

## Discovery of New High-Pressure Phase of $\text{MgCO}_3$

High-pressure X-ray diffraction measurements have revealed that magnesite ( $\text{MgCO}_3$ ) changes into a new high-pressure phase at pressures higher than 130 GPa. The crystal structure of the new phase synthesized in our study is in good agreement with that predicted by first-principles calculations. This new phase is stable at high pressures corresponding to the bottom of the Earth's lower mantle. These findings have important implications for the carbon circulation in the Earth's interior.

Magnesite ( $\text{MgCO}_3$ ) is the dominant carbon-bearing phase in the Earth's crust, and acts as a buffer for the long-term cycling of  $\text{CO}_2$  between the atmosphere, oceans, and solid Earth. It is unsurprising, therefore, that the high-pressure stability and behavior of  $\text{MgCO}_3$  and related phases have attracted considerable interest. Most carbon must be present as a separate phase, such as magnesite, in the upper mantle, because the carbon solubility in olivine, which is a major phase in the Earth's interior, is exceedingly low. In order to understand carbon recycling in the mantle, there have been a number of investigations into the pressure response of magnesite. It is generally known that magnesite is stable at high P-T that corresponds to the crust and the upper mantle. However, it is unknown whether magnesite transforms to a new high-pressure phase at the Earth's deep mantle. In this study, therefore, the high-pressure stability limit of magnesite was investigated.

High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell ap-

paratus [1]. The diamonds had a culet of 100  $\mu\text{m}$  and gaskets were pre-indented to a thickness of 30  $\mu\text{m}$ . The starting material of magnesite had the trigonal structure, space group  $R\bar{3}c$ . Gold powder was mixed with the sample to absorb the laser radiation. It was also used as an internal pressure calibrant. A pressure-transmitting medium was not used to avoid a reaction between the sample and the pressure-transmitting medium. The samples were heated with an infrared laser to overcome any potential kinetic effects on any potential phase transitions. After the desired pressure was achieved, the sample was heated to  $\sim 2000$  K. The heated samples were probed using angle-dispersive X-ray diffraction at the synchrotron beam line BL-13A. A monochromatic incident X-ray beam was collimated to a diameter of 30  $\mu\text{m}$ , and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate. The experimental method used in this study has been described elsewhere [2].

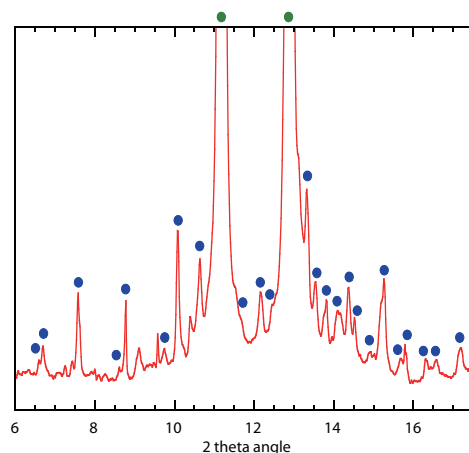


Figure 1 X-ray diffraction pattern of magnesite-III. Data was acquired after laser heating at a pressure of 140 GPa. The blue circles denote peaks from magnesite-III. Gold powder, the diffraction peaks of which are shown as green circles, was used as the pressure calibrant. The wavelength of the monochromatic incident X-ray beam was  $\lambda = 0.4274$  Å.

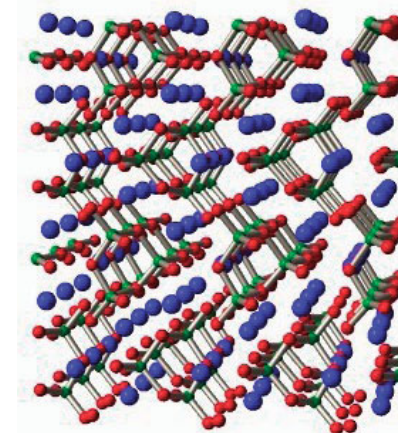


Figure 2 Crystal structure of magnesite-III. The blue, green and red spheres denote magnesium, carbon and oxygen atoms, respectively.

A typical diffraction pattern after heating the sample is shown in Fig. 1. In this run, the pressure was increased directly to  $\sim 150$  GPa at room temperature. After the desired pressure was achieved, the sample was heated to  $\sim 2000$  K, and the X-ray diffraction data of the sample were acquired after temperature quenching. In addition to the peaks arising from gold, other peaks were observed, indicating that the starting material had transformed into a new high-pressure phase. These peaks belonged to a monoclinic cell, which was different from magnesite. The new peaks were assigned to a pyroxene-type structure having space group  $P2_1$ , because of the excellent agreement between the observed X-ray powder diffraction pattern and the simulated pattern for the pyroxene-type structure (magnesite-III) predicted by Oganov et al. [3] was confirmed.  $\text{MgCO}_3$  magnesite has  $\text{C}^{4+}$  cations exhibiting a three-fold coordination with the oxygen ions. However, in the case of the new pyroxene-type structure, the  $\text{C}^{4+}$  cations exhibit a four-fold coordination (Fig. 2). Four-fold coordinated structures are commonly observed in many silicate minerals under ambient conditions. According to other experiments, the phase boundary was determined to be  $\sim 130$  GPa at high temperatures.

Generally speaking, magnesite is stable in the normal mantle composition of the Earth. The mantle rock contains Mg-rich minerals, such as olivine, wadsleyite, ringwoodite, perovskite and ferropericlase. The saturated-MgO component could stabilize magnesite at the Earth's deep mantle. In this study, we observed that  $\text{MgCO}_3$  magnesite transforms into the pyroxene-type phase (magnesite-III) in conditions the same as those at the base of the Earth's lower mantle. The host phases of carbon in Mg-rich rocks are the pyroxene-type structures at the core-mantle boundary. Our finding supports the assertion that a certain amount of carbon is likely to be buried in the Earth's deep mantle.

### REFERENCES

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### BEAMLINE

13A (This work was carried out at the former BL-13A.)

S. Ono (JAMSTEC)