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LETTER

High-pressure transition of $CaCO_3$

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ABSTRACT

Calcite, $CaCO_3$, is a common carbon-bearing mineral found on the Earth's surface. As carbon dioxide in the atmosphere can be sequestered in carbon-bearing minerals (carbonates), the stability of carbonate minerals is of great interest to earth science. In our study, in-situ X-ray diffraction observations indicate that calcium carbonate ($CaCO_3$) transforms to an orthopyroxene-type structure that has fourfold coordination of carbon cations, when heated to temperatures >1500 K at pressures >130 GPa, which is in agreement with theoretical predictions from ab initio calculations. The volume reduction of this transition is ~0.5%, and the high-pressure phase did not quench on decompression to ambient pressure. Although the post-aragonite phase, which has threefold coordination of carbon cations, shows strongly anisotropic compressibility of each axis of the unit-cell parameter, no obvious anisotropy in the pyroxene-type phase was observed. The stability of this new calcium carbonate implies that the carbon dioxide could be storable at the base of the lower mantle.

Keywords: Calcium carbonate, phase transition, high pressure, diamond anvil cell

INTRODUCTION

To understand the carbon circulation in the Earth's system, we need to know the high-pressure behavior of carbonates (e.g., $MgCO_3$ and $CaCO_3$), because a large volume of carbonate rocks sink into the deep mantle at subduction zones. Theoretical calculations on the behavior of $MgCO_3$ and $CaCO_3$ at high pressures (Skorodumova et al. 2005; Oganov et al. 2006) predict that both carbonates will transform into a pyroxene-type structure. The transition pressures of $MgCO_3$ and $CaCO_3$ were calculated to be 100 and 137 GPa, respectively (Oganov et al. 2006). However, no evidence of these high-pressure phases has been observed in high-pressure X-ray diffraction studies. Magnesite ($MgCO_3$) is stable from the Earth's surface to the mid-lower mantle (Fiquet et al. 2002). The high-pressure phase of $MgCO_3$ (>100 GPa) observed in experiments (Isshiki et al. 2004) is different from that predicted by calculations (Skorodumova et al. 2005; Oganov et al. 2006). In contrast, the high-pressure phase of $CaCO_3$ (>100 GPa) has not been investigated in high-pressure experiments.

Calcite phase transitions under static and dynamic compression have been performed in many studies. The pioneering work of Bridgman (1939) indicated that two polymorphs of calcite ($CaCO_3$) exist at high pressures. Several investigations into the pressure response of the structure of calcite have followed (Jamieson 1957; Ahrens and Gregson 1964; Fong and Nicol 1971; Merrill and Bassett 1975; Singh and Kennedy 1974; Tyburczy and Ahrens 1986; Liu and Mernagh 1990; Biellmannet al. 1993; Fiquet et al. 1994; Suito et al. 2001; Ivanov and Deutsch 2002). Aragonite ($CaCO_3$) is known to be a more important phase at pressures corresponding to the mantle. Therefore, the stability and structure of aragonite at high pressures were also investigated by many researchers (Vizgirda and Ahrens 1982; Kraft et al. 1991; Santillán et al. 2004; Ono et al. 2005a). Recently, both theoretical and experimental studies confirmed that the structure of the post-aragonite phase is orthorhombic (space group *Pmmn*) at pressures higher than ~40 GPa (Oganov et al. 2006; Ono et al. 2005a).

In this study, we conducted laser-heated diamond anvil cell experiments combined with X-rays from a synchrotron radiation source to acquire data on $CaCO_3$ phases at high pressures up to 192 GPa. We report the results of in situ X-ray powder observations of a new orthorhombic $CaCO_3$ phase identified here for the first time.

EXPERIMENTAL METHODS

To clarify whether a structural phase transition occurs, we carried out a high-pressure an in situ X-ray diffraction study of $CaCO_3$ heated to temperatures >1500 K, corresponding to temperatures in the Earth's mantle for $P > 100$ GPa. Heating carbonate samples is often necessary to overcome any kinetic barriers to phase transitions (Ono et al. 2005a). Our sample consisted of polycrystalline calcite mixed with platinum (8 wt%), which acted as both an absorber of the laser beam power for heating and as a pressure standard (Holmes et al. 1989). Rhenium gaskets were pre-indented to a thickness of 40 μm and then drilled to give a 50 μm hole. The sample pellet was loaded into a motor-driven diamond anvil cell with a 50° conical aperture (Ono et al. 2007). The samples were heated with a TEM_{01}-mode Nd:YLF laser or a multimode Nd:YAG laser. Sample temperatures were measured using a spectroradiometric method, which consists of a thermoelectrically cooled CCD

