

# A GENESIS OF CARBONATITIC MELT WITHIN SUBDUCTING OCEANIC CRUSTS: HIGH-PRESSURE EXPERIMENTS IN THE SYSTEM MORB-CaCO<sub>3</sub>

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## INTRODUCTION

In the convergent plate margin, some carbonate sediments accrete to the continental crust, and at least some of them subduct into the upper mantle. What is the fate of the subducted carbonate in the mantle? The possible link between carbonatitic melt and subducted carbonate has been paid much attention in recent literatures. Some metasomatic agent is considered to have originated from recycle carbonates in the arc system (Papua New Guinea; McInnes and Cameron 1994) and in hot spot (Hauri et al. 1993). Hoernle et al. (2002) discussed that the carbonatite magma in the Cape Verde Islands originated from the subducted carbonate sediments.

### PREVIOUS EXPERIMENTAL STUDIES IN THE BASALTCARBONATE SYSTEM

Although the role of carbonate in mantle eclogite is very important, earlier experiments have been carried out at < 3 GPa for carbonate-bearing eclogite. Yaxley and Green (1994) and Shirasaka (1998) studied high-pressure phase relations in the system MORB-CaCO<sub>3</sub>-H<sub>2</sub>O at < 3.0 GPa and < 2.5 GPa respectively. These experiments showed that calcite or dolomite coexists with silicate melt of andesite to dacitic compositions at relatively lower temperatures.

Yaxley (1999) carried out the partial melting of carbonated eclogite at 3 and 3.5 GPa, the first melt coexisting with calcite is carbonatitic. Shirasaka and Takahashi (in preparation) conducted high-pressure experiments on carbonated eclogite system, up to 8 GPa with lesser carbonate contents in bulk composition than Yaxley's study (1999). The following three important results were obtained in our previous work; (1) solidus shape with a cusp at around 5 GPa (see Fig.2), (2) Ca-rich dolomitic to calcitic melt compositions above 3.5 GPa, and (3) carbonate phase changes from calcite to dolomite, and finally aragonite + magnesite.

Production of carbonatitic melt by partial melting of carbonated eclogite has been recognized. However, no experimental study has been carried out at pressures higher than dolomite breakdown at solidus. This study investigates the solidus temperature and melt

compositions in the pressure range 12 to 15 GPa where dolomite becomes unstable in eclogite system.

## EXPERIMENTAL PROCEDURES

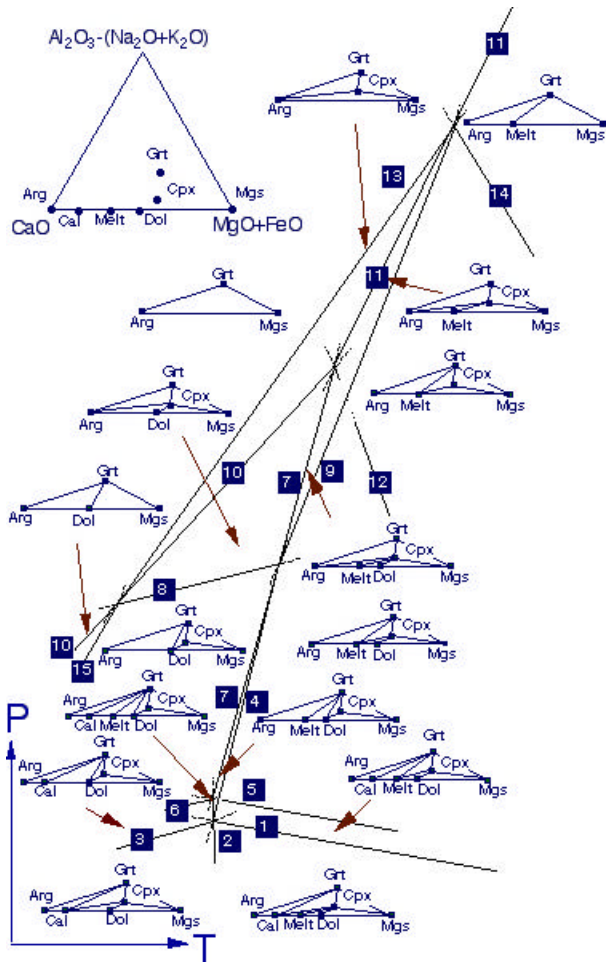
The details of experimental and analytical procedures of this study are described in Shirasaka and Takahashi (in preparation), and here we present the outlines and pertinent to the present experiment. The high-pressure experiments conducted with the mixture of 90 wt% of the MORB glass and 10 wt% of high purity CaCO<sub>3</sub> powder.

