Ab initio study of the structure and stability of CaMg(CO$_3$)$_2$ at high pressure

Natalia V. Solomatova$^{1,*}$ and Paul D. Asimow$^1$

$^1$Division of Geological and Planetary Sciences, Caltech, Pasadena, California 91125, U.S.A.

ABSTRACT

Dolomite is one of the major mineral forms in which carbon is subducted into the Earth’s mantle. End-member CaMg(CO$_3$)$_2$ dolomite typically breaks down upon compression into two carbonates at 5–6 GPa in the temperature range of 800–1200 K (Shirasaka et al. 2002). However, high-pressure X-ray diffraction experiments have shown that dense high-pressure polymorphs of dolomite may be favored over single-cation carbonates (Santillán et al. 2003; Mao et al. 2011; Merlini et al. 2012). Here we compare calculated dolomite structures to experimentally observed phases. Using density functional theory interfaced with a genetic algorithm that predicts crystal structures (USPEX), a monoclinic phase with space group C2/c was found to have lower energy at pressures above 15 GPa than all previously reported dolomite structures. It is possible that this phase is not observed experimentally due to a large activation energy of transition from dolomite I, resulting in the observed second-order phase transition to a metastable dolomite II. Due to the complex energy landscape for candidate high-pressure dolomite structures, several structurally unique metastable polymorphs exist. We calculate the equation of state of a set of lowest-energy dolomite polymorphs with space groups P$_T$, P2/c, and C2/c up to 80 GPa. Our results demonstrate a need for calculations and experiments on Fe-Mn bearing high-pressure carbonate phases to extend our understanding of Earth’s deep carbon cycle and test whether high-pressure polymorphs of double-cation carbonates represent the main reservoir for carbon storage within downwelling regions of Earth’s mantle.

Keywords: Dolomite, ab initio, global carbon cycle, lower mantle, high pressure

INTRODUCTION

Carbon is exchanged between the surface and Earth’s interior through ingassing by subduction and through both passive and volcanic outgassing (Kelemen and Manning 2015). Carbon is subducted into the mantle primarily in the form of carbonate (CO$_3^2$)-bearing minerals as metasomatically calcium-enriched basaltic rock (rodingite), calcified serpentinites (ophiicarbonates), and sedimentary carbonaceous ooze (Brenker et al. 2006). Evidence of carbon-bearing phases in the Earth’s mantle includes: the release of CO$_2$ in volcanic eruptions, dissolved CO$_2$ in magmatic glasses and glass inclusions (Mörner and Etiope 2002), diamonds and carbonate minerals in mantle xenoliths (Eggler 1987; Sobolev and Shatsky 1990), and the existence of carbonatite and kimberlite magmas (Wyllie et al. 1990). Carbon has low solubility in mantle silicates (Shcheka et al. 2006), such that significant carbon storage or transport in the mantle requires formation of carbon-rich phases. Decomposition of carbonates can produce free CO$_2$, which lowers the viscosity and melting temperature of the surrounding mantle (Eggler 1976) and enables rapid recycling of carbon through subduction-related volcanism rather than deep subduction and long-term storage. Identifying and characterizing the stability of carbonate phases is therefore a necessary step toward understanding the transport and storage of carbon through the Earth’s deep carbon cycle (Hazan et al. 2013). The identification of a new, more stable carbonate phase that is able to host carbon under conditions where known carbonates may decompose has the potential to substantially change estimates of the geochemical fluxes of carbon.

It has been suggested that magnesite is the dominant carbonate phase in relatively oxidized regions of the mantle (Brenker et al. 2006; Ishikii et al. 2004; Skorodumova et al. 2005), reasoning by analogy to silicates, examined the stability of magnesite in selected pyroxene and perovskite structures, finding that magnesite could transform into a C2/c pyroxene structure with fourfold coordination of carbon by oxygen at 113 GPa. Using USPEX, however, Oganov et al. (2008) searched a vastly larger space of possible structures and found that magnesite undergoes a phase transition at 84 GPa to a monoclinic phase (“phase II”) with space group C2/m, containing rings of (C:O)$_2^+$, and subsequently at 138 GPa transitions to an orthorhombic phase (“phase III”) with space group P2$_1$, containing chains of CO$_3^2$ tetrahedra. Their calculations show that the C2/c pyroxene structure has a higher energy than either phase II or phase III at all relevant pressures. Calcite, on the other hand, transitions to aragonite at 2 GPa, which transitions to the post-aragonite phase (space group Pmmn) at 42 GPa, persisting up to core-mantle boundary pressures (Ono et al. 2005; Oganov et al. 2006).

End-member CaMg(CO$_3$)$_2$, dolomite typically breaks down into two carbonates at about 5–6 GPa in the temperature range of 800–1200 K (Shirasaka et al. 2002). However, X-ray diffraction experiments have proposed that dense high-pressure phases of dolomite may be more stable or comparable in stability to single-cation carbonates above 35 GPa. High-pressure dolomite may be resistant to decomposition into single-cation carbonates prior to the transformation of trigonal magnesite to monoclinic phase II.