shown in the schematic phase

diagram (figure 8(a)), a metastable phase transition between orthorhombic and hexagonal aragonite occurs at 510 K, and the dT/dP slope of the phase boundary between these phases is estimated at about $1.25 \times 10^3 \text{ K GPa}^{-1}$.

The stable region of calcite can be divided into two metastable regions: a relatively low-temperature region below the phase transition temperature, where orthorhombic aragonite is more stable than the hexagonal phase; and a higher temperature region, where hexagonal aragonite is more stable than the orthorhombic phase (figure 8(b)). If we assume that hexagonal aragonite forms within the stable region of calcite, because CO_3 prefers six-coordination in the stable region of calcite, then it is possible that hexagonal aragonite forms metastably under highly supersaturated conditions. Below the transition temperature, hexagonal aragonite is less stable than

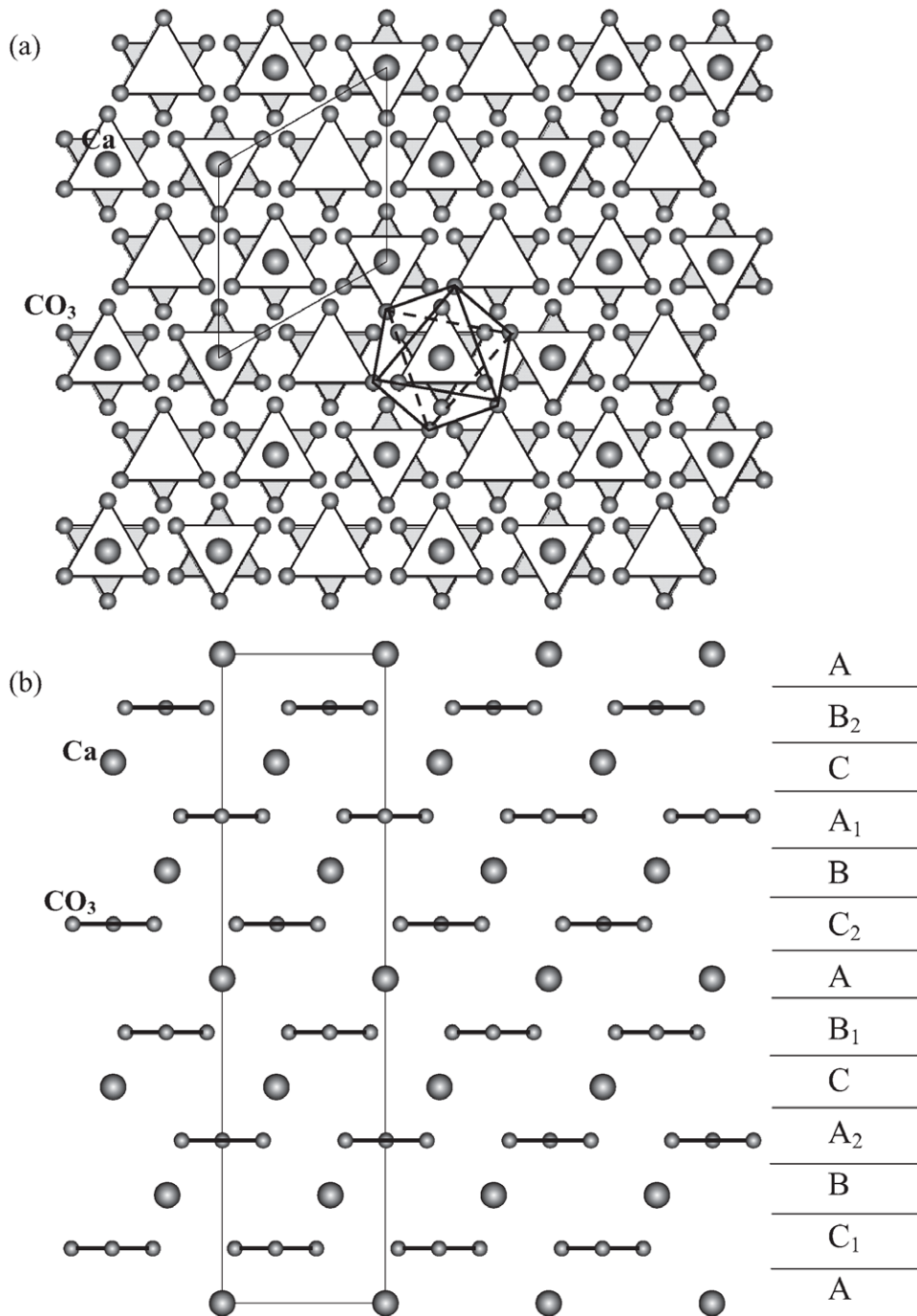


Figure 7. Atomic arrangement of the calcite structure projected along (a) the *c* axis and (b) the *a* axis. The unit cell is shown by thin lines. In panel (a) the CaO₆ octahedron is shown by solid and dashed lines. In panel (b) stacking is shown (A, B, C, A₁, B₁, C₁ . . . , etc.).

