

In Situ X-ray Observation of the Stability of MgCO₃ Magnesite throughout Earth's Lower Mantle

Carbonates, such as CaCO₃ calcite and aragonite, MgCO₃ magnesite, and CaMg(CO₃)₂ dolomite, are important constituents of marine sediments and play a fundamental role in the long-term recycling of carbon into Earth's deep interior via oceanic plates subduction. It has been demonstrated that these subducted carbonates react with surrounding silicates and/or decompose to CO₂-bearing assemblages at certain depths in the upper mantle (a region of 30-660 km depths), and therefore, MgCO₃ magnesite is believed to be the major carbonate in the deeper part of the upper mantle near 660 km [1].

A study of the stability of magnesite under the pressure and temperature corresponding to those of entire mantle conditions down to 2900 Km depth (P = ~ 136 GPa and T = ~ 4000 K) is thus crucial in modelling the carbon circulation in the entire Earth system. However, such experiments have been limited to upper mantle conditions (P < 24 GPa) with few exceptions [2]. Moreover, most of these studies adopted a quench method, and no *in situ* X-ray diffraction measurements have been made under simultaneous high pressure and high temperature conditions of the lower mantle.

We firstly made an *in situ* X-ray diffraction study of the stability of magnesite under P-T conditions approaching the mantle-core boundary using a laser heated diamond anvil cell (LHDAC) at beamline BL10XU (Fig. 1) [3], the details of which have been reported by Isshiki *et al.* [4]. We found the magnesite persists at pressures up to about 100 GPa at

temperatures up to 3000 K, without dissociation into a CO₂-bearing assemblage (Figs. 2(a-c)). However, we noted that several new peaks appeared at the expense of those of magnesite when the temperature and the pressure were increased to 2200 K and ~115 GPa, respectively (Fig. 2(d)). These new peaks were present at room temperature after quenching under pressure (Fig. 2(e)), but completely disappeared when pressure was released (Fig. 2(f)), and only the diffraction peaks of magnesite were observed in the recovered sample. These new peaks did not correspond to any possible dissociation products of magnesite, and the presence of only the diffraction peaks of magnesite in the recovered sample also precludes its dissociation and/or reaction with the surrounding Al₂O₃ pressure medium.

Thus we conclude that magnesite transforms to a new high-pressure form (magnesite II) at pressures above ~ 115 GPa at temperatures of 2100 – 2200 K (equivalent to a depth of ~ 2600 km in the lower mantle), although we were unable to refine its crystal

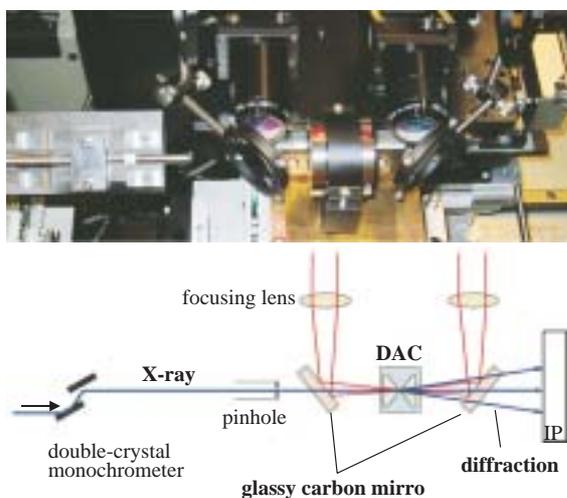


Fig. 1. LHDAC system at BL10XU used in the present study.

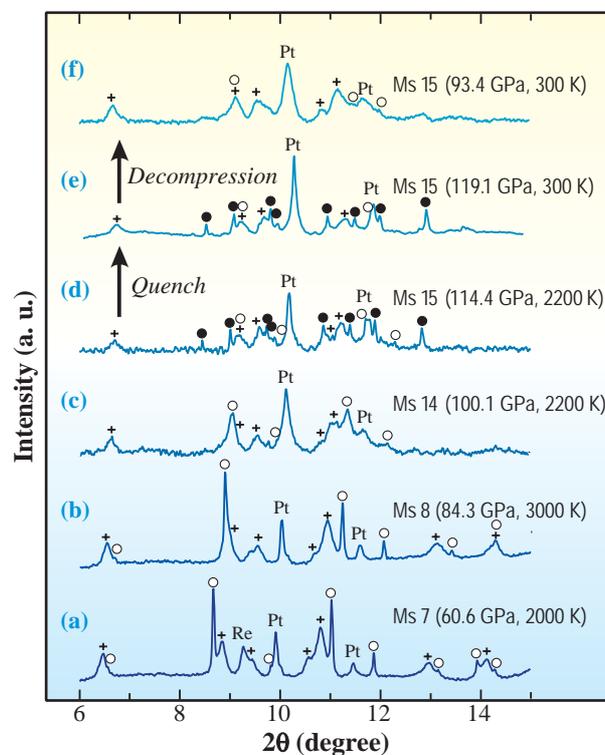


Fig. 2. X-ray diffraction profiles with increasing pressure at maximum temperatures in selected experiments. ○, Magnesite; ●, Magnesite II; Pt, Platinum; Re, Rhenium; +, Al₂O₃ [4].

