



Experimental determination of carbon isotope fractionation between graphite and carbonated silicate melt under upper mantle conditions



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ABSTRACT

Carbon isotope fractionation between graphite and carbonated silicate melt was determined at 5 GPa and in the temperature range between 1400 and 1900 °C. High pressure experiments were carried out in the carbon-saturated model harzbergite system (Enstatite–Magnesite–Olivine–Graphite), where carbonated silicate melt and graphite were the two stable carbon-bearing phases in the run products. Carbonated silicate melting resulted in an isotopic fractionation between graphite and carbon in the silicate melt, where the carbon in the melt is ¹³C enriched than co-existing graphite. ¹³C enrichment in carbonate melt when compared to graphite was further confirmed in experiments where redox melting between olivine and graphite produced carbonate melt as well as carbonate reduction experiments to form graphite. Although a quantitative estimate of fractionation between carbonate melt and graphite could not be obtained, our results indicate that mantle melting in the presence of graphite can result in progressive ¹³C carbon isotope enrichment in carbonate melt and depletion in graphite, which can be an alternate explanation for the carbon isotopic heterogeneity observed in the mantle derived carbon.

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1. Introduction

Carbon is the fourth most cosmic abundant element in the Solar system and its global cycle is important in the study of Earth's system because of its role in the evolution of life and environment. Carbon also controls the redox conditions in the interior of the Earth. For several billions of years, the surface carbon such as organic matter and carbonate minerals in marine sediment is carried to the Earth's interior by subduction processes (Sleep and Zahnle, 2001; Dasgupta et al., 2004), and inflow of the carbon to mantle can reach up to $6.1\sim 11.4 \times 10^7$ tons per year (Dasgupta and Hirschmann, 2010). Subsequently, carbon returns to the surface in different or the same forms owing to volcanism. Recently, there have been many discussions on the “deep carbon cycle” with renewed attention on the function and formation of carbonate melts that play a critical role in carbon geodynamic cycle in the Earth's interior. If carbon exists in the form of carbonates, then partial melting in the mantle could be more pronounced, leading to efficient extraction of carbon from the deep interior (Dasgupta and Hirschmann, 2006). Thus, carbon further acts as an agent of mass transfer in the form of mobile carbonate-rich melts.

Recent studies also suggest the importance of carbonated silicate melting, which satisfactorily explain the geochemical and geophysical properties of mantle, and restrict the stability of carbonatite in the Earth's deep upper mantle and help in understanding the deep carbon cycle (Dasgupta et al., 2013; Yoshino et al., 2012; Stagno et al., 2013).

One of the most efficient tools to understand the carbon cycle is the isotopic composition of carbon. Surface carbon is deposited on or precipitated in the ocean floor as organic matter ($\delta^{13}\text{C} \approx -25\text{‰}$) and carbonates ($\delta^{13}\text{C} \approx 0\text{‰}$), and part of it is transported into the mantle via subduction of oceanic lithosphere. The carbon isotopic composition of the mantle has been long considered to be homogeneous ($\delta^{13}\text{C} \approx -5.5\text{‰}$) and often approximated as the composition of the “bulk silicate Earth” (Marty, 2012; Deines, 2002; Matthey, 1991). Carbonatites (e.g., Deines, 1989) and kimberlites (e.g., Deines and Gold, 1973) typically have similar $\delta^{13}\text{C}$ value, between -7‰ and -5‰ . In addition, the $\delta^{13}\text{C}$ values of carbonate assemblages in hypabyssal kimberlites vary from -3.5 to -8‰ , which is similar to those for primary igneous carbonatite (Wilson et al., 2007). Fractionation of carbon isotopes is ‘traditionally’ considered as resulting from low temperature surface processes into different surface reservoirs, such as carbonate, organic matter and the atmospheric CO₂. However, the range of carbon isotope variation of mantle derived diamond

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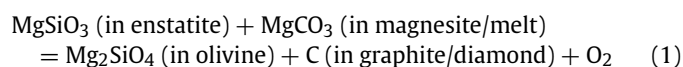
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Table 1
Experimental run conditions and phase relations.

Run No.	Comp.	T (°C)	Time (min)	Capsule	Phase relations						
1K1687	EMOG	1600	240	Pt	Ol	Opx		Gr	Carb-Si-melt		
1K1766	EMOG	1700	240	Pt	Ol	Opx		Gr	Carb-Si-melt		
1K1523	EMOG	1750	180	Pt	Ol	Opx		Gr	Carb-Si-melt		
1K1786	EMOG	1900	60	Re	Ol			Gr	Carb-Si-melt		
1K1980	CMASN + CO ₂	1400	720	Pt	Ol	Opx		Gnt	Gr	Carb-Si-melt	
1K1984	CMASN + CO ₂	1400	1440	Pt	Ol	Opx	Cpx	Gnt	Gr	Carb-Si-melt	FeC
1K1986	CMASN + CO ₂	1600	720	Pt	Ol	Opx		Gnt	Gr	Carb-Si-melt	
1K2011	EMOG (oxidized)	1700	240	Re	Ol	Opx			Gr	Carb-melt	
1K2012	EMOG (reduced)	1700	160	Pt	Ol				Gr	Carb-Si-melt	
1K2013	Fe + CaCO ₃	1400	420	MgO					Gr	Carb-melt	fper

