

New high-pressure phase of CaCO₃

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Introduction

Calcite is the dominant carbon-bearing phase in the Earth's crust, and acts as a buffer for the long-term cycling of CO₂ between the atmosphere, oceans, and solid Earth. It is unsurprising, therefore, that the high-pressure stability and behaviour of CaCO₃ and related phases has attracted considerable interest. In order to understand carbon recycling in the mantle, there have been a number of investigations into the pressure response of the structure of CaCO₃ polymorphs. It is known that calcite transforms to aragonite, which often occurs in high-pressure metamorphic rocks, at high P-T that correspond to the lower crust and the uppermost upper mantle. However, it is unknown whether aragonite transforms to a new high-pressure phase at the deep mantle. In this study, therefore, the high-pressure stability limit of aragonite was investigated using a laser-heated diamond anvil cell combined with a synchrotron X-ray diffraction method.

Experimental methods

High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell high-pressure apparatus. Synthetic powdered CaCO₃ was loaded into a 100 μm diameter hole that was drilled into a rhenium gasket. Platinum powder was mixed with the sample to absorb the laser radiation to provide a heat source, and was also used as an internal pressure calibrant. The samples were heated with a YAG laser to overcome any potential kinetic effects on possible phase transitions. The samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam lines BL13A, Photon Factory in Japan [1]. A monochromatic incident X-ray beam with a wavelength of about 0.42 angstrom was used. The X-ray beams were collimated to a diameter of 30 μm, and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate (Rigaku).

Results and Discussion

In the first set of experiments using the pressure transmitting medium, the pressure was increased directly to about 40 GPa at room temperature, and an X-ray diffraction pattern of the sample was recorded. A strain-broadening of the diffraction peaks occurred, because a large differential stress was induced in the diamond anvil cell experiments as pressure increased. After the desired pressure was achieved, the sample was heated to about 1500-2000 K to relax the differential stress and to overcome potential kinetic effects on possible phase transitions. After the heating, some new peaks appeared

in the diffraction pattern. This implies that the starting material transformed to a new high-pressure phase (post-aragonite phase). The experimental pressures of this study were from 11 to 86 GPa. The transition pressure from aragonite to the post-aragonite phase was located at about 35 GPa and room temperature after the heating (Fig. 1). The crystal structure of the post-aragonite phase is likely to have an orthorhombic symmetry. The number of molecules of this phase in a unit cell (*Z*) is 2. The lattice parameters at 66.4 GPa and 300 K, for example, are *a* = 4.101(12) Å, *b* = 4.561(4) Å and *c* = 3.964(3) Å, with a unit cell volume of 74.1(2) Å³ for the orthorhombic cell [2]. Recently, the phase transition of SrCO₃, which seems to be an analog material of CaCO₃, from aragonite-type to orthorhombic structure (*P2₁2₁2*) was reported at 10 GPa [3]. The phase transition sequence of CaCO₃ observed in this study agrees with that of SrCO₃. As seen in Fig. 1, a discontinuity in volume between aragonite and the post-aragonite phase indicates that this is a first-order phase transformation. At 35 GPa, the relative volume change is about 5%.

References

- [1] Ono et al., J. Appl. Phys. 97, 073523 (2005).
- [2] Ono et al., Am. Mineral. 90, 667 (2005).
- [3] Ono et al., Phys. Chem. Mineral. 32, 8 (2005).

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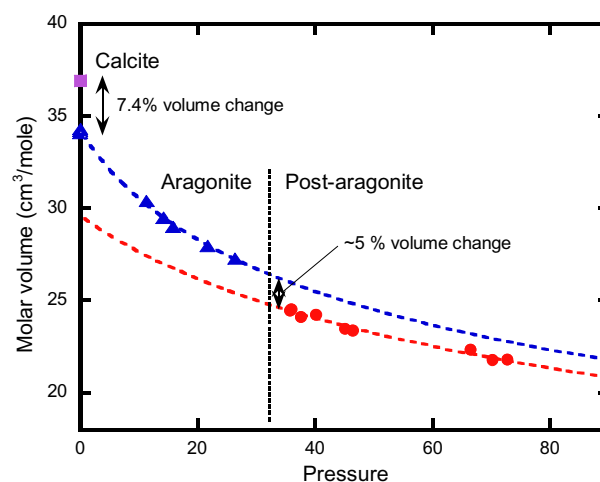


Figure 1. Pressure-volume data for the CaCO₃ phases at 300 K. Dashed curves are Birch-Murnaghan equation fits. Blue, aragonite; red, post-aragonite.