

High-pressure phase transitions of MgCO₃ under the lower mantle conditions

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MgCO₃ is one of the important carbonate minerals in the deep Earth because it can be a carbon carrier from the surface to the mantle in subduction processes. Such deep carbonates may be involved in melting of subducted rocks and formation of deep diamonds in the mantle transition zone or lower mantle. MgCO₃ has especially been suggested to be the most stable carbonate under the high-pressure and temperature conditions.

Recent experimental and theoretical studies reported high-pressure phase transitions of MgCO₃ under the lower mantle conditions. A report of the high-pressure polymorph was started from 'magnesite II' at 115 GPa in Isshiki et al. (2004). Several recent studies supported a monoclinic MgCO₃ ('phase II') as a post-magnesite phase above ~80 GPa.

Phase II was revealed to be composed of (C₃O₉)-ring units which were constituted by three CO₄ tetrahedra sharing three oxygen atoms. However, the structure of phase II has a little difference between the previous studies: the space groups of phase II were reported as C2/m and P2₁/c in Oganov et al. (2008) and Boulard et al. (2011), respectively. Moreover the latest study by Pickard and Needs (2015) observed a new high-pressure polymorph having a triclinic lattice as a post-magnesite phase above 85 GPa, which changed to phase II at 101 GPa.

In addition to the difference of the post-magnesite phase and phase-II structures, none of the above studies decided the phase boundary of the high-pressure phase transitions at high temperature.

Therefore, we have been studied the phase relation of MgCO₃ up to the lowermost mantle conditions based on high-pressure and temperature experiments. We especially focused on the phase boundary of the high-pressure polymorphs at high temperature and a true post-magnesite phase.

The starting material was a natural magnesite from Bahia in Brazil. The experimental conditions were up to 138 GPa and 2900 K generated using a double-sided laser-heated diamond anvil cell (LHDAC). Culet diameters of diamond anvils used were between 130 and 250 μm. The sample was loaded into a sample chamber in a tungsten gasket which was pre-indented to 40–60 μm in thickness and drilled a 60–80-μm hole in diameter. Laser heating was conducted using a fiber laser. Pt or Au was used as a laser absorber. Run products were detected using synchrotron X-ray diffraction (XRD) measurements at beamline BL10XU of SPring-8 in Hyogo, Japan. Experimental pressures were measured using a thermal equation of state of Pt or Au (Fei et al., 2007) and thermal pressures were calculated using Mie-Grüneisen-Debye model (e.g., Fei et al., 1992). XRD patterns were analyzed using IPAnalyzer and PDIndexer software (Seto et al., 2010).

We observed the two high-pressure polymorphs of MgCO₃, which might be monoclinic phase II and triclinic phase reported in Oganov et al. (2008) and Pickard and Needs (2015), respectively. Phase II was observed mainly above 90 GPa and the lattice constants were estimated to be $a = 8.209 \text{ \AA}$, $b = 6.575 \text{ \AA}$, $c = 6.978 \text{ \AA}$, $\beta = 104.06^\circ$, and $V = 365.3 \text{ \AA}^3$ at $100 \pm 2 \text{ GPa}$ and $2080 \pm 230 \text{ K}$ when fitted using the Oganov's space group, C2/m. The triclinic phase might be appeared as a post-magnesite phase around 90 GPa: The XRD patterns were not explained only by magnesite and phase II. Strong peaks near 104 diffraction of magnesite are considered to be derived from the triclinic phase although we could not fit their patterns and estimate the lattice constants due to lack of the peak number to fit the triclinic unit cell. We could estimate the phase boundaries of high-pressure polymorphs based on the above observations.

The triclinic post-magnesite phase may have a very narrow stability field in the P-T phase diagram. The triclinic phase might buffer the significant structural change from magnesite (CO_4 triangles) to phase II (C_3 O_9 rings composed of three CO_4 tetrahedra).

Keywords: magnesite, high-pressure polymorph, lower mantle, LHDAC