has broadened to more than 40‰ (Galimov, 1991; Kirkley et al., 1991; Cartigny 2005, 2010; De Stefano et al., 2009; Bulanova et al., 2010), which has raised concerns about the homogeneous distribution of carbon isotopes in the upper mantle (Deines et al., 2009). Additionally, the low $\delta^{13}\text{C}$ compositions of diamonds with inclusion derived from potentially deep mantle sources has been interpreted as evidence for the presence of recycled light carbon derived from subducted organic material (Walter et al., 2011; Smart et al., 2011). Recently Palot et al. (2012) suggested that low $\delta^{13}\text{C}$ composition of diamonds derived from the deep mantle possibly reflect both mixing between mantle-derived and recycled organic source of carbon and Rayleigh fractionation process. Despite several strong evidences that points to the low-temperature surface carbon fractionation for the origin of light carbon in the mantle, a recent experimental investigation of carbon isotope fractionation in the Fe–C system at high-temperature and high-pressure conditions has hypothesized a possibility of Earth's core as a light carbon reservoir, thereby proposing a new possible source for light carbon flux from core-mantle boundary (Satish-Kumar et al., 2011). To what extent the wide range of carbon isotope variation of diamond is a result of mantle fractionation processes, whether they preserve primordial heterogeneities (Cartigny, 2010; Deines et al., 2009), or an interplay of recycling of surface carbon and those released from the core still remain unanswered (Wood et al., 2013).

In this study, we present results on the experimental determination of fractionation of carbon isotopes under high-pressure and high-temperature conditions in the Mg–Fe–Si–C–O system with excess carbon. This system provides a simple chemical model for understanding the relationships between silicate, carbonate and oxidized/reduced carbon phase in the mantle. Mg-rich olivine and orthopyroxene are the major minerals of mantle peridotites in the upper mantle. Magnesite is a stable carbonate phase, which stores oxidized carbon in mantle related assemblages of peridotite and eclogite at above 4.5 GPa (e.g. Dalton and Presnall, 1998; Hammouda, 2003; Yaxley and Brey, 2004; Dasgupta et al., 2004; Gudfinnsson and Presnall, 2005). In general, the stable carbon phase in the mantle depends on oxygen fugacity. Some studies have also assessed the $f\text{O}_2$ behavior on the diamond/graphite stability field in the presence of carbonate melt such as 'redox melting' in the upper mantle (Stagno and Frost, 2010). At upper mantle conditions, the reaction between magnesite or carbonate melt and graphite or diamond with enstatite and olivine can be approximated by the equilibrium (Eggler and Baker, 1982)



This equilibrium takes the acronym EMOG and defines a fixed oxygen fugacity above which carbonate become stable at upper mantle conditions. To further characterize the redox melting effect on carbon isotopes we have also examined redox melting in

the EMOG system (reverse reaction-1) as well as reductive melting of carbonate to graphite. The resulting carbon isotope fractionation between graphite and carbonated silicate melt at temperatures and pressures corresponding to upper mantle conditions was evaluated to characterize the distribution of carbon in the mantle, and we discuss the carbon isotope systematics during melting of carbonated mantle in the presence of graphite.

2. Method

2.1. Experimental

High-pressure experiments were performed using a Kawai type multi-anvil high-pressure apparatus (1000 ton press) at the Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan. All experiments were carried out at a pressure of 5 GPa. Pressure media was composed of a Cr₂O₃-doped MgO octahedron with 18 mm edge length. Cylindrical graphite was used as a heater. Pyrophyllite was used as gaskets. Cell assembly parts, except the graphite heater, were preheated in an oven at 1000 °C for an hour to remove absorbed water. In order to reduce the temperature gradient within the capsule, starting materials enclosed in metal capsules were placed in the central portion of a heater, surrounded by an MgO sleeve and spacers. The capsule length was 3.0–4.0 mm. In majority of experiments, a platinum capsule was used and tightly sealed to avoid exchange of components of starting materials with surrounding materials. Only for the experiments at 1900 °C, a rhenium capsule was used. The temperature was monitored with a W₉₇Re₃–W₇₅Re₂₅ thermocouple covered with an alumina sleeve, and the junction was located at the center of the capsule. The cell assembly was compressed using tungsten carbide cubes with 11 mm truncation edge length. The experiments were quenched by turning off the power applied to the heater. Total 10 runs were carried out at varying temperature conditions between 1400 °C and 1900 °C (Table 1).

2.2. Starting materials

Four experiments were carried out in the Mg–Fe–Si–C–O system, where natural enstatite (Mg# = 90.0), synthetic magnesite, San Carlos olivine (Mg# = 91.5) and pure graphite (sp-1) were used. These minerals were mixed at a molar ratio of 3:2:1:3 using an agate mortar under ethanol. This mixture is considered as a simplified carbonate harzburgite in the upper mantle. In order to easily obtain graphite from the run product for isotope measurements, experiments were done with an excess of carbon such that the experiments were saturated in graphite.

Three experiments were carried out with a starting material composition assumed to a carbonated fertile peridotite, which is more close to natural system, named as CMASN + CO₂ system in this paper. The chemical composition of the starting material in this

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