Experimental studies on carbon isotope fractionation in the deep Earth

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Carbon is the fourth most abundant element in the solar system. It has a key role in the melting phase relations of mantle rocks [1] and metallic core [2]. Carbon further acts as an agent of mass transfer in the form of mobile carbonate-rich melts [1]. An efficient tool to understand the carbon cycle, both in the shallow and deep Earth environments, is by using carbon isotopic composition. However, our understanding of carbon isotopic composition of deep Earth is very limited. Here we present results of experimental determination of partitioning of carbon isotopes at high-pressure high-temperature conditions, in systems analogous core formation environment and carbonate melting in the mantle conditions.

High-pressure experiments were performed using a Kawai type multi-anvil high-pressure apparatus at the ISEI, Okayama University, Misasa, Japan. Two types of starting materials were used. First type is a mixture of Fe + 9.0wt% C with known carbon isotopic composition. Second set of experiments were carried out in the Mg-Si-C-O system, where San Carlos enstatite and olivine was mixed with graphite and magnesite. Experiments were carried out at a pressure of 5 and 10 GPa at temperature conditions between 1200 ºC and 2100 ºC. Carbon isotope measurements were carried out using an IRMS.

The distribution of carbon isotopes between iron carbide melt and graphite/diamond at high-pressure high-temperature conditions shows the presence of large and measurable carbon isotope fractionation in the Fe-C system. These results were also consistent with the carbon isotope distribution between graphite and cohenite (Fe_3C) in iron meteorites. A temperature-dependent fractionation of carbon isotopes between iron carbide melt and graphite/diamond, as reported in [3], is believed to have created a “^{12}C-enriched core” with a significant difference in the distribution of carbon isotopes between the carbon core and bulk silicate Earth during accretion and differentiation of early Earth. In order to further characterize the carbon movement in the mantle, the carbon isotope systematics during melting of carbonated mantle in the presence of graphite/diamond were investigated in the Mg-Si-C-O system. Preliminary results indicate that carbon isotopes show considerable partitioning between graphite/diamond and carbonate melt at temperatures and pressures corresponding to upper mantle conditions. We attempt to discuss the carbon isotope systematics in the mantle and core based on our experimental results.

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δ^{26}Mg of brachiopod shells and the composition of past seawater

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The Mg isotope composition of marine carbonates can provide information on the dynamics of the Mg cycle through geological times (e.g. [1]). Brachiopods were extensively used for tracking both physicochemical conditions and secular isotopic variations of past oceans (e.g. [2]). Articulated brachiopods shells are made of low-Mg calcite, which is relatively resistant to most diagenetic processes [3]. However, significant intravariability in oxygen and carbon isotope ratios have been shown for several species, mainly due to kinetic and metabolic effects operating during calcite formation (e.g. [4]).

Magnesium, oxygen and carbon isotopes were measured in various fragments of a fossil *Terebratula scillae* (2.1 Ma) in order to test whether brachiopod shells could constitute valuable proxies of the seawater Mg isotope composition. The external parts of the shell, including the primary layer and external contamination were physically removed before analyses. Mg isotope ratios were measured by MC-ICP-MS Neptune *Plus*, with an external 2σ error of 0.15‰. Oxygen and carbon isotope ratios were measured by IRMS, with an 2σ error of 0.04‰.

The ventral and dorsal valves have similar isotope compositions and variability: δ^{26}Mg ranges from -2.95 to -2.02 ‰, δ^{18}O ranges from 2.57 to 3.15‰ and δ^{13}C ranges from 1.12‰ to 2.00‰. No correlation is observed with Mg/Ca ratio. A negative trend can be observed between δ^{26}Mg and δ^{18}O. The lowest δ^{26}Mg values correspond to isotope equilibrium determined for inorganic calcite relative to seawater Mg (Saulnier et al., submitted), and are systematically observed in the fragments located at the outer parts of the shell. This suggests that the outermost parts of brachiopod shells can be used to track the Mg isotope composition of past seawter. This aspect will be tested by studying ancient brachiopods with geological ages spanning from 0 to 54 Ma.

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