Effects of hydrostaticity and Mn-substitution on dolomite stability at high pressure

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ABSTRACT

Studying the structural evolution of the dolomite group at high pressure is crucial for constraining the deep carbon cycle and mantle dynamics. Here we collected high-pressure laser Raman spectra of natural Mg-dolomite CaMg(CO₃)₂ and Mn-dolomite kutnohorite Ca₁₁Mn₀₉(CO₃)₈ samples up to 56 GPa at room temperature in a diamond-anvil cell (DAC) using helium and neon as a pressure-transmitting medium (PTM), respectively. Using helium or neon can ensure samples stay under relatively hydrostatic conditions over the investigated pressure range, resembling the hydrostatic conditions of the deep mantle. Phase transitions in CaMg(CO₃)₂ were observed at 36.1(25) GPa in helium and 35.2(10) GPa in neon PTM from dolomite-II to -III, respectively. Moreover, the onset pressure of Mn-dolomite Ca₆₃Mn₀₉(CO₃)₂-III occurs at 23−25 GPa, about 10 GPa lower than that of Mg-dolomite-III, suggesting that cation substitution could significantly change the onset pressure of the phase transitions in the dolomite group. These results provide new insights into deep carbon carriers within the Earth’s mantle.

Keywords: Deep carbon cycle, Raman spectroscopy, high pressure, dolomite, phase transition

INTRODUCTION

Carbon geochemistry of mantle-derived material suggests that the flux of ca. 2.4−4.8 × 10²³ g carbon enters the Earth’s interior through subduction slabs each year (Dasgupta and Hirschmann 2010; Plank and Manning 2019). A part of carbon has been stored and transported into the deep mantle as accessory minerals (e.g., carbonates, diamond, and carbides) due to their relatively low solubility in silicates (Shcheka et al. 2006). Geochemical and petrologic evidence further indicates that carbon is mainly subducted as carbonate minerals under cold slab conditions, involving the crustal materials cycle and crust-mantle interaction (Sanchez-Valle et al. 2011). The presence of carbonate minerals can dramatically affect the physical and chemical properties of the mantle, such as phase stability, melting, viscosity, electrical conductivity, thermal conductivity, and elasticity (Fu et al. 2017; Gaillard et al. 2008; Yao et al. 2018; Zhao et al. 2019; Gui et al. 2021). Thus, studying the structural evolution of carbonate minerals at high pressure is crucial to constrain the deep carbon cycle as well as mantle dynamics (Farsang et al. 2021a; Fu et al. 2017; Isshiki et al. 2004; Liu et al. 2015; Mao et al. 2011; Merlini et al. 2012, 2017; Vennari and Wayne 1989; Rividi et al. 2010). Furthermore, dolomite inclusions in super-deep diamonds evidence their existence in the deep mantle (Brenker et al. 2007; Logvinova et al. 2019).

Thus far, a good number of experiments and theoretical calculations have concentrated on the structure and phase transition of Mg,Fe-dolomite Ca(Mg,Fe,Mn)(CO₃)₂ under high pressures and/or high temperatures (Binck et al. 2020b; Efthimiopoulos et al. 2018; Mao et al. 2011; Merlini et al. 2012, 2017; Vennari and Williams 2018; Zhao et al. 2020). A series of high-pressure phase transitions were reported from dolomite-I (abbreviated as Dol-I) to Dol-II at ~8−11 GPa, then to Dol-II at ~14−19 GPa, and subsequently to Dol-III at ~35−43 GPa with increasing pressure at room temperature (Binck et al. 2020b; Efthimiopoulos et al. 2017; Zhao et al. 2020). The Dol-IV and -V phases are only detected at simultaneous high-temperature and pressure (P-T) conditions (Binck et al. 2020b; Merlini et al. 2017). In particular, those high-pressure phases of (Mg,Fe)-dolomite are considered to be important carbon carriers in the deep mantle (Mao et al. 2011; Merlini et al. 2012). Recently, it has been found that improved hydrostaticity can greatly influence the structural evolution of MgCO₃ at high pressure up to 80 GPa, where the pressure-transmitting medium (PTM) was helium (Zhao et al. 2020).