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# Carbonate stability in the reduced lower mantle

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## ABSTRACT

Carbonate minerals are important hosts of carbon in the crust and mantle with a key role in the transport and storage of carbon in Earth's deep interior over the history of the planet. Whether subducted carbonates efficiently melt and break down due to interactions with reduced phases or are preserved to great depths and ultimately reach the core-mantle boundary remains controversial. In this study, experiments in the laser-heated diamond anvil cell (LHDAC) on layered samples of dolomite $(Mg,Ca)CO_3$ and iron at pressure and temperature conditions reaching those of the deep lower mantle show that carbon-iron redox interactions destabilize the $MgCO_3$ component, producing a mixture of diamond, $Fe_7C_3$, and $(Mg,Fe)O$. However, $CaCO_3$ is preserved, supporting its relative stability in carbonate-rich lithologies under reducing lower mantle conditions. These results constrain the thermodynamic stability of redox-driven breakdown of carbonates and demonstrate progress towards multiphase mantle petrology in the LHDAC at conditions of the lowermost mantle.

## 1. Introduction

Carbonates are the major minerals responsible for transportation of carbon from the Earth's surface to its deep interior. Their behavior at depth is critical to the storage capacity and fluxes of the geologic carbon cycle. Recent estimates of the flux of carbon trapped in carbonate minerals that reach the deep Earth range from 0.0001 to 52 megatons annually (Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015). The uncertainty in this range hinges on poor constraints on the budget of carbon retained by subducting slabs. Transport of carbon to at least transition zone depths is demonstrated by carbonate inclusions in diamonds (e.g. Brenker et al., 2007; Wang et al., 1996), but whether any carbonates remain in the lower mantle is controversial. Most subducted carbon is expected to melt and/or break down and return to Earth's surface via volcanism (Dasgupta and Hirschmann, 2010; Kelemen and Manning, 2015; Thomson et al., 2016). However, relatively oxidizing conditions, low temperatures, and resulting slow kinetics within subducting slabs may result in transportation of carbonates magnesite, siderite, calcite, and their solid solutions to great depths (Martirosyan et al., 2016). Subducted carbonates in slabs that reach the base of the lower mantle will undergo multiple phase transitions and encounter reducing conditions, to be finally buffered by metallic iron at or near the CMB.

Carbon provides key constraints on the chemical evolution of the deep Earth through its role as a proxy for mantle redox conditions, as its speciation is largely governed by oxygen fugacity, or $fO_2$ (Frost and McCammon, 2008). Evidence of deep mantle chemistry (Walter et al., 2011) and redox state (Ryabchikov and Kaminsky, 2013; Smith et al., 2016) in local environments of diamond formation can likely be inferred from diamond inclusions. Diamonds and their inclusions indicate widely varying local $fO_2$ (Brenker et al., 2007; Walter et al., 2011; Ryabchikov and Kaminsky, 2013; Smith et al., 2016; Kaminsky, 2012), though $fO_2$ is expected to generally decrease with mantle depth (Frost and McCammon, 2008; Rohrbach and Schmidt, 2011). Both isotopic evidence (e.g. Harte, 2010; Tappert et al., 2005) and carbonate inclusions in diamonds (e.g. Wang et al., 1996) suggest that diamonds are (at least in part) formed by reduction of subducted carbonate minerals or carbonate melts. Reduction of carbonates to diamond takes place by interactions with mantle silicates (Pal'yanov et al., 2002; Stagno et al., 2011, 2013, 2015) or metal (Arima et al., 2002; Siebert et al., 2005; Rouquette et al., 2008; Pal'yanov et al., 2013).

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These redox reactions contribute to the barrier to carbonate transport to the deep Earth (Rohrbach and Schmidt, 2011; Thomson et al., 2016). The key to determining the amount of oxidized carbon in the deep Earth is the dependence of both the thermodynamics and the kinetics of redox reactions in carbonates on temperature, pressure, and $fO_2$.

Petrologic observations, experiments and computational studies on stability and breakdown kinetics of carbonates have determined that magnesite is the most stable carbonate phase throughout most of the mantle (e.g. Dasgupta and Hirschmann, 2010; Rohrbach and Schmidt, 2011), but calcite and siderite polymorphs have also attracted interest. Relative to aragonite (Spivak et al., 2011) or siderite (Tao et al., 2013), magnesite is more likely to subduct to the deep mantle due to its higher melting temperature (Isshiki et al., 2004; Katsura and Ito, 1990; Martinez et al., 1998; Solopova et al., 2014). Melting experiments on carbonated peridotite (Dasgupta and Hirschmann, 2010; Ghosh et al., 2014; Rohrbach and Schmidt, 2011) and eclogite (Thomson et al., 2016) systems confirm that calcium and iron carbonate components are more likely to enter a melt phase than magnesium carbonate in silicate lithologies. At sub-solidus temperatures, $MgCO_3$ is also favored in carbonate–silicate mixtures by the reaction $CaCO_3 + MgSiO_3 \rightarrow MgCO_3 + CaSiO_3$ at lower-mantle pressures up to 80 GPa (Biellmann et al., 1993; Seto et al., 2008). Due to its broad solid solution with siderite (Lin et al., 2012; Liu et al., 2015), magnesite in the mantle will host iron. An (Mg, Fe)-carbonate in the lowermost mantle may have mixed redox state and coexist with diamond (Boulard et al., 2012). However, both $(Mg,Fe)CO_3$ (Brenker et al., 2007; Kaminsky et al., 2016; Phillips and Harris, 1995; Ryabchikov and Kaminsky, 2013) and $CaCO_3$ (Brenker et al., 2007; Meyer and McCallum, 1986) have been observed in inclusions in diamonds, including ultra-deep diamonds from the transition zone or possibly the lower mantle (Brenker et al., 2007). These inclusions demonstrate that both $(Mg,Fe)CO_3$ and $CaCO_3$ may be preserved by kinetic effects within carbonate-rich sediment in cold subducting slabs, consistent with slow breakdown kinetics observed in experiments at transition zone conditions (Martirosyan et al., 2016). The relative stability of $(Mg,Fe)CO_3$ and $CaCO_3$ may also change at depth due to polymorphism. If $(Mg,Fe)CO_3$ or $CaCO_3$ reaches the base of the lower mantle, density functional theory calculations (Oganov et al., 2008; Pickard and Needs, 2015) and experiments (Boulard et al., 2011; Ono et al., 2007) suggest these carbonates will transform to tetrahedrally-coordinated structures. If the transition in $CaCO_3$ occurs at a shallower depth than the analogous transition in $MgCO_3$, as predicted by Pickard and Needs (2015), $CaCO_3$ would be the denser and more energetically-favored carbonate in the deep lower mantle.

