



# The CaCO<sub>3</sub>–Fe interaction: Kinetic approach for carbonate subduction to the deep Earth's mantle



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## ABSTRACT

The CaCO<sub>3</sub>–Fe<sup>0</sup> system, as a model for redox reactions between carbonates and reduced lithologies at the slab-mantle interface during subduction or at core-mantle boundary, was investigated systematically at temperatures from 650 to 1400 °C and pressures from 4 to 16 GPa using multi-anvil apparatus. CaCO<sub>3</sub> reduction via reaction: 3 CaCO<sub>3</sub> (aragonite) + 13 Fe<sup>0</sup> (metal) = Fe<sub>7</sub>C<sub>3</sub> (carbide) + 3 CaFe<sub>2</sub>O<sub>3</sub> (Ca-wüstite) was observed. The thickness of the reaction-product layer ( $\Delta x$ ) increases linearly with the square root of time in the time-series experiments ( $t$ ), indicating diffusion-controlled process. The reaction rate constant ( $k = \Delta x^2/2t$ ) is log-linear relative to  $1/T$ . Its temperature dependences was determined to be  $k$  [m<sup>2</sup>/s] =  $2.1 \times 10^{-7} \exp(-162[\text{kJ/mol}]/RT)$  at 4–6 GPa and  $k$  [m<sup>2</sup>/s] =  $2.6 \times 10^{-11} \exp(-65[\text{kJ/mol}]/RT)$  at 16 GPa. The sluggish kinetics of established CaCO<sub>3</sub>–Fe<sup>0</sup> interaction suggests that significant amount of carbonates could survive during subduction from metal saturation boundary near 250 km depth down to the transition zone and presumably to the lower mantle if melting of carbonates is not involved.

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## 1. Introduction

The Earth's mantle is a chemically heterogeneous system with complex structure, which consists of fertile and depleted peridotite and magmatic or recycled pyroxenite and eclogite, formed during evolution of the Earth (Hart, 1988; Hofmann, 2003). The subduction of oceanic slabs would be an important source of heterogeneity in the upper mantle, transition zone, and even in the lower mantle. Volatiles, notably H<sub>2</sub>O from hydrous minerals and CO<sub>2</sub> from carbonates, released by oceanic crust, affect the mantle oxidation state, trigger partial melting, alter major and trace element composition and rheological properties of ambient mantle rocks (Dasgupta and Hirschmann, 2006, 2010; Ghosh et al., 2014; Litasov and Ohtani, 2009, 2010; Litasov et al., 2013a,b; Rohrbach et al., 2007).

High-pressure behavior of carbonates is an important issue for the global geodynamic processes, mantle metasomatism, diamond formation, and deep carbon cycle. Experimental and theoretical studies (Boulard et al., 2012; Isshiki et al., 2003; Katsura and Ito, 1990; Litasov, 2011; Oganov et al., 2008; Ono et al., 2007) confirm

possible carbonate stability under the  $P$ - $T$  conditions of the upper and lower mantle.

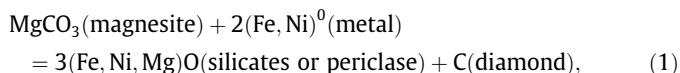
The evidence for deep ( $\geq 150$  km depths) subduction of carbonates within the slabs originates from the findings of Ca-Mg carbonates associated with diamond in CO<sub>2</sub>-bearing inclusions in xenoliths from forearc magmatic rocks in southwest Japan (Murakami et al., 2008). Besides, findings of syngeneic CaCO<sub>3</sub>-bearing mineral inclusions in sublithospheric diamonds from São Luiz, Brazil and some others localities suggest their crystallization from carbonatite melt derived from a chemically distinct Ca-rich carbonate-silicate reservoir (Brenker et al., 2007; Walter et al., 2008; Bulanova et al., 2010; Zedgenizov et al., 2014b). Several aspects, e.g. the C-isotopic composition of the host diamonds (Walter et al., 2008; Bulanova et al., 2010; Zedgenizov et al., 2014a) and Eu-anomalies of CaSiO<sub>3</sub> (Stachel et al., 2000), attribute the Ca-rich lithologies to subduction processes. The finding of CaSiO<sub>3</sub> in association with bridgmanite and ferropericlase within these diamonds confirms their ultra-deep origin (Joswig et al., 1999; Brenker et al., 2007).

