

Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University

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Name of the research project: The interaction of magnesium carbonates with reduced peridotite and eclogite containing metallic iron at P-T parameters of the Earth's upper mantle.

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Research report:

1. Introduction

The findings of syngenetic inclusions of calcium and magnesium carbonates in the diamonds from kimberlites (Bulanova et al., 2010; Jablon and Navon, 2016; Stachel et al., 1998, 2000; Zedgenizov et al., 2014 a, b), and carbonate - bearing rocks from the ultrahigh-pressure metamorphic terranes, such as The Kokchetav Massif (Korsakov et al., 2009, 2011; Sobolev and Shatsky, 1990), confirm the existence of carbonates deep in the upper mantle, transition zone, or even the lower mantle and their role in diamond formation.

Although MgCO_3 and CaCO_3 are stable in a wide range of P-T conditions (Boulard et al., 2015; Lobanov et al., 2017), the deeper part of the mantle can be too reduced to favor presence of carbonates. Studies of the ferric – ferrous equilibria reconstructed from the garnet peridotites suggest that mantle rocks become progressively more reduced (Frost and McCammon, 2008). Thermodynamic calculations and experiments suggest that mantle becomes metal saturated at 250 km depth and in all mantle regions below (Frost et al., 2004; Rohrbach et al., 2007). Findings of metallic iron and iron carbides as inclusions in diamonds (Kaminsky and Wirth, 2011; Smith et al., 2016; Stachel et al., 1998) are in good agreement with this concept.

Thus, it is evident that the significant chemical heterogeneity in the redox conditions exists in the mantle, and the oxygen fugacity varies from the CCO buffer in the carbonate-bearing

subducted rocks to the Fe-FeO buffer in the Fe⁰-saturated surrounding mantle. As consequence of the existing redox gradient redox reactions will occur, and diamonds or other reduced carbon species can be formed directly by the reduction of carbonates or carbonatite melts. The mechanism and kinetics of these processes are extremely important for understanding the carbon behavior and distribution in the deep Earth.

Current state of issue

Most of the previous experimental and theoretical studies on the reactions of carbonates with metallic iron examine simplified carbonate-Fe⁰ systems: 1) MgCO₃-Fe⁰ at 6 and 25 GPa (Gao et al., 2016; Martirosyan et al., 2015b); 2) CaCO₃-Fe⁰ at 6 and 16 GPa (Martirosyan et al., 2015a, 2016); 3) (Ca,Mg)CO₃-Fe⁰ at 6–7 GPa and 40–110 GPa (Dorfman et al., 2015; Palyanov et al., 2013). All the works above revealed the occurrence of the redox reactions with the formation of graphite/diamond, Fe₃C/Fe₇C₃ carbide and magnesiowistite or calcium wustite, depending on the initial composition of the carbonate.

Despite the wide interest to the carbonates reduction in the presence of metallic iron, there are only few works, which model the process in the presence of silicates. Among them are investigation of Bataleva et al. (2015) in the (Mg,Ca)CO₃-SiO₂-Al₂O₃-Fe⁰ system at 6.3 -7.5 GPa, and experiments with carbonated peridotite conducted by Rohrbach and Schmidt (2011) at 14–23 GPa.

It is evident that for the further understanding of this issue, experimental study in the model systems, close to natural, are required.

Aims of the project

In the present project we studied the interaction of Fe with magnesite in the complex natural systems with peridotite and eclogite composition at 6-10 GPa and 900-1400°C. Based on the results the model of the redox reaction of calcium and magnesium carbonates with metallic iron will be reconstructed.

2. Experimental results

Methods

High-pressure experiments were carried out using uniaxial presses equipped with the split-sphere guide blocks, USSA-1000 installed at the Institute for Planetary Materials, Okayama University, Misasa, Japan (IPM). Octahedra made of Cr-doped MgO semi-sintered ceramics were employed as pressure-transmitting media. The cell assembly with a/b = 18/11, where a is an

octahedron edge length and b is a truncation edge length, were employed at 6 and 10 GPa. Graphite tubular heaters were used to generate high temperatures. The temperature was controlled using a $W_{97}Re_3$ – $W_{75}Re_{25}$ thermocouple with a junction at the centre of the heater. The high-pressure cell contained two graphite capsules, placed symmetrically to the thermocouple junction, and separated from the heater by a MgO sleeve.

Natural magnesite, Fe powder or plates (99.9% Rare Metallic Co) were used as starting reagents. Silicate part of the sample was presented by San Carlos olivine (Fo 90.1%), or natural eclogite and dunite with known compositions (Ragozin et al., 2006). The starting reagents were dried before the experiments at 320 °C.

To see more clearly the reaction front we used layered loading of the experimental capsules. Iron and carbonates were initially separated by the silicate layer. The following systems were studied:

- Magnesite – dunite/olivine – Fe;
- Magnesite – eclogite – Fe;

Overall 12 samples were obtained and analysed by EDS.

