High-pressure and high-temperature experimental study of carbon isotope fractionation in the Mg-Si-C-O system

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Carbon is the fourth most cosmic abundant element in the solar system. It has a key role in the melting phase relations of mantle rocks and can move within mantle as carbonate rich melts [1]. Additionally, carbon is deposited in the ocean floor as carbonate minerals and organic matter, and is recycled into the mantle during subduction. Carbon isotopic composition serves as an efficient tool to understand the carbon cycle, both in the shallow and deep Earth environments. Recently, the presence of low $\delta^{13}C$ diamonds was considered to provide evidence for deep cycling of surface carbon of the organic matter origin [2], however recent experimental results in the Fe-C system suggests an alternate possibility of light carbon in the core [3]. Therefore, it is essential to understand the carbon isotope fractionation at mantle *P-T* conditions. Here, we present results on experimental determination of partitioning of carbon isotopes at high-pressure and high-temperature conditions, analogous to melting of carbonated mantle in the presence of graphite/diamond, and discuss the carbon movement in the mantle.

High-pressure experiments were performed in the Mg-Si-C-O system using a Kawai type multi-anvil high-pressure apparatus at the Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan. Starting materials comprise of natural enstatite, synthetic magnesite ($\delta^{13}C$ = -32.8‰), San Carlos olivine and pure graphite ($\delta^{13}C$ = -16‰), that were mixed in the molar ratio 3:2:1:1 or 3:2:1:3. This mixture is assumed as simplified carbonated harzburgite in a upper mantle. Experiments were carried out at pressures of 5 and 10 GPa at varying temperature conditions between 1100 ºC and 1800 ºC. Retrieved samples from HPHT experimental runs were mounted in epoxy and cut into two halves and polished. One half was used for petrographic observations and chemical analysis using an electron microprobe and the other half for carbon isotope measurements. Run products were mechanically and/or chemically separated and carbon isotope measurements were carried out using a conventional gas source isotope ratio mass spectrometer (IRMS).

Preliminary results indicate that runs at 5 GPa and above 1500 ºC have melted and the chemical composition of the melt varied widely, such as C-rich melt or Si-rich melt. Carbon isotope results show considerable partitioning between graphite/diamond and carbonate melt at temperatures and pressures corresponding to upper mantle conditions. We discuss the carbon isotope systematics during melting of carbonated mantle and implications for deep carbon cycle based on our experimental results.

[1] Dasgupta & Hirschmann (2006) *Nature*, **440**, 659-662 [2] Walter et al., (2011) *Science*, **334**, 54-57 [3] Satish-Kumar et al., (2011) *Earth Planet. Sci. Lett.* **310**, 340-348

Influence of DOM quality on arsenic mobilization in a Bangladesh Aquifer

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There is broad consensus that the main mechanism for the mobilization of arsenic (As) in reducing groundwater is the microbial reductive dissolution of iron (Fe) oxyhydroxides driven by the oxidation of labile organic matter (Figure 1). There is increasing evidence that the chemical quality of dissolved organic matter (DOM) may have an additional influence on arsenic (As) mobilization in reducing groundwater. [1] For example, humic substances, a major part of the DOM pool, are known electron shuttles that may also be involved in metal complexation (Figure 1). We used UV-vis absorbance and novel fluorescence techniques to characterize DOM in groundwater with dissolved As concentrations ranging from 2 to >400 µg/L and spanning a wide spatial extent in Araihazar, Bangladesh. For a subset of wells, we also determined % fulvic acid and performed elemental and ^{13}C-NMR analyses on fulvic acid isolates.

Our results consistently showed that terrestrially-derived aromatic organic compounds with low protein-like character were found where dissolved As concentrations are elevated. Moreover, the lowest As concentrations were found in village wells that had sewage pollution-derived DOM signatures. Together with highly significant relationships between arsenic and aromaticity and fluorescence of the fulvic acid isolates, our results provide strong evidence that humic substances have an important role in arsenic mobilization and potentially its maintenance in solution (Figure 1).

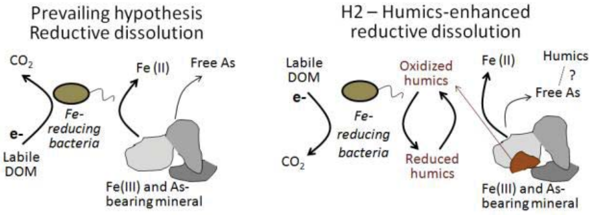

Figure 1: Conceptual diagram showing the "reductive dissolution" hypothesis (left) and an expanded "humics-enhanced reductive dissolution" hypothesis (H2; right) in which labile DOM and reactive DOM (including humic quinones) serve to donate and shuttle electrons, and are involved in complexation reactions. Sedimentary organic matter sources of labile and reactive DOM shown in brown.

[1] Mladenov, N. et al. (2010) *Env. Sci. Tech.* **52**, 47-59.