Although carbonates and carbonate-bearing melts are stable in a wide range of  $P$ - $T$  conditions (Boulard et al., 2012; Litasov et al., 2013b), the redox state of the mantle can highly diminish their stability (Stagno et al., 2015). In contrast to subduction zones, large part of the ambient mantle is suspected to be significantly reduced. Studies of peridotite xenoliths show that mantle  $f(\text{O}_2)$  continuously

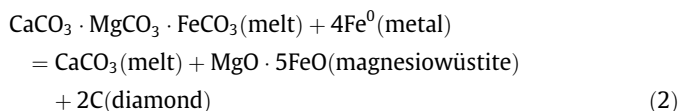
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decreases with increasing pressure (Woodland and Koch, 2003), such that carbonates should not be stable at depth greater than 120 km (Frost and McCammon, 2008; Stagno et al., 2013). Thermodynamic calculations and experiments (Frost et al., 2004; Rohrbach et al., 2007) suggest that mantle should be metal-saturated below 250 km depth, resulting from  $\text{Fe}^{2+}$  disproportionation in garnet, pyroxene and bridgmanite to structural  $\text{Fe}^{3+}$  and metallic  $\text{Fe}^0$ . As it was observed for carbonate-bearing peridotite, formation of  $\text{Fe}^0$  can trigger carbonates reduction with diamond formation (Rohrbach and Schmidt, 2011). Large contrast in the redox conditions between carbonate-bearing subducted slab and  $\text{Fe}^0$ -saturated surrounding mantle causes redox interactions. According to the high-pressure experiments magnesite reduction occurs via reaction (Rohrbach and Schmidt, 2011):



whereas dolomite-ankerite melt reacts with iron as (Palyanov et al., 2013):



Rohrbach and Schmidt (2011) suggested that carbonatite melts formed from recycled carbonates at depths greater than 250 km are unstable and have been reduced to immobile diamond when infiltrating ambient mantle.

On the other hand, it is not clear what will happen with carbonates remaining in solid state, which is quite possible for alkali- and water-poor compositions under  $P$ - $T$  conditions of subducted slabs (Shatskiy et al., 2015). To understand this process one can study mechanism and kinetics of redox reactions between carbonates and reduced mantle species. Carbonate-iron interaction is a simplified model of processes occurring between  $\text{Fe}^0$ -saturated mantle and oxidized subducted crust, representing one of the involved redox interactions at slab-mantle interface (Martirosyan et al., 2015a,b). We chose  $\text{CaCO}_3$  as a model carbonate, as nearly all  $\text{CO}_2$  enters subduction zones in the form of  $\text{CaCO}_3$ . It can be stable in sediment and eclogite assemblages in experiments (Litasov et al., 2013b; Kiseeva et al., 2013) and coexist with ultra-deep phases in natural diamond inclusions (Brenker et al., 2007).

In the present study, we report the results on the Ca-carbonate and Fe interaction at pressures of 4, 6 and 16 GPa and temperatures ranging from 650 to 1400 °C in experiments with different run duration. Using obtained data, the reaction rate constants and parameters for the Arrhenius equation were calculated. Based on the results, the mechanism and kinetics of the redox interaction between carbonated slab and  $\text{Fe}^0$ -saturated mantle were discussed. The results are also important for fundamental kinetic relations in the Earth's mantle minerals, since this type of reactions at high pressures was not investigated before.

## 2. Experimental and analytical methods

High-pressure experiments were performed using uniaxial split-sphere multianvil apparatus, USSA-5000 and USSA-1000, installed at the Institute for study of the Earth's Interior (ISEI), Okayama University, Misasa, Japan (Kawai et al., 1973; Shatskiy et al., 2011). A Cr-doped MgO octahedra with 14 and 18 mm edge-lengths were used as a pressure transmission medium (PM) (Shatskiy et al., 2010). The PM was compressed by WC anvils with truncated edge lengths of 8 and 11 mm. We placed pyrophyllite gaskets, 5 mm in width, between anvils near truncations to minimize extrusion of the PM and to improve stress distribution inside

the cell. The cell assemblies with octahedron/anvil truncation edge-length ratios of 18/11 and 14/8 mm were employed in experiments at 4–6 and 16 GPa, respectively. The details of pressure calibration are given in Shatskiy et al. (2011).