both calcite and aragonite and tends to transform to either of those two phases. Hexagonal aragonite can transform into orthorhombic aragonite with only a slight movement of CO₃ groups. In contrast, the transition from calcite to orthorhombic aragonite, or from calcite to hexagonal aragonite, requires much structural rearrangement. Therefore, when hexagonal aragonite is formed, we suggest that it is easier for it to transform into orthorhombic aragonite than into calcite, even within the stable region of calcite. Thus, it is possible that the existence of hexagonal aragonite in the stable range of

calcite plays an important part in the metastable formation of orthorhombic aragonite. Recently, Kawano *et al* [9] pointed out the importance of the temperature dependence of surface free energy in the nucleation of aragonite in precipitation experiments. They showed that the surface free energy of aragonite at relatively low temperature (around 25 °C) should be much higher than that at higher temperature (around 80 °C), which explains successfully the experimental result for aragonite nucleation. A possible explanation for this temperature dependence is the difference between the surface

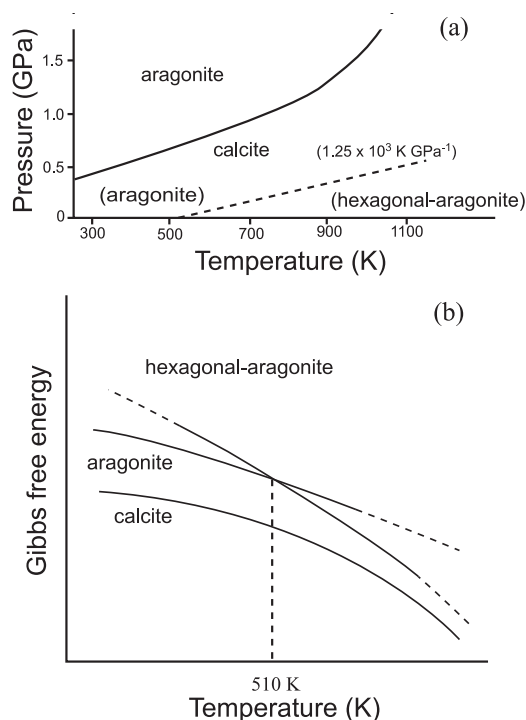


Figure 8. (a) Schematic phase diagram of CaCO_3 polymorphs based on the summarization by Carson [2]. Dashed lines are metastable phase boundaries between orthorhombic and hexagonal aragonite estimated by the present calculations. The gradient of the phase boundary (dT/dP) was about $1.25 \times 10^3 \text{ K GPa}^{-1}$. (b) Free energy curves for CaCO_3 polymorphs with temperature at 1 atm. Calcite is a stable phase over the whole temperature range and the metastable phase transition between orthorhombic and hexagonal aragonite occurs around 510 K.

free energies of orthorhombic and hexagonal aragonite. That is, hexagonal aragonite is possible to nucleate first as a precursor to aragonite.

The orthorhombic structure of aragonite commonly appears in the form of sector trilling [10], which might suggest the transition of hexagonal aragonite to orthorhombic aragonite. The a -axis lengths of orthorhombic and hexagonal aragonite are almost identical (figure 1). When hexagonal aragonite transforms to orthorhombic aragonite, there are three possible directions in which the common a axis can

be retained. Therefore, if the hexagonal aragonite exists first, the sector trilling of aragonite might occur during its transformation to the orthorhombic phase. Formation of sector trilling in this manner has been reported for the phase transition from hexagonal indialite to orthorhombic cordierite [11]. On the other hand, the phase transition from hexagonal aragonite to orthorhombic aragonite did not occur in our simulation (figure 1). One of the limitations of the present simulation is the possibility that the MD cell size and the periodic phase boundary conditions might influence the phase transition with cooling. Namely, because three kinds of orthorhombic phase with the different directions from each other might nucleate in the smaller MD cell than the natural crystal simultaneously, hexagonal aragonite could not transform to the orthorhombic phase.

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