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ORIGINAL PAPER

Decarbonation reaction of magnesite in subducting slabs at the lower mantle

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Abstract High-pressure and temperature experiments (28–62 GPa, and 1,490–2,000 K, corresponding to approximately 770–1,500 km depth in the mantle) have been conducted on a $MgCO_3$ + SiO_2 mixture using a laser-heated diamond anvil cell combined with analytical transmission electron microscope observation of the product phases to constrain the fate of carbonates carried on the subducting basalt into the lower mantle. At these conditions, the decarbonation reaction $MgCO_3$ (magnesite) + SiO_2 (stishovite) $\rightarrow$ $MgSiO_3$ (perovskite) + CO_2 (solid) has been recognized. This indicates that above reaction takes place as a candidate for decarbonation of the carbonated subducting mid ocean ridge basalts in the Earth's lower mantle.

Keywords High-pressure solid CO_2 · Carbonate · Slab · Diamond

Introduction

Stability relations of carbonate minerals in the deep mantle are important to our understanding not only of magmatic processes involving CO_2; i.e., genesis and origin of kimberlite and carbonatite magmas, but also of the fate of carbon in the Earth's deep mantle. Carbonates possibly play a fundamental role in the recycling of carbon into the Earth's interior via the subducted slabs, producing one of the carbon budgets in the entire Earth's system. Carbonation reactions for olivine-bearing ultramafic rocks up to 50 GPa have been studied extensively by several workers (e.g., Canil and Scarfe 1990; Katsura and Ito 1990; Biellmann et al. 1993). In these assemblages, the carbonation reactions invariably involve olivine or pyroxene reacting with CO_2 to form carbonate without dissociation into a CO_2-bearing assemblage. Contrast to this, in eclogite rocks, Luth (1995) experimentally studied the following reaction; dolomite + 2coesite = diopside + $2CO_2$ (vapor). Also, Knoche et al. (1999) reported that the reaction; 3 magnesite + kyanite + 2coesite = pyrope + $3CO_2$ (vapor) in the upper mantle. However, it is still an open question how the eclogite rocks-CO_2 system behaves in the lower mantle.

Eclogite rocks transform into garnetite rocks from the mantle transition zone to the upper part of the lower mantle (Irifune et al. 1986). One of the essential points in eclogite rocks is that the mineral assemblage involves stishovite. Also, the major carbonates in marine sediments ($CaCO_3$ calcite, $CaCO_3$ aragonite, and $CaMg(CO_3)_2$ dolomite) have been shown to transform to magnesite-bearing assemblages (e.g., Biellmann et al. 1993), and magnesite may be the only stable carbonate throughout most parts of the lower mantle (Isshiki et al. 2004).

Here, we report a phase relation of $MgCO_3$ (magnesite) + SiO_2 (stishovite) at the lower mantle condition in order to constrain the fate of carbonates carried on the subducted ocean floor in the lower mantle.

Experimental

A powder mixture (1:1 in mol) of α-quartz and natural magnesite with a composition of $(Mg_{0.994}Ca_{0.006})CO_3$

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was used as starting material. The sample was mixed with a small amount (<10 wt%) of platinum powder, which works as a laser-radiation absorber. The laser-heated diamond-anvil cell (LHDAC) experiments were carried out at about 28–62 GPa and 1,490–2,000 K for 60 min, at which conditions magnesite is solid (Fiquet et al. 2002; Katsura and Ito 1990) (Fig. 1). The sample was loaded into a 100 μm hole in a rhenium gasket and compressed by 300 μm culet diamond anvils. The sample was embedded between layers of NaCl in the hole in order to avoid a large axial temperature gradient. Heating was made with a focused TEM_{01*} YLF laser mode using a double-sided heating technique that minimizes both radial and axial temperature gradients, producing a heating spot size of ~40 μm in diameter. Temperature was monitored from one side using the spectroradiometric method. Although it is difficult to measure the absolute temperature, we could measure the temperature distribution across the hot spot on heating and monitored the temperature at intervals of about 10 s. The radial and temporal temperature variations in the heated region were within 100 K, but it was difficult to estimate axial temperature variations. Pressure was determined using ruby-fluorescence techniques after heating (Mao et al. 1978). Present estimation of pressure does not include a correction for a thermal pressure.

