Equation of state and structural evolution of manganese dolomite (kutnohorite) under high pressures

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ABSTRACT

Understanding the structural evolution of carbonate minerals with increasing pressure is essential to decoding the role of Earth’s mantle in the global carbon cycle and long-term climate change. Here, we carried out synchrotron single-crystal X-ray diffraction measurements on a natural sample of manganese dolomite [kutnohorite, CaMn_{10}CO_{32}] in a diamond-anvil cell up to 51.2 GPa at room temperature with neon as the pressure-transmitting medium. The manganese dolomite sample remains stable in the rhombohedral structure from 1 bar to ~13.3 GPa. The equation of state of CaMn_{10}CO_{32} was determined: \( V_0 = 334.06 \pm 0.29 \AA^3 \), \( K_0 = 99.9 \pm 4.7 \) GPa, and \( K_0' = 4.3 \pm 0.9 \); when \( K_0' \) is fixed at 4.0, \( V_0 = 334.04 \pm 0.24 \AA^3 \), and \( K_0 = 101.4 \pm 1.5 \) GPa. Upon further compression at room temperature, the split and disappearance of diffraction spots were observed. That is, the rhombohedral structure of manganese dolomite becomes highly distorted to lose its long-range order at 13.3–51.2 GPa at room temperature. Moreover, our single-crystal X-ray diffraction results reveal the mechanisms of the reported lattice and internal Raman mode splits of the same manganese dolomite sample approximately at 13 and 24 GPa, respectively. These results suggest manganese-bearing carbonates may play a distinct role in the deep carbon cycle.

Keywords: High pressure, manganese dolomite, X-ray diffraction, deep carbon cycle; Physics and Chemistry of Earth’s Deep Mantle and Core

INTRODUCTION

Carbonate minerals are the important forms of carbon carriers from shallow subduction zones to the deep mantle (Plank and Manning 2019). Those carbonate minerals could account for the major constituent of the global carbon fluxes, with about 100 megatons of deep carbon entering the Earth’s interior via subducting slabs each year (Dasgupta and Hirschmann 2010; Farsang et al. 2021). Little to no carbon can be incorporated into the crystal lattice of mantle silicate minerals, leading to the deep carbon being mostly stored and transported as carbonates, together with graphite, diamond, and carbides (Shcheka et al. 2006). The physical, chemical, and transport properties of the deep mantle could be significantly influenced by the presence of carbonates involving the crust-mantle interactions (Lavina et al. 2009; Lin et al. 2012; Dorfman et al. 2018). In particular, it remains enigmatic how those carbonate minerals evolve in subducted slabs. This holds the key to better decoding the global carbon cycle, long-term climate dynamics, as well as mantle dynamics (Kelemen et al. 2011; Sanchez-Valle et al. 2011; Malusà et al. 2018).

Thus far, the structural evolution and chemical reactions of carbonate minerals have been investigated by a battery of probes under high-pressure and high-temperature conditions (e.g., Boulard et al. 2011; Zhao et al. 2020). Calcium carbonate (e.g., calcite and aragonite) could react with pyroxene to form the dolomite group minerals [CaM(CO_3)_2] with M = Mg, Fe, Mn, etc.] under relatively shallow depths of 100–150 km (Kushiro 1975). Dolomite minerals exhibit a rhombohedral structure (space group \( R \bar{3} \)) in which MO₃ units alternate along the c-axis. The dolomite group minerals undergo a series of high-pressure phase transformations including dolomite-II, -III, -IIIC, -IV, and -V (e.g., Santillan et al. 2003; Mao et al. 2011; Merlini et al. 2012, 2017; Wang et al. 2022). Dolomite minerals and their high-pressure polymorphs likely occupy up to half of the Earth’s accessible carbonate reservoirs (Bincik et al. 2020). Among all the dolomite group minerals investigated under high pressures, the high-pressure behavior of manganese dolomite [CaMn(CO_3)_2] is the least constrained in the literature. Palaich et al. (2015) reported the bulk modulus and phase stability of a natural manganese dolomite sample [CaMn_{10}CO_{32}] (hereinafter referred to as “Ca76”) in the Ne-NaCl pressure-transmitting medium. Notably, varying pressure-transmitting media (e.g., NaCl, Ar, Ne, and He) can have distinct effects on the structural transition paths and electronic states with increasing pressure (Efthimiopoulos et al. 2017, 2019; Merlini et al. 2017; Bincik et al. 2020; Zhao et al. 2021). The use of NaCl generally induces a very large deviatoric stress of >5–10 GPa in a diamond-anvil cell (DAC), whereas Ne can keep the sample under relatively hydrostatic conditions that more closely resemble the deep mantle (Klotz et al. 2009).