High-pressure experiments below 3.5 GPa were carried out with a Boyd-England type piston-cylinder apparatus at the Magma Factory, Tokyo Institute of Technology (TITECH). Experiments at > 4.0 GPa were conducted using a multi-anvil apparatus SPI 1000 at the Magma Factory (Takahashi et al. 1993). Experiments at 12-15 GPa were conducted with MgO octahedral of 10 mm edge length (10M) and WC cubes with 5 mm truncations. Details of the cell assembly in other PT condition were described in Shirasaka and Takahashi (in preparation).

The capsule was mounted in epoxy resin and polished under ethanol. The surface of the charge was polished with diamond and coated with carbon. The compositions of all phases were determined by a wavelength dispersive electron microprobe analyzer (JEOL JXA 8800) in TITECH. All phases were analyzed with a focused beam using an acceleration voltage of 15 kV and a beam current of 12 nA.

## EXPERIMENTAL RESULTS

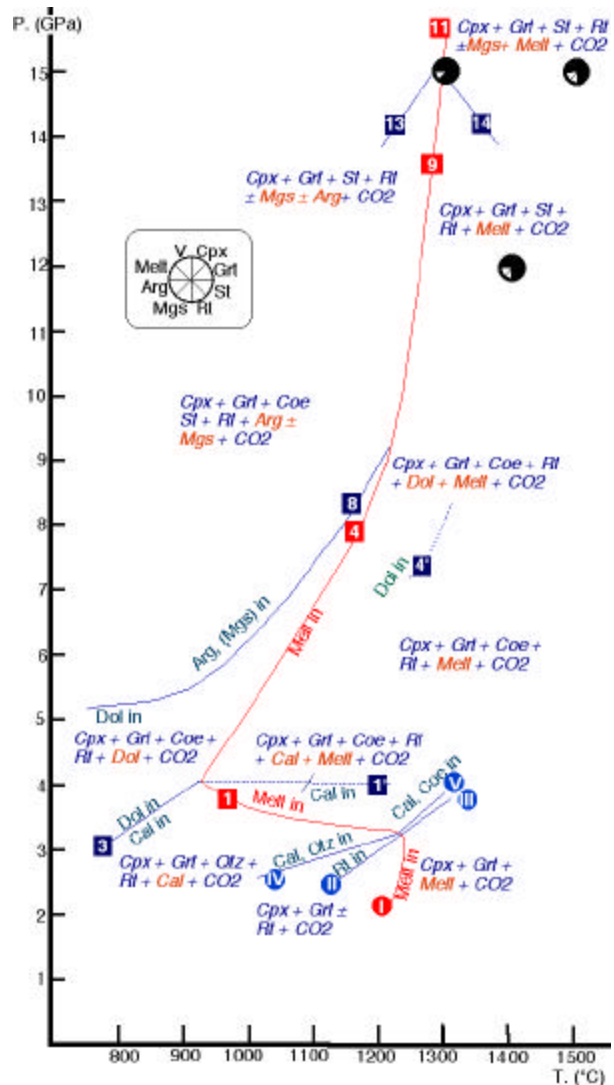
At 12-15 GPa, Clinopyroxene (Cpx), garnet (Grt), stishovite (St), rutile (Rt), melt and CO<sub>2</sub> (vapor, V) are present in all runs. Additionally, magnesite (Mgs) is present. Based on experimental results and previous studies, we draw ACF-grids (Fig. 1). Phase relations in the system 90 wt.% MORB-10 wt.% CaCO<sub>3</sub> at 2.7-15 GPa are given in Fig. 1b. Some reactions in ACF-grids (Fig. 1) apply to phase relations (Fig. 2).