structure, partly because of the possible overlap of the diffraction peaks with those of corundum, platinum, magnesite and rhenium. The unquenchability of magnesite II also made it difficult to determine its crystal structure from the observed diffraction profile. Nevertheless, we found that the X-ray diffraction peaks of magnesite II can be reasonably indexed on the basis of an orthorhombic symmetry, yielding a density of 5.20 g/cm³ at ~ 120 GPa, which is about 17% denser than that of magnesite (4.46 g/cm³) under the same P/T conditions.

Figure 3 shows the present experimental conditions and the results, and depicts a typical geotherm in the mantle and the predicted boundary for the dissociation of MgCO₃. It is seen that the dissociation of magnesite into MgO and CO₂ is unlikely to occur throughout the mantle. Subducted oceanic plates are significantly colder than the surrounding mantle into the uppermost part of the lower mantle, and accordingly, magnesite should survive and be transported down to the upper mantle-lower mantle boundary at ~ 660 km depth without dissociation into a CO₂-bearing assemblage. Moreover, parts of the stagnant plates at these depths may ultimately sink into the lower mantle after they are accumulated to a critical size to form a megalith structure [5]. Thus, magnesite is likely to be transported further into the lower mantle, where it is transformed into magnesite II at 110 - 120 GPa, as illustrated in Fig. 4.

The present results suggest that magnesite II is the major host for oxidized carbon in the D'' layer, and some of the "missing carbon" may be stored in this phase at the base of the mantle. It is also possible

that a certain amount of carbon is incorporated into the iron core and/or reduced to form diamond in the D'' layer if it is in sufficiently low oxygen fugacity. On the other hand, magnesite II may dissociate to MgO + CO₂ in the D'' layer, as a result of the predicted dramatic temperature increase with depth in this region (Fig. 3). Release of CO₂ from magnesite II may trigger partial melting of materials present in the D'' layer, which should contribute to initiate rising plumes from this region.

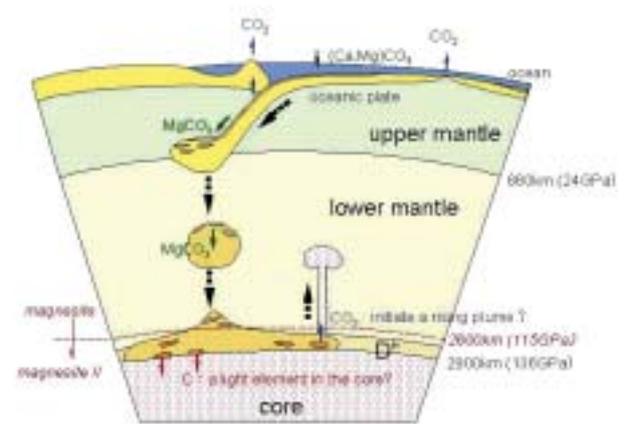


Fig. 4. Schematic illustration of possible carbon circulation in the deep mantle.

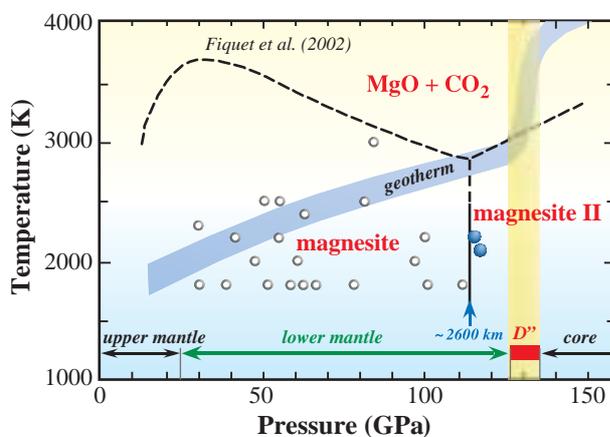


Fig. 3. Possible phase relations of MgCO₃ and a typical geotherm in the deep mantle [4].

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