

Carbonates in deep mantle

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Carbonate minerals are thought to play an important role in the carbon cycle at deep Earth's mantle. The mantle provides CO₂ to the surface through degassing of the magmatism, whereas carbonate minerals in the sediments and/or altered oceanic crusts can be recycled into the mantle through subduction. Therefore, we have investigated the pressure-induced phase transition of carbonate minerals in several compositions using high-pressure experiments and the first-principles calculations.

High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell apparatus. The samples were heated with either a YLF or YAG laser to overcome any potential kinetic effects on the possible phase transitions. The heated samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam lines at the Photon Factory or at SPring-8. Powdered samples (MgCO₃, CaCO₃, SrCO₃, BaCO₃, MnCO₃, and PbCO₃) were used in this study.

The ab initio calculations based on DFT were performed using the VASP code. The interactions between the electrons and the ionic cores were described using the projector augmented wave (PAW) method with the generalized gradient approximations, known as PBE. We calculated the free energies of possible structures to find stable phases in MgCO₃, CaCO₃, SrCO₃, and BaCO₃. We could discover several high-pressure phases in our project [1-6]. Although the crystal structure of a couple of new phases has not been identified (e.g., [7, 8]), two types of structure were confirmed. One is the post-aragonite structure, which appears in CaCO₃, SrCO₃, and BaCO₃ [1, 3, 6, 7]. This structure has C₄₊ cations exhibiting a three-fold coordination with the oxygen ions, which is same coordination of other known carbonates. Another is the pyroxene-type structure, which was confirmed in MgCO₃ and CaCO₃ [2, 4, 5]. In the case of the pyroxene-type structure, the C₄₊ cations exhibit a four-fold coordination. Four-fold coordinated structures are commonly observed in many silicate minerals under ambient conditions. Our study indicates that the pressure-induced phase transition with coordination change from three to four is likely to occur in many carbonate minerals.

Our studies indicate that MgCO₃ and CaCO₃, which are possible host phases of carbon in the deep mantle, have a major change in the crystal chemistry within the lowermost mantle. The change in the crystal chemistry confirmed in our studies might influence the physical properties of carbonates. We discuss the possibility of CO₂ release at the very bottom of the mantle, which could enhance partial melting of mantle rocks.

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