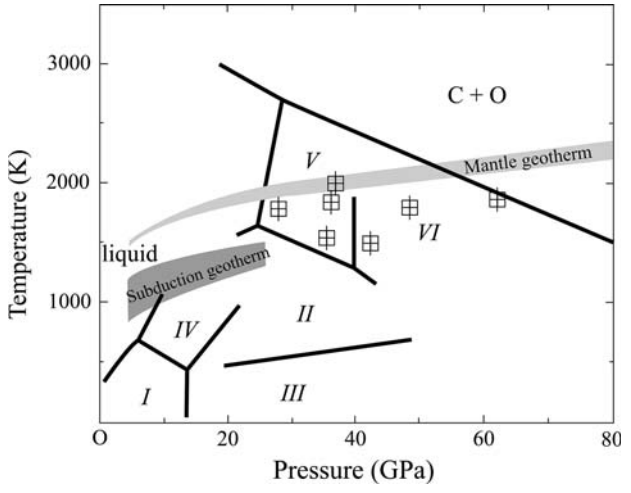

Fig. 1 Phase diagram of CO_2 determined at high pressure and temperature, based on previous laser-heating experiments (e.g., Iota and Yoo 2001; Tschauner et al. 2001; Santoro et al. 2004). Early high pressures studies have reported the existence of many high pressure phases of CO_2 (CO_2-I, II, III, IV, V, VI) and a decomposition reaction from CO_2 to C + O. But, CO_2-VI, which was suggested to be a precursor of the decomposition of carbon dioxide into molecular oxygen and carbon, was not observed in the study of Santoro et al. (2004). The mantle geotherm is after Akaogi et al. (1989) and Brown and Shankland (1981). The subduction geotherm is after Thompson (1992) and Komabayashi et al. (2004). *Squares* are the experimental points in the present study

Samples recovered from the LHDAC were Ar ion-thinned after trimming off the insulation layers and investigated with a JEOL-2010 transmission electron microscope (TEM) operating at 200 kV. Chemical analyses were made using a NORAN Instruments/Voyager (EDS) analytical system attached to TEM. We calculated the chemical compositions from the measured X-ray intensities using experimentally determined k-factors under the same operational conditions to those described previously (Takafuji et al. 2004).

Results and discussion

A total of seven runs were performed using LHDAC at lower temperatures than that of the typical mantle geotherm (Table 1, Fig. 1). Phase assemblages in the run products were identified by analytical TEM. Figure 2a shows a transmission electron photomicrograph of the recovered sample at 36.9 GPa and 2,000 K. The TEM image shows the $MgSiO_3$ perovskite phase with abundant voids but also shows magnesite and stishovite, the same assemblage as starting materials. Magnesite and stishovite are thought to be unreacted starting materials, because magnesite and stishovite were never contacted with each other. Voids usually have highly irregular shapes and widely varying sizes (several ~100 nm). Similar textures were observed in all the run products in this study. Figure 2b is an example of the selected area electron diffraction (SAED) pattern obtained from $MgSiO_3$ perovskite. No diamond could be found in the recovered samples. Considering chemical stoichiometry and no detection of diamond, the present results provide a chemical reaction as follows:

$$MgCO_3\ (\text{magnesite}) + SiO_2\ (\text{stishovite}) \rightarrow MgSiO_3\ (\text{perovskite}) + CO_2 \quad (1)$$

This decomposition reaction of magnesite was confirmed in all the run products of this study.

The voids suggest the presence of a CO_2 phase which was formed according to reaction Eq. 1. Although the voids should be filled with a CO_2 phase at high pressure, CO_2 evaporated during releasing pressure and the voids remained.

Katsura and Ito (1990) also observed abundant voids with forsterite crystals in the experiment at 2.5 GPa and 1,600°C with starting material of enstatite

Table 1 Pressure and temperature conditions in the present study

Run no.	Pressure (GPa)	Temperature (K)	Duration (min)
1	27.8	1,780	60
2	35.3	1,550	60
3	36.2	1,830	60
4	36.9	2,000	60
5	42.2	1,490	60
6	48.6	1,810	60
7	62.0	1,850	60

50% + magnesite 50% in the mole. They interpreted that the voids suggest the presence of CO_2 fluid which was formed according to the reaction:

$$MgSiO_3 \text{ (enstatite)} + MgCO_3 \text{ (magnesite)} \rightarrow Mg_2SiO_4 \text{ (forsterite)} + CO_2$$

