Experiments on CaCO$_3$-MgCO$_3$ solid solutions at high pressure and temperature

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ABSTRACT

Multi-anvil experiments have been performed in the system CaCO$_3$-MgCO$_3$ at pressures of 5.0–7.0 GPa and temperatures of 800–1600 °C. The reaction dolomite = aragonite + magnesite has been reversed and located near 750 °C at 5.0 GPa, 900 °C at 6.0 GPa, and 1000 °C at 7.0 GPa. Between 5 and 6 GPa, the reaction boundary is strongly curved and its dP/dT slope increases from 2 to 12 MPa/°C, expanding the stability field of dolomite. This increase is attributed to increasing Ca-Mg disorder in the dolomite. In addition to the reaction boundary, an isobaric section of CaCO$_3$-MgCO$_3$ has been determined at 6.0 GPa. There is a two-phase field of aragonite + dolomite on the Ca-rich side, which closes before minimum melting temperatures of 1350 °C are reached. The two-phase field on the Mg-rich side, where dolomite + magnesite coexist, intersects with the solidus. Inferred minimum melts are close to dolomite composition suggesting congruent melting of dolomite at 6 GPa. The melt compositions and temperatures in the pure carbonate system are surprisingly similar to solidus phase relations in the CMAS-CO$_2$ system, implying that minimum melting conditions in carbonated peridotite at high pressures are dominated and controlled by the carbonate component.

Keywords: experimental petrology, high-pressure studies, phase equilibria, metamorphic petrology

INTRODUCTION

Previous experimental studies demonstrate that magnesite and dolomite should be stable at mantle conditions, and may carry carbon in subducting lithospheric plates into the deep upper mantle (Biemann et al. 1993; Blundy et al. 1991; Dalton and Wood 1995; Eggler et al. 1976; Gillet 1993; Katsura et al. 1991; Kraft et al. 1991; Kushiro et al. 1975; Zhu and Ogasawara 2002). Occurrences of magnesite in mantle-derived kimberlites, high-pressure metamorphic ultramafics, and eclogites support these experimental results (Lappin and Smith 1978; Ogasawara et al. 2000; Ogasawara et al. 1998; Okay et al. 1993; Shatsky and Sobolev 1995; Zhang et al. 1997).

The reaction dolomite = magnesite + aragonite, delimiting the possible coexistence of carbonate minerals at high pressures, has been determined by many authors with quite diverging interpretations of the reaction boundary (Fig. 1a). It is the scope of this experimental study to reverse this reaction and investigate the extent of compositional gaps between orthorhombic aragonite, trigonal dolomite, and trigonal magnesite in the CaCO$_3$-MgCO$_3$ system at high pressures and temperatures under subsolidus and supersolidus conditions.

EXPERIMENTAL AND ANALYTICAL PROCEDURE

The starting materials consist of mixtures of pure synthetic calcite, natural virtually pure dolomite from Adamello (Italy, Gieré 1990), and pure natural magnesite from Oberdorf (Austria, Philipp 1998). The starting materials were ground, dried at 220 °C for ≥16 h, and subsequently stored at 110 °C.

Part of the experiments (Table 1) were run at ETH Zurich in a Walker-type multi-anvil module (Walker et al. 1990) using welded 1.6 mm O.D. Pt capsules. The capsule, surrounded by a BN insulating sleeve, was placed in a stepped graphite furnace with MgO end-spacers, which in turn was contained within a castable ceramic octahedron of 19 mm edge length. Temperature was measured with a lateral Pt-Pt$_{90}$Rh$_{10}$ thermocouple placed in contact with the capsule(s). Details of pressure calibration are given by Ulmer and Sweeney (2002). About 1/3 of the 60 experiments were run at University of Alberta (UA) in a USSA-2000 split-sphere multi-anvil apparatus. These experiments were run in 1.5 mm O.D. Pt capsules dried at 120 °C for ≥16 h before welding. Assemblies consisted of a prefabricated MgO + 5% Cr$_2$O$_3$ octahedron of 18 mm edge length, containing a stepped graphite furnace surrounded by a ZrO$_2$ insulating sleeve, and inner MgO spacers. Pyrophylrite gaskets were used; details of the experimental setup and calibration are given by Luth (2001). In both setups, no pressure correction was applied to the emf of the thermocouple, and quench rates were 500–700 °C/s. Pressure is accurate to ±0.3 GPa, and temperature precision is ~15–20 °C.

Capsules were embedded in epoxy and ground to expose longitudinal cross sections. Phase assemblages in the run products were identified by Micro-Raman spectroscopy, and analyzed by electron microprobe for chemical composition. Raman spectra were acquired at ETHZ using a Dilor Labram 2 Raman microprobe using the 632 nm line of a He-Ne-laser. All 4 different carbonate minerals, calcite, dolomite, aragonite, and magnesite could be distinguished by Raman spectroscopy. All samples were analyzed by electron microprobe using 15 kV acceleration voltage either on a Cameca SX50 at ETH or a JEOL 8900R at UA. Textural relationships between the phases were studied using backscattered electron (BSE) imaging. Volatilization of carbonates under the electron beam can be a serious problem. Thus, the probe current was reduced to 6 nA, and the spot size broadened to 10 µm where possible. The counting time was 20 s on peak and 10 s on background. Carbonate standards were used, and carbon (as carbonate) was calculated by stoichiometry. With due care and adequate standards, it was possible to obtain acceptable analytical totals (including stoichiometric CO$_2$) of 100 ± 5 wt%. Only data that met this standard have been used in this study.

RESULTS

Dolomite = Aragonite + Magnesite

At pressures above ~5 GPa, almost pure aragonite and magnesite react to form dolomite with increasing temperature. The experiments reverse and bracket the reaction at 750–850 °C between 5.0–5.3 GPa, at 900 °C between 5.0–6.0 GPa, and...