This study examines a Mg–Fe–Ca carbonate system in the petrologic context of a subducted carbonate assemblage in contact with metallic iron. Metallic iron may be present at the percent level throughout the mantle (Frost et al., 2004), and the outer core provides an unlimited reservoir of iron. Subducted carbonates may contact reduced core–mantle mixing regions if they reach depths within ∼10s km from the base of the mantle (Frost and McCammon, 2008; Otsuka and Karato, 2012). Previous studies of carbonates at lower mantle pressures have investigated mineralogical stability of single phases as a function of pressure and temperature alone (Isshiki et al., 2004; Solopova et al., 2014; Boulard et al., 2011; Ono et al., 2005), or used mixtures of carbonates and silicates which complicate textural analysis of run products (Biellmann et al., 1993; Thomson et al., 2014). In contrast, we examine reaction interfaces between multiple carbonates and iron; similar previous studies have been limited to transition zone conditions (Martirosyan et al., 2016; Pal'yanov et al., 2013). We determine the relative stability and metastability of Mg-, Fe-, and Ca-carbonates as host phases for oxidized carbon storage in the lower mantle.

**Table 1**
Pressure, temperature, and heating duration for all experiments. Pressures given were obtained before heating from the equation of state of the iron foil (Mao et al., 1990). Temperature differences between downstream and upstream sides were typically observed to be ∼100 K and varied by ∼100 K over the heating duration.

| Pressure before heating (GPa) | Temperature (K) | Duration (min) |
|---|---|---|
| 51 | 1800–2050 | 15 |
| 66 | 1900–2200 | 10 |
| 77 | 1900–2200 | 20 |
| 113 | 2400–2500 | 10 |

## 2. Methods

To bring experimental petrology of carbonates to the Mbar pressures and 1000s K temperatures of the core–mantle boundary, experiments must be miniaturized: sample geometry must be controlled within the ∼50 × 50 × 10-micron chamber of the laser-heated diamond anvil cell, and analysis must be performed with ∼100-nm-scale spatial resolution of typical grain sizes of run products. Dolomite, a major constituent of subducted marble, provides a unique advantage as a starting material as it has a mixed Mg–Fe–Ca carbonate composition homogeneous to <nm scale. Natural dolomite crystals with composition determined to be $(Mg_{0.38}Ca_{0.59}Fe_{0.03})CO_3$ by X-ray fluorescence spectroscopy and structure confirmed by X-ray diffraction were used as starting materials. Single dolomite crystals were polished to ∼10-micron thickness and dried in a 120 °C oven overnight before loading. 3-micron thick 99.85% iron foil was machined into discs with a ps-pulsed 532-nm laser or cut with a razor blade. Iron foils were loaded sandwiched between dolomite crystals in symmetric diamond anvil cells. No other pressure standard or medium was loaded in order to prevent reactions with other components and contamination of the chemical system. Sample sandwiches were loaded within chambers cut in Re gaskets in diamond anvil cells. Diamond anvils with flat culets of 200 micron diameter or beveled culets of 150 micron diameter were chosen to generate pressures corresponding to the lower mantle.

Samples were compressed to pressures of 51, 66, 77, and 113 GPa, as determined by the equation of state of the iron foil (Mao et al., 1990) before laser heating (Table 1). Pressures were not measured during heating due to chemical reaction of the iron foil with the dolomite, but were likely ∼7–10 GPa higher than those reported here due to thermal pressure. Laser heating was performed with *in situ* X-ray diffraction at the GSECARS sector of the Advanced Photon Source (Prakapenka et al., 2008). The laser spot was focused to a diameter of ∼10 microns with a flat-top beam shape. Each sample was heated for 10–20 min at 1800–2500 K.

After recovery to ambient conditions, each heated spot was sectioned using a Zeiss NVision 40 dual-beam scanning electron microscope and focused $Ga^+$ ion beam (Centre Interdisciplinaire Microscopie de Electronique (CIME), EPFL). Each sample was coated with 15 nm Au to reduce charging in the scanning electron microscope. To protect the samples from damage by the $Ga^+$ ion beam, an additional ∼1–2 micron thick layer of Pt or C was deposited across the centers of heated spots. Thin sections of each heated spot were extracted and polished to electron transparency (∼100 nm thickness).

Imaging of recovered thin sections was performed with scanning transmission election microscopy (S/TEM) and energy-dispersive X-ray spectroscopy (EDX) in a FEI Tecnai Osiris analytical TEM (CIME, EPFL). Accelerating voltage for these measurements was 200 kV. The Osiris TEM is equipped with four wide-solid-angle