The CO_2 phase produced in the upper mantle conditions would be fluid due to the lower melting point of CO_2 at such conditions (Iota and Yoo 2001; Tschauner et al. 2001; Santoro et al. 2004). However, the CO_2 phase in the present study is considered to be solid by the following reason. It is known that several solid CO_2 phases (I, II, III, IV, V, and VI) are stable at high pressure and temperature (e.g., Yoo et al. 1999, 2002; Iota et al. 1999; Iota and Yoo 2001; Tschauner et al. 2001, Park et al. 2003) (Fig. 1). Tchauner et al. (2001) also reported that there is no sign of melting up to 2,800 K above 50 GPa. These results suggest that the CO_2 phases in the present study are considered to be solid and CO_2-V and CO_2-VI should be stable in the present experimental conditions. To evaluate the volume change associated with reaction Eq. 1 theoretically, we calculated the molar volumes of perovskite plus CO_2-V and magnesite plus stishovite based on the existing data on the equations of state of magnesite (Fiquet et al. 2002), stishovite (Andrault et al. 2000), perovskite (Shim and Duffy 2000) and CO_2-V (Yoo et al. 1999). Because no EOS data of CO_2-V at high temperature has been available so far, all the EOS data used in this calculation were reported for compression at a room temperature. Figure 3 shows the total molar volumes of perovskite plus CO_2-V (solid) and magnesite plus stishovite (dashed) at pressures. It is clear that the assemblage of perovskite plus CO_2-V has a smaller molar volume than that of magnesite plus stishovite over the entire range of pressures in the present study. Although the relationship of the molar volumes of these phases at high temperature is not clear at the moment and also the stability of materials depends on not only volume, this indicates that perovskite plus CO_2-V might be much stable than magnesite plus stishovite at the lower mantle.

The present study clearly indicates that magnesite coexisting with stishovite is not stable at the lower mantle and possibly produces magnesium silicate perovskite and solid CO_2 phases. Since physical properties of the solid CO_2 phases in the lower mantle conditions have not been known so far, how the solid CO_2 phases behave at the lower mantle is still unclear. However, the solid CO_2 phases might be decomposed

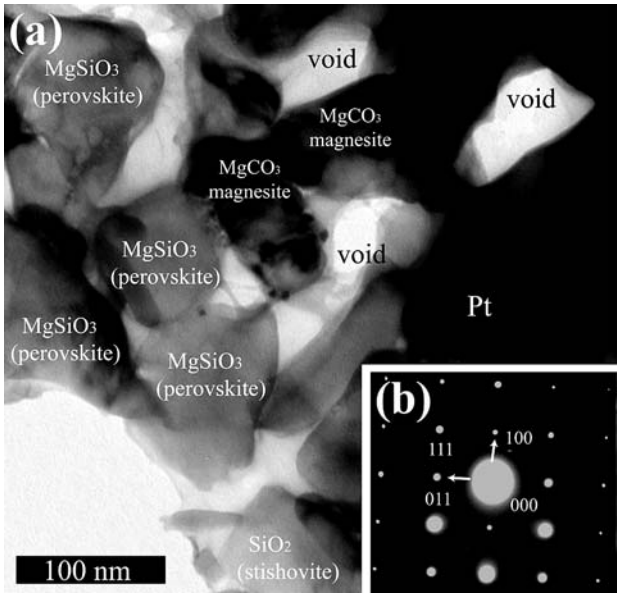

Fig. 2 **a** TEM image of $MgSiO_3$ perovskite, SiO_2 stishovite, and $MgCO_3$ magnesite recovered from 36.9 GPa and 2,000 K. The recovered sample is rich in voids of irregular shape. **b** Selected area electron diffraction pattern of $MgSiO_3$ perovskite

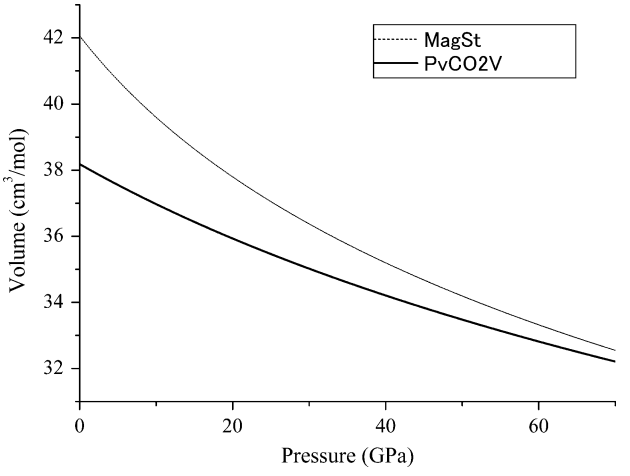

Fig. 3 Comparison of molar volumes of perovskite plus CO_2-V (*solid*) and magnesite plus stishovite (*dashed*) at high pressure. We did not use the thermodynamic data of CO_2-VI since Santoro et al. (2004) did not observe CO_2-VI

into diamond and a solid oxygen phase at higher pressure and temperature (Tschauner et al. 2001). When the eclogitic slab goes down to the lower part of the lower mantle, it may be possible that the formation of diamond originated from carbonate minerals occurs. Further discussion of the diamond formation at the lower mantle must need more experimental data, especially on the stability field of CO_2 phases at the lower mantle.

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