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detector and a spectrograph. The samples were probed by angle-dispersive X-ray diffraction using the synchrotron beam line of BL13A, Photon Factory (Ono et al. 2005b) and BL10XU, SPring-8 (Ono et al. 2005c). A monochromatic incident X-ray beam was used, with its beam size collimated to a diameter of 20–30 μm diameter. Angle-dispersive X-ray diffraction patterns were obtained on an imaging plate (RigakuRAXIS-IV) with exposure times of typically 3–15 min. The 2D diffraction images were integrated using Fit2D software (Hammersley et al. 1996). Further experimental details are described elsewhere (Ono et al. 2005b, 2005c). The diffraction peak positions were determined using a peak-fitting program (Origin v7.5), and the unit-cell parameters and volumes of the sample and platinum were calculated using a least-squares fit of each diffraction peak position. In diamond anvil cell experiments, X-ray diffraction data were acquired at each pressure increment before and after laser heating had been carried out. After the desired pressure had been reached, the sample was heated to relax the differential stress and to overcome any potential kinetic effects on the phase transition. Typical heating duration times were 10–20 min. After heating, the diffraction peaks were observed to sharpen due to the relaxation of the differential stress and the recrystallization. In some heating cycles, X-ray data were also acquired during laser heating. At each temperature increment, the laser heating was performed to relax the differential stress for a period of 2–3 min before each X-ray measurement. Pressure was estimated from the observed unit cell volumes using the equation of state (EOS) of platinum (Holmes et al. 1989). During the laser heating, pressure increased, because of the thermal pressure of the sample. Typical pressure uncertainty at high temperatures was less than 10 GPa.

Results and discussion

Typical diffraction patterns after heating the sample are shown in Figure 1. In this run, the pressure was increased directly to ~200 GPa at room temperature. After the desired pressure was achieved, the sample was heated to ~2000 K, and the X-ray diffraction data of the sample were acquired after a temperature quench. The exposure time was 10 min. In addition to the peaks arising from platinum, other peaks were observed, indicating that the starting material had transformed into a new high-pressure phase. These peaks belonged to an orthorhombic cell, which was different from other high-pressure phases of $CaCO_3$ reported in previous high-pressure experiments (Ono et al. 2005a). The new peaks were assigned to a pyroxene-type structure having space group $C222_1$, because of the excellent agreement between the observed X-ray powder diffraction pattern and the simulated pattern for the pyroxene-type structure predicted by Oganov et al. (2006). Moreover, the a/c and b/c ratios of the cell parameters obtained for the pyroxene-type phase, 1.703 and 2.128, respectively (at 152 GPa), are close to the theoretical values of 1.725 and 2.156, respectively (at 150 GPa). Other known high-pressure phases of $CaCO_3$ have C^{4+} cations exhibiting a threefold coordination with the oxygen ions. However, in the case of the new pyroxene-type structure, the C^{4+} cations exhibit fourfold coordination (Fig. 1). Fourfold-coordinated structures are commonly observed in many silicate minerals under ambient conditions.

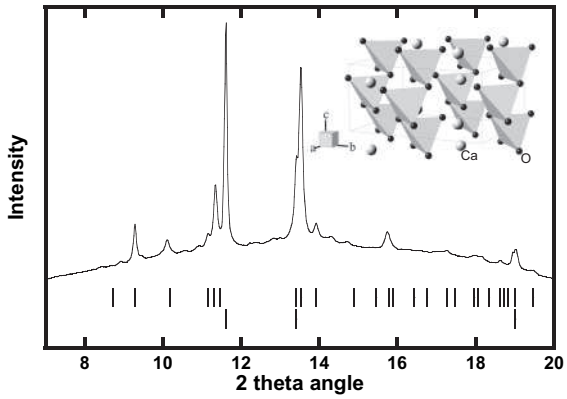

Figure 1. An example of the observed X-ray diffraction patterns acquired at P = 182 GPa and T = 300 K after heating. The vertical bars indicate the calculated positions of the diffraction lines of each phase. Upper bars = pyroxene-type $CaCO_3$ ($C222_1$), a = 5.464 Å, b = 6.852 Å, and c = 3.206 Å; lower bars = platinum, a = 3.552 Å. The wavelength of the monochromatic incident X-ray beam was 0.4150 Å. The upper right-hand figure shows the crystal structure of pyroxene-type $CaCO_3$. The dark and gray spheres denote oxygen and calcium atoms, respectively. The tetrahedrons denote CO_4 units. Wyckoff symbols and coordinates of each atom from Oganov et al. (2006) are Ca, 4b, (0, 0.8287, 0.25); C, 4a, (0.3538, 0, 0); O1, 4b, (0, 0.3881, 0.25); O2, 8c, (0.2736, 0.3875, 0.7324).