**Figure 1:** The grids in ternary systems in  $\{Al_2O_3 - (Na_2O + K_2O)\}/2 - CaO - (MgO + FeO)$  saturated in  $SiO_2$ ,  $TiO_2$  and  $CO_2$ . Numbers of lines mean following reaction, which shift to right with increasing temperatures; (1)  $Cpx + Cal = Grt + Melt$ , (2)  $Dol + Cal = Melt$ , (3)  $Grt + Dol = Cpx + Cal$ , (4)  $Grt + Dol = Cpx + Melt$ , (5)  $Cal = Arg + Melt$ , (6)  $Arg + Dol = Cal$ , (7)  $Dol + Arg = Melt$ , (8)  $Cpx + Arg = Grt + Dol$ , (9)  $Cpx + Arg = Grt + Melt$ , (10)  $Arg + Mgs = Dol$ , (11)  $Arg + Mgs = Melt$ , (12)  $Dol = Mgs + Melt$ , (13)  $Grt + Arg + Mgs = Cpx$ , (14)  $Cpx = Grt + Mgs + Melt$ , (15)  $Grt + Dol + Mgs = Cpx$

### ACF-GRIDS

This study uses ACF-grids, which are saturated in  $SiO_2$ ,  $TiO_2$  and  $CO_2$ . Trace amounts of  $MnO$  and  $B_2O_5$  are disregarded. Sodium and potassium oxides are subtracted from aluminum oxide in order to examine reactions using Tschermakite (not jadite) component in clinopyroxene. Existing phases, Grt, Cpx, Arg, Cal, Dol, Mgs and Melt, in this ACF-grids are solid solutions, and then all reactions form divariant fields.



**Figure 2:** Phase relations in the system 90 wt% MORB–10 wt%  $CaCO_3$ . The solid sectors in the symbols indicate the presence of those particular phases. Arabic numbers of lines mean the reaction in Fig 1. Roman Numbers of lines mean following reactions, which shift to right with increasing temperatures; (I)  $Cpx + Grt = Melt$ , (II)  $Rt$  dissolves in  $Cpx$ , (III)  $Rt$  dissolves in  $Melt$ , (IV)  $Cal$  and  $Qtz$  dissolve in  $Cpx$  and/or  $Grt$ , (V)  $Cal$  and  $Coe$  dissolve in  $Cpx$ ,  $Grt$  and/or  $Melt$  (Details in Shirasaka and Takahashi in preparation).

Relative arrangements of the divariant reactions are decided to satisfy the following criteria; Arg at higher pressure than Cal, assemblage Arg + Mgs at higher pressure than Dol, and melting of Mgs at higher temperature than Cal, Arg or Dol. We supplemented carbonate-grids (Arg–Cal–Melt–Dol and Arg–Melt–Dol–Mgs) for the  $CaCO_3$ – $MgCO_3$  system with the ACF-grids.

The formation of magnesian calcite from aragonite and dolomite was studied experimentally up to 2.2 GPa by Goldsmith and Newton (1969). It is not proved that the reaction 6 takes place at pressures higher than the invariant point (Grt, Cpx, Cal, Dol, Melt). If the reaction 6 occurs at lower pressure than this point, reactions 3 and 6, 1 and 5 overlap each other.

According to these ACF-grid analyses, magnesite-bearing eclogite is stable in extensive PT field. Whereas the stable area of other carbonate phases or melt is limited. With increasing pressure, calcite changes to dolomite, and lastly to aragonite (or magnesite).

