A novel carbon bonding environment in deep mantle high-pressure dolomite

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ABSTRACT

The main source of carbon entering the deep Earth is through subduction of carbonates, including CaMg(CO3)2-dolomite. We examine the high-pressure structure and stability of dolomite to understand the means through which carbon can be sequestered as it enters the deep Earth carbon cycle. Dolomite is investigated to 86 GPa using Raman spectroscopy at room temperature: this includes spectroscopic characterization of dolomite-III, a phase stable at deep mantle pressures and temperatures. Between 63–86 GPa, within the dolomite-III structure, we observe spectroscopic evidence for the evolution of a subpopulation of carbonate ions characterized by weaker C-O bonds, with anomalous pressure shifts: this abnormal bonding change is explained by the onset of a 3+1 coordination of the carbon in some of the carbonate ions in the dolomite-III structure, confirming an earlier prediction of Merlini et al. (2012). The wide suite of carbonate ions (both normal threefold and 3+1 coordinate) within this phase at the highest pressures should give rise to a large variety of cation sites; as such, dolomite-III could represent a major host for incompatible elements in the deep mantle, implying that incompatible element distribution may be closely linked to carbon cycling within the deep Earth.

Keywords: Dolomite, high pressure, Raman spectroscopy, carbon, distorted cation sites, deep Earth

INTRODUCTION

Carbonate minerals have long been accepted as the primary carriers of carbon into the deep Earth. Carbonates are present in and on oceanic plates, and when slabs are subducted, oxidized carbon is brought into the deep Earth (e.g., Alt and Teagle 1999). Carbon can have a strong influence on the chemical and physical properties of the mantle (e.g., Shcheka et al. 2006; Hirshmann and Dasgupta 2009), so its manner of retention at depth is critical for clarifying its role in deep Earth geophysical and petrologic processes. In higher temperature slabs, carbonates likely decompose and release CO2, which facilitates melting in the Earth’s deep upper mantle (e.g., Rosenthal et al. 2015) and can explain carbon dioxide’s ubiquity in back arc volcanoes. However, in high pressure and temperature experiments that mimic cold slab geotherms, carbonate and peridote phase equilibria indicate that carbonate minerals could persist at least down to the transition zone, and possibly deeper (e.g., Litasov et al. 2013). Moreover, primordial carbon could also be retained within Earth’s deep mantle, in addition to recycled carbon from subduction (e.g., Hirshmann and Dasgupta 2009).

Dolomite [CaMg(CO3)2] is a common carbonate on the surface of the Earth, is found in sedimentary environments and vein deposits, and crystallizes with rhombohedral symmetry in the space group R3. There have been several previous high-pressure experiments on dolomite at room temperature (300 K). Using spectroscopy and X-ray diffraction (XRD), two well-defined transitions of dolomite to dolomite-II and dolomite-III have been identified at 15–20 and 36–38 GPa, respectively (Santillán et al. 2003; Santillán and Williams 2004; Mao et al. 2011; Merlini et al. 2012; Efthimiopoulos et al. 2017). Merlini et al. (2012), using single-crystal X-ray diffraction reported a triclinic, calcite-II-like structure for dolomite-II above 17 GPa and a larger triclinic, calcite-III unit cell for dolomite-III above 35 GPa. Most importantly, Merlini et al. (2012) heated their samples to 2200 K at up to 72 GPa, and Mao et al. (2011) to ~1500 K to 83 GPa, and their results demonstrate that dolomite-III is stable at these extreme conditions. Hence, dolomite-III represents a likely carbon repository at the conditions of Earth’s lower mantle. The dolomite-III structure reported by Merlini et al. (2012) is structurally novel, as extrapolated trends of their refinements of interatomic distances to 60 GPa indicate that some of the carbonate ions could adopt a 3+1 coordination with the O atoms at pressures of 60–80 GPa. Experimental and theoretical evidence of fourfold coordinate carbon in oxides at high pressures has been previously described (Ishikii et al. 2004; Oganov et al. 2006; Sun et al. 2009; Boulard et al. 2011, 2015; Cerantola et al. 2017; Merlini et al. 2017).

Here, we utilize vibrational spectroscopy to probe the local bonding environment of the carbonate ion (and Ca/Mg cations) within dolomite to 86 GPa: a substantially higher pressure range than previous vibrational studies and nearly 50 GPa higher than where a previous study (Efthimiopoulos et al. 2017) was unable to resolve any Raman bands from dolomite. Our goals are to evaluate whether dolomite-III undergoes the predicted continuous transition to partial 3+1 coordination of carbon and to probe the character of the bonding environment of the carbon ion within dolomite-III at these extreme conditions.

EXPERIMENTAL METHODS

Dolomite, Ca10Mg5Fe8O(CO3)24, from New Almaden, California (UCSC mineral collection no. 7206) was used for this experiment: this composition was confirmed using a JEOL JXA-8230 electron microprobe. The sample identity was confirmed using Raman spectroscopy and single-crystal XRD, and our results are in excellent agreement with previous studies of nearly end-member dolomite (e.g., Nicola et al. 1976). The samples were single crystals with approximate dimensions of 20 × 20 × 10 μm. High pressures were generated with a symmetric-type Princeton type diamond-anvil cell equipped with type Ia diamonds with 250 μm culets. Neon