Next, the sample was gradually decompressed to investigate the stability of the pyroxene-type $CaCO_3$. After each pressure decrement, the sample was heated to overcome any transition kinetics. We confirmed that the new phase was stable at pressures >143 GPa. However, the diffraction peaks were observed to disappear after decompression to ambient pressure. This indicated that the high-pressure phase was not stable at low pressures, and became amorphous during decompression. In the next run, the pressure was gradually increased from 116 to 144 GPa. At P = 116 GPa and T = 1700 K, a post-aragonite $CaCO_3$ with space group *Pmmn* (Ono et al. 2005a; Oganov et al. 2006) was synthesized. When the pressure was increased to P = 141 GPa at T = 1700 K, the pyroxene-type phase appeared. The experimental results are shown in Figure 2. From our current data, the phase boundary is likely to occur at P ~130 GPa. The volume reduction of this phase transition was ~0.5%, which was in general agreement with that predicted by theoretical calculation (Oganov et al. 2006). However, further experiments are necessary to determine the dP/dT slope of this phase transition and the exact phase relationships of $CaCO_3$.

The effect of pressure on the unit-cell parameters and the volume of the high-pressure phases of $CaCO_3$ are shown in Table

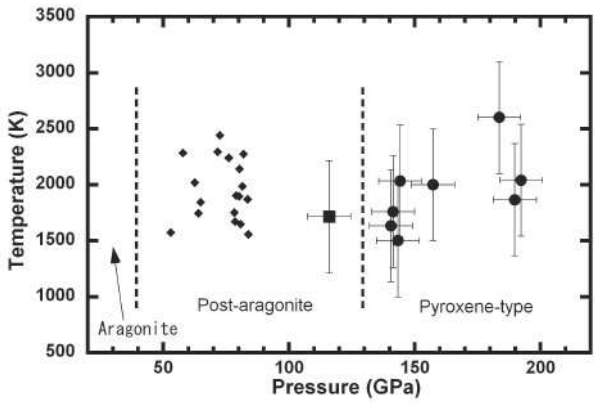

Figure 2. Experimental results and the phase boundary determined from in situ X-ray observations. The solid squares and circles denote the conditions where post-aragonite and pyroxene-type $CaCO_3$ are stable. The dashed lines are the inferred phase boundaries. The diamonds denote conditions where post-aragonite was observed in a previous study (Ono et al. 2005a).

1. All data were acquired after the laser annealing to release the accumulated stress. The *P-V* data of the pyroxene-type phase ($C222_1$) were fitted to a third-order Birch-Murnaghan equation of state to determine the elastic parameters (Birch 1947). Due to lack of data at low pressures, it is difficult to constrain V_0 and K_0 at ambient conditions from our data set. We have therefore calculated the volume and the bulk modulus at 120 GPa. When the value of the first pressure derivative of the isothermal bulk modulus was set to 4, the isothermal bulk modulus and the volume at 120 GPa and room temperature were determined to be K_{120} = 627(85) GPa and V_{120} = 130.3(9) Å^3, respectively.

Figure 3 shows axial ratios of the pyroxene-type phase. Both *b*/*a* and *c*/*a* ratio are markedly less pressure dependent. In contrast, both *b*/*a* and *c*/*a* ratios of the post-aragonite phase increase strongly with increasing pressure. This difference is due to the drastic change of fundamental structure from threefold to fourfold coordination of the C^{4+} cations. In the case of known calcium carbonates, except for pyroxene-type phase, the triangular CO_3^{2-} units have parallel arrangement. This structure leads to anisotropy of the physical properties, such as the strong pressure dependence of the axial ratios. In contrast, the pyroxene-type phase is composed of corner-sharing CO_4^{4-} tetrahedra that result in less pressure dependence of the axial ratio.

