New experimental data on phase relations for the system Na$_2$CO$_3$-CaCO$_3$ at 6 GPa and 900–1400 °C

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ABSTRACT

Phase relations in the system Na$_2$CO$_3$-CaCO$_3$ have been studied in the compositional range, $X$(Na$_2$CO$_3$), from 100 to 10 mol%, at 6.0 GPa and 900–1400 °C. Below 1100 °C, the system has three intermediate compounds: Na$_2$Ca(CO$_3$)$_3$, Na$_2$Ca$_2$(CO$_3$)$_4$, and Na$_2$Ca$_4$(CO$_3$)$_6$. The Na$_2$Ca(CO$_3$)$_3$ and Na$_2$Ca$_2$(CO$_3$)$_4$ compounds melt congruently slightly above 1200 and 1300 °C, respectively. The eutectics were established at 70 and 52 mol% near 1200 °C and at 21 mol% near 1300 °C. The Na$_2$Ca$_2$(CO$_3$)$_4$ compound decomposes to the Na$_2$Ca$_4$(CO$_3$)$_6$ + aragonite assembly at 1100 °C. Maximum solid solution of CaCO$_3$ in Na$_2$CO$_3$ is 6–8 mol% at 1100–1300 °C. Melting of Na$_2$CO$_3$ occurs between 1350 and 1400 °C. Na solubility in aragonite does not exceed the detection limit (<0.5 mol%). Aragonite remains a liquidus phase at 1300 and 1400 °C.

Keywords: Na-Ca carbonate, high-pressure, aragonite, natrite, shortite, nyerereite, natrocarbonatite, Earth’s mantle

INTRODUCTION

It has been shown that the presence of CO$_2$ substantially lowers the melting temperature of mantle rocks (Wyllie and Huang 1975; Dalton and Pressnall 1998; Dasgupta and Hirschmann 2006; Litasov and Ohtani 2009, 2010; Dasgupta et al. 2011) and plays an essential role in mantle metasomatism (Green and Wallace 1988; Haggerty 1989; Yaxley et al. 1991; Walter et al. 2008) and diamond formation (Akaishi et al. 1990; Kanda et al. 1990; Pal’yanov et al. 1999, 2002; Shatskii et al. 2002; Palyanov et al. 2007). According to studies of the melt inclusions in diamonds (Navon 1991; Schrauder and Navon 1994; Klein-BenDavid et al. 2009; Weiss et al. 2009; Logvinova et al. 2011; Zedgenizov et al. 2011) and melting experiments (Wallace and Green 1988; Brey et al. 2011; Grassi and Schmidt 2011; Litasov et al. 2013), the specific feature of these melts is high alkali contents. It is, therefore, essential to know the phase relations in simple alkali-alkaline earth carbonate systems under mantle conditions.

As part of an investigation of those systems, Na$_2$CO$_3$-CaCO$_3$ is important, given the Na and Ca abundances in natrocarbonatite lavas (Dawson 1962; Hay 1983; Zaitsev and Keller 2006) and in the groundmass of fresh kimberlites (Watkinson and Chao 1973; Cooper and Gittins 1974; Kamensky et al. 2004, 2007). The given system is also important in view of the Na and Ca abundances in carbonate melts entrapped by olivine and Cr-spinel from kimberlites (Kamensky et al. 2009, 2012), sheared peridotite xenoliths (190–220 km depth) (Korsakov et al. 2009; Golovin et al. 2012), and some “fibrous” diamonds (Klein-BenDavid et al. 2004, 2007; Kaminsky et al. 2009).

Although phase relations in alkali-earth carbonate systems were studied extensively from upper down to lower mantle conditions, e.g., (Ono et al. 2005, 2007; Buob et al. 2006; Merlini et al. 2012a, 2012b; Spivak et al. 2012), the studies of alkali-bearing carbonate systems and in particular the system Na$_2$CO$_3$-CaCO$_3$ (Fig. 1), were limited by 0.1 GPa (Eitel and Skalidis 1929; Cooper et al. 1975). In this study we extended an available pressure range for this system and studied phase relations at 6 GPa and 900–1400 °C.

EXPERIMENTAL METHODS

In this study we conducted multi-anvil experiments to constrain phase relations in the system Na$_2$CO$_3$-CaCO$_3$ using DIA- and wedge-type presses at Tohoku University (Sendai, Japan) (Shatskiy et al. 2011b) and BARS apparatus at V.S. Sobolev’s IGEM SB RAS (Novosibirsk, Russia) (Palyanov et al. 2010; Shatskiy et al. 2011a). All experiments were performed using graphite sample capsules, which are conventionally employed to seal alkali-carbonate melts in long duration experiments (up to 20–40 h) under 6.0 ± 0.5 GPa pressures and temperatures up to 1650 °C (Kanda et al. 1990; Shatskii et al. 2002). The experimental methods employed in the present study were the same as in our recent manuscript (Shatskiy et al. 2013). Here, we will only focus on peculiarities of measurement of chemical composition of carbonate phases in the Na$_2$CO$_3$-CaCO$_3$ system using energy-dispersive scanning electron microprobe.

Samples were studied using a JSM 5410 scanning electron microscope equipped with Oxford Instruments Link ISIS Series 300 energy-dispersive X-ray spectrometer (EDS) at Tohoku University (Sendai, Japan). The EDS spectra were collected by rastering the electron beam over a surface area available for the analysis with linear dimensions from 10 to 300 μm at 15 kV accelerating voltage and 10 nA beam current. The EDS was calibrated at the same conditions by rastering the electron beam over a sample cross-section area, up to 0.5–0.8 mm in linear dimensions. For that purpose, we employed post-experimental samples with known compositions and a homogeneous texture (i.e., samples that underwent complete melting and samples synthesized well below eutectic temperatures). We also...