#### **PHASE RELATIONS IN THE SYSTEM 90 WT% MORB–10 WT% CaCO<sub>3</sub>**

The carbonate undersaturated solidus up to ~3 GPa (the reaction I; Cpx + Grt = Melt) has a positive Clapeyron slope. The solidus temperature decreases from ~1200°C at ~3 GPa to ~950°C at ~4.5 GPa (the reaction 1; Cpx + Cal = Grt + Melt) dramatically due to the appearance of dolomite below solidus. At 3.5–4.0 GPa, calcite is stable in solidus. With increasing pressure, dolomite is stable in solidus and carbonatitic melt is produced above ca. 4.5 GPa, and then, dolomite saturated solidus temperature increase up to ca. 1250°C with pressure (the reaction 4; Grt + Dol = Cpx + Melt). Aragonite appears in the solidus at higher pressure than dolomite dissolution (the reaction 9). At 15 GPa, solidus temperature is below 1300°C. Then, the Clapeyron slope of solidus is gentle at pressures from 8 to 15 Pa.

On the other hand, dolomite breaks down to aragonite + magnesite under subsolidus conditions above 5.5 GPa (Luth 2001, Shirasaka et al. 2002). Some runs show the phase assemblage Grt + Cpx + Arg + Mgs in this study, however there are no fields on the ACF grids that these four phases coexist except for those on the divariant reaction 13. It is also possible that aragonite or magnesite is metastable in this run product, or different sets of carbonate appeared due to the fluctuation of the local bulk chemistry.

#### **MELT COMPOSITIONS**

Melt above 3.5 GPa has calcic-dolomite to calcitic composition and is low in SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O contents. The solidus melt composition is strongly influenced the carbonate phase stable at solidus. Melt of calcite saturated solidus is magnesian calcitic composition. Ca-rich dolomitic melt appears at dolomite saturated solidus. Above 3.5 GPa, melt becomes in more calcitic composition with increasing temperature. At solidus of 15 GPa, melt coexists with aragonite and/or magnesite. At 15 GPa, dolomitic melt

is produced at 1300°C. At 1500°C, melt is calcitic composition.

## **DISCUSSIONS**

#### **COMPARISON WITH EXPERIMENTAL STUDIES FOR CARBONATED PERIDOTITES**

Over the past few decades, a considerable number of studies have been conducted on high-pressure experiments in the system peridotite–CO<sub>2</sub>. Carbonate phase is dolomite or magnesite at pressures above an invariant point (Fo–En–Di–Dol–Melt, ~2.7 GPa) in the lherzolite–CO<sub>2</sub> system. The experimental study of anhydrous peridotite–CO<sub>2</sub> system (Dalton and Presnall 1998) showed that the carbonate-saturated solidus has a positive Clapeyron slope, and is 1430°C at 7 GPa. Extrapolated their peridotite–CO<sub>2</sub> solidus to 15GPa is higher in temperature than that of the present study. Melt composition in the lherzolite–CO<sub>2</sub> system is dolomitic or more magnesite-rich, and there is no condition to yield calcitic melt.

Partial melting of carbonated wehrlite at pressures below the invariant point may produce calcitic melt. For example, Dalton and Wood (1993) showed that Ca-carbonatitic melt is present in wehrlite. On the other hand, in the eclogite–CO<sub>2</sub> system, calcitic melt occurs at solidus of ~3.5 GPa. Moreover, at temperatures higher ~100°C than solidus in very wide pressures of 4.5–15 GPa, calcitic melt coexists with eclogite.

#### **GENESIS OF CARBONATITIC MELT IN SUBDUCTION ZONES**

Shirasaka and Takahashi (in preparation) showed that, in the subduction zone with relatively cold oceanic lithosphere with carbonated sediments, carbonate is stable at least up to 8 GPa. Based on the present study, behavior of carbonate in deeper subducted slabs can be discussed. Peacock et al. (1994) calculated geotherms on the surface of slab. The calculated geotherm for 50 Ma old slab crosses the carbonated eclogite solidus in the present study at ~15 GPa. There is a possibility that carbonated eclogite produces carbonatitic melt under various depth conditions in the upper mantle, because the solidus has a small Clapeyron slope and the cross over could take place over a wide pressure range. The melt composition formed along the solidus is dolomitic to calcitic, and then a Ca-rich carbonatitic melt would metasomatize mantle peridotite.

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