From geological observations, the most dominant carbonates at the Earth's surface are calcite ($CaCO_3$) and dolomite [$(Mg,Ca)CO_3$]. Marine sediments and hydrothermally altered oceanic crust containing these carbonates are likely to subduct into the deep mantle (Selverstone and Gutzler 1993; Massonne et al. 2007). However, dolomite is not stable in the deep mantle, because dolomite decomposes into magnesite, $MgCO_3$, and aragonite, $CaCO_3$, in the upper mantle (Martinez et al. 1996; Sato and Katsura 2001; Luth 2001; Shirasaka et al. 2002). Therefore, it is important to clarify whether these carbonates break down into two oxides or remain stable in the Earth's mantle, because carbon dioxide produced from carbonate decomposition would change the physical properties of the mantle rock and would influence carbon circulation in the Earth's system on the geological time scale. The phase relations of carbonate-bearing rock in the upper mantle are subject to debate (Hammouda 2003; Yaxley and Brey 2004; Dasgupta et al. 2004). Generally speaking, magnesite is stable in a pyrolite mantle composition. The pyrolite rock contains Mg-rich minerals, such as olivine, wadsleyite, ringwoodite, and ferropericlase (e.g., Irifune 1987; Ono and Oganov 2005). The saturated-MgO component could stabilize magnesite at the deep mantle. On the other hand, high-pressure phases of $CaCO_3$ seem to be stable at deep mantle conditions in Ca-rich rocks,

Table 1. Lattice parameters and volumes of $CaCO_3$ phases to 182 GPa at 300 K

P (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	Volume (Å^3)
Post-aragonite				
111.0	3.857(11)	4.441(13)	3.882(12)	66.48(33)
Pyroxene-type				
130.7	5.586(27)	7.104(39)	3.242(41)	128.6(19)
136.1	5.562(4)	6.986(5)	3.244(2)	126.1(2)
152.2	5.545(7)	6.928(15)	3.256(11)	125.1(5)
164.4	5.488(9)	6.898(7)	3.227(12)	122.2(5)
182.1	5.464(11)	6.852(6)	3.206(6)	120.0(3)

Notes: Numbers in parentheses are the standard uncertainties. Pressures were determined from the observed unit-cell volume of platinum.

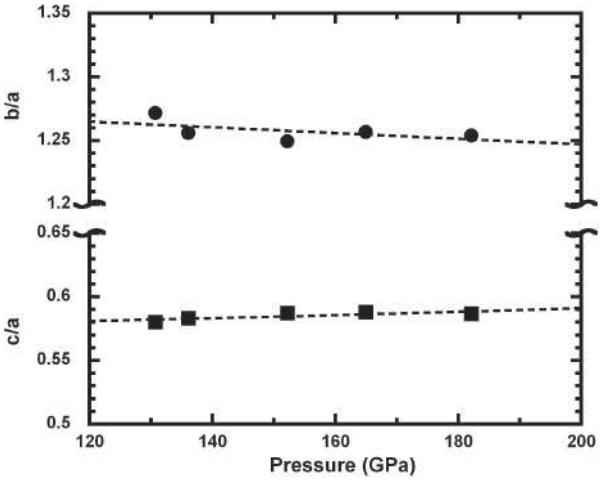

Figure 3. Pressure dependence of the axial ratios of pyroxene-type $CaCO_3$. The solid squares and circles denote *c*/*a* and *b*/*a* ratio, respectively. The dashed lines denote the linear fit of each.

such as subducted sediments and basaltic rocks (e.g., Irifune and Ringwood 1993; Ono et al. 2005d). In this study, we observed that post-aragonite $CaCO_3$ remains stable under lower mantle conditions, and finally transforms into the pyroxene-type phase at conditions the same as those at the base of the lower mantle. The host phases of carbon in the Ca-rich rocks are the pyroxene-type structures at the core-mantle boundary. Our finding supports the assertion that a certain amount of carbon, which is carried by subducted oceanic plates, is likely to be buried in the deep mantle.

The density of pyroxene-type $CaCO_3$ was calculated using the equation of state that we determined. The density of pyroxene-type $CaCO_3$ is 5–7% lower than those of the pyrolite mantle and subducted basalt at 130 GPa and room temperature. This indicates that the existence of pyroxene-type $CaCO_3$ contributes buoyancy to the subducted oceanic plate. This conclusion is not in agreement with a $MgCO_3$ study, which estimated that the high-pressure phase of $MgCO_3$ could contribute to negative buoyancy (Isshiki et al. 2004).

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