3. Results and discussion

System Magnesite – peridotite – Fe

The Magnesite – olivine – Fe and Magnesite – dunite – Fe systems were studied at 6 and 10 GPa in the temperature range 1100–1400 °C in experiments with various durations from 3 to 26 hours (Fig. 1). The formation of magnesiowüstite (Mws) and graphite (Gr) was observed. Gr crystallized up to a temperature of 1400 °C, at which the diamond (Dia) was detected. In the silicate part of the sample, modal composition of olivine changes toward more Fe rich variety.

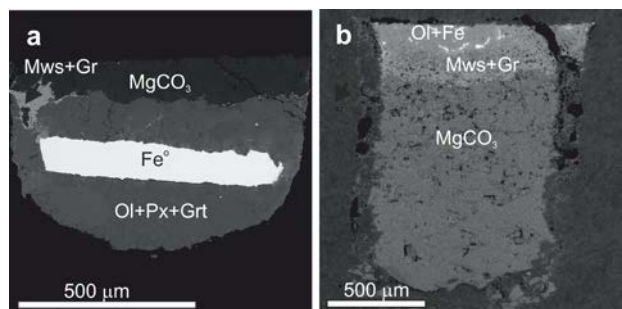
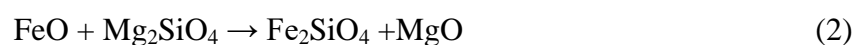
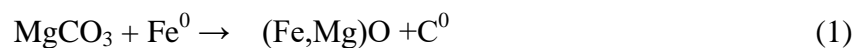


Fig. 1 BSE images of the samples from the 6GPa experiments: (a) $MgCO_3$ –dunite–Fe (1100°C, 26 h) ; (b) $MgCO_3$ –olivine–Fe

Based on our observations the following reactions could be proposed:



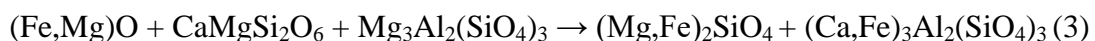
The reaction rate in the Magnesite – peridotite – Fe system increases exponentially with temperature. After 26 hours of heating at 1100°C, only a small amount of Mws and Gr was found near the carbonate / silicate interface (Fig. 1a). At the same time, a significant part of MgCO₃ and Fe remain unaltered. At 1200 °C, the reaction zone reaches 200 microns after 12 hours of heating (Fig. 1b), while in 20 hours MgCO₃ and Fe completely react.

System Magnesite – eclogite – Fe

The experiments in the Magnesite-eclogite-Fe system were carried out at 6 GPa and 1100 ° C with a heating duration of 3 to 26 hours. Same as in Magnesite - peridotite – Fe system, the formation of Mws and Gr is observed.

Mws reacted with diopside (Cpx), resulting in the formation of Ol. In the 26h experiment, we detected only relicts of magnesite and iron. Cpx was completely replaced by Ol. It is clear that the reaction carbonate-iron reaction is faster in the eclogite system, compared to that in peridotite system.

The redox reaction in the system could be described by the equation (1). Additionally, the formation of olivine and disappearance of Cpx allows to propose the following reaction:



4. Conclusions

In this project, we conducted experiments in the MgCO₃ - peridotite / eclogite - Fe systems at 6-10 GPa using multi-punch presses. The layered loading of reagents in experiments with different durations and temperatures made it possible to establish the sequence of reactions occurring in the systems under study.

The redox reaction of carbonate with Fe in all experiments was accompanied by the formation of Gr or Dia and Mws. It was found that oxide is not stable in silicate systems under the parameters of the upper mantle and react with Ol, Cpx and to form Fe-Ol.

Based on the obtained data, it can be concluded that in natural systems where carbonates and iron are separated by silicate media, the reaction is limited by slow diffusion rates in silicates and

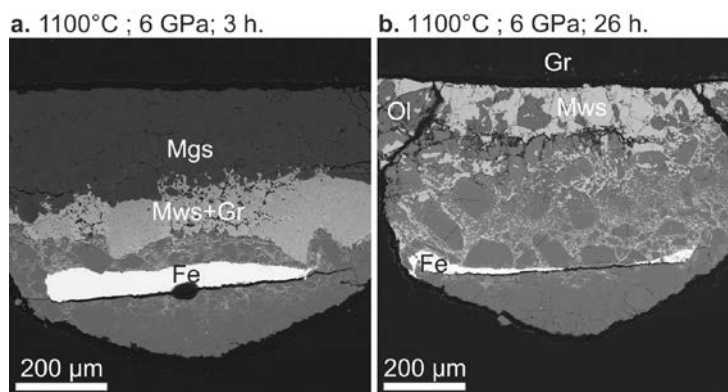


Fig. 2 BSE images of the samples from the Dolomite – eclogite-Fe experiment at 1100°C, 6GPa: (a)after 3h of heating; (b) 26h.

will not have a significant effect on the preservation of magnesite in the conditions of subduction zones (hot geotherm - 6 GPa, 1100 °C). At the same time, under the parameters of the mantle adiabat, the reaction rate is sufficient to lead to a complete or significant substitution of magnesite by Dia and Mws / Ol.

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