Additional runs at 6 GPa, were performed using uniaxial presses equipped with wedge-type and DIA-type guide blocks at Tohoku University (Sendai, Japan). In these experiments, we used Ca-doped  $\text{ZrO}_2$  octahedra with 20.5 mm edge length, WC anvils with 12-mm truncation edge length, and pyrophyllite gaskets, 4 mm in width and thickness. The details of cell assembly design and pressure calibration are given in Shatskiy et al. (2013).

Sample heating was achieved by using a tubular graphite (at 4–6 GPa) and  $\text{TiB}_2$  (at 16 GPa) heaters embedded in a  $\text{ZrO}_2$  sleeve for thermal insulation (Fig. 1). The sample temperature was monitored using a  $\text{W}_{97\%}\text{Re}_3\%-\text{W}_{75\%}\text{Re}_{25\%}$  thermocouple inserted in the center of the PM through the heater walls. High-pressure cell contained two iron capsules, prepared from high-purity Fe-foil (99.9%). Capsules were separated from heater by MgO sleeve, and placed symmetrically relative to the thermocouple junction in the center of the cell. The thermocouple was sandwiched between two MgO disks to prevent Fe contamination. One capsule was filled with  $\text{CaCO}_3$  powder (99.9%, Wako Pure Chem. Ind., Ltd., Japan) and remaining capsule was filled with magnesite (Martirosyan et al., 2015a). The loaded sample capsules were dried at 140 °C for several hours prior to experiments. In all experiments, pressure was first increased at room temperature to the target load in about 2–3 h. Then, sample was heated to the desired temperature in less than 10 min and annealed at fixed temperature. Temperature was maintained within 0.5 °C of desired value ranging from 650 to 1400 °C. Experiments were terminated by shutting off the electrical power of the heater, followed by slow decompression.

After the experiments, the recovered samples were mounted into epoxy and sectioned perpendicular to the capsule caps (i.e., to the Fe- $\text{CaCO}_3$  interface). Finally, samples were polished using 3- $\mu\text{m}$  diamond paste. The phase composition of the run products was examined using micro-focused X-ray diffractometer and scanning electron microscope with energy-dispersive X-ray spectrometer (EDS). We employed a Tescan MYRA 3 LMU scanning electron microscope coupled with INCA Energy dispersive X-ray microanalysis system 450 equipped with the liquid nitrogen-free large area EDS X-Max-80 Silicon Drift Detector (Oxford Instruments) at Institute of Geology and Mineralogy SB RAS (Novosibirsk, Russia). Operating conditions were 20 kV accelerating voltage, 1 nA

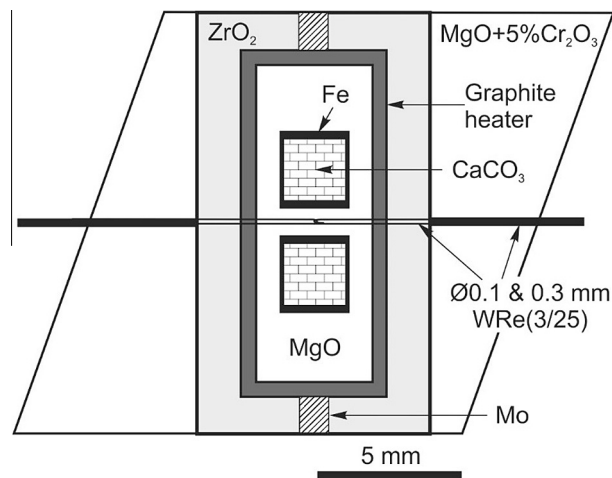


Fig. 1. Design of the cell assembly to study kinetics of  $\text{CaCO}_3$  reaction with metallic iron at 4–6 GPa. Two sample capsules can be loaded simultaneously into the cell. Thermocouple junction is located at the center of the cell.

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