The Dolomite-Fe Interaction at High Pressure and High Temperature: Implications for Carbonate Subduction in the Transition Zone

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Abstract: Carbonates are the most abundant carbon-bearing minerals in the Earth's crust and can be dragged down into the deep Earth by subduction of oceanic lithosphere. Seismological, geological and geochemical studies have extended the subduction processes to the transition zone and even to the core-mantle boundary (Dorfman et al., 2018), during which carbonates undergo a series of complex changes (e.g. melting, decomposition, phase transition, interactions with the surrounding mantle) (Boulard et al., 2011; Drewitt et al., 2019). Thus their behaviors during sinking processes could provide unique insights into the mineralogy, geochemistry and petrology of the Earth's interior. Rohrbach and Schmidt (2011) proposed that with the increase of depth (>~250 km), carbonate reduction occurs to form diamond driven by decrease of oxygen fugacity. The $MgCO_3$-Fe system has been studied at 6.5–7.5 GPa 1500–1700 K, which presents a redox mechanism of diamond formation (Palyanov et al., 2013). The interaction between dolomite $CaMg(CO_3)_2$ and iron shows that at pressure-temperature conditions reaching to the lower mantle, the $MgCO_3$ -component decomposed whereas the $CaCO_3$ remained stable (Dorfman et al., 2018). So far limited experimental data on carbonate-iron couple is available that remains elusive in unlocking the carbon reduction pathways. Here we use laser-heated diamond anvil cells (DACs) to generate high pressure-temperature conditions to model the fate of carbon during the deep subduction processes.

The starting materials were mixtures of high-purified dolomite and iron powder. Two runs of experiments were conducted with dolomite/Fe molar ratio of 1:1. The target pressure of run-1 is 20.2 GPa and of run-2 is 15.7 GPa. Gem-quality diamonds with cult of 300 μm and 400 μm were mounted in symmetry-type DACs, respectively. The hole of 150 μm and 200 μm in-diameter were drilled in two rhenium gaskets with a pre-indented thickness of ~38 μm and ~40 μm, respectively. The sample mixture was compressed into thin slices of ~25 μm in-thickness and then loaded into the chamber in a sandwich configuration by two pieces of LiF slice with 7–8 μm in thickness, which act as thermal insulation material, pressure-transmitting medium and pressure calibrant. In prior to the experiments, the sample was first pressurized to the target pressure and then was heated by double-side laser heating for ~1 h until the reaction completion. The temperature was ~1500 K. The quenched reaction products were identified by X-ray diffraction (XRD) and Raman spectroscopy. In situ synchrotron radiation XRD experiments were performed at 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF). A monochromatic X-ray beam with a wavelength of 0.6199 Å was used with the beam size of 30×8 μm^2. The XRD patterns were recorded using a CCD detector with exposure times of 500s or 700s per pattern. After the pressure was released, we removed the sample out of the DACs and placed it on a slide, then performed ex-situ Raman measurements for the recovered sample. The Raman spectroscopy experiments were performed on Reinshaw 1000 Laser Raman spectrometer in Peking University, China. A 514.5 nm Ar^+ ion laser was employed as the excitation light source. The laser light was focused using a Leica microscope with a 50× microscope objective to a beam size of ~1.5 μm in-diameter. The collection time for each pattern was 180s.

Our results show that dolomite can be reduced to diamond by metallic mantle under pressure-temperature conditions corresponding to the transition zone. The element carbon extracted from dolomite was dominantly in the form of graphite yet the weak peak at 1331 cm^{-1} in Raman spectra strongly document the formation of diamond. The conversion from graphite to diamond is influenced by the molar ratio of the initial materials. In addition, an accompanying product (Mg, Fe)O was detected which has long been considered as an indicator of the deep mantle. The present study demonstrates a formation mechanism of ultradeep diamond via redox reaction between dolomite and iron.

Key words: deep Earth carbon cycle, carbonates, slab-mantle interaction, dolomite, high pressure

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