Microvolume stable isotope measuremetns and its applicaiton for high-pressure high-temperature experimental run products

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Light elements are very important in deep earth processes. Its composition in the lower mantle and core is still not well constrained. Stable isotope composition can be effectively used as an independent proxy. Although isotope fractionation in the deep earth occur in a narrow range, the volume of light element content in the mantle and core are extremely high, which can effectively cause significant natural isotopic compositional variations. It is necessary to accurately measure the isotope composition accurately in micro to nanomole scales, because the high-pressure experimental run products are small in volume. Recent studies have predicted the presence of isotope fractionation even at lower mantle and core *P-T* conditions, especially in magma ocean environment and during the core segregation. Despite the necessity of the micro-volume stable isotope measurement, there is always a tradeoff between the accuracy and the sample size.

At Niigata University, a MAT-253 mass spectrometer (Thermo Fisher Scientific) was installed through the MEXT Grant-in-Aid for Scientific Research on Innovative Areas. Carbon and oxygen isotopic compositions are measured using $CO_2$and multiple sulfur isotopic composition are measured using SF_6gas. A new micro-volume inlet system was installed and fundamental parameters such as pressure effect and capillary flow effect were tested. Using the micro-volume inlet system the minimum volume required for analysis is 1 micro-mole sample gas, and the precession for carbon and oxygen isotopic composition are better than 0.1‰. The precession for sulfur isotopes is ±0.3‰ and ±0.01‰ (1s) for $\delta^{34}S$ and $D^{33}S$, respectively, based on the repeated analyses of standard Ag_2S (IAEA S-1).Multiple sulfur isotope measurement system consists of 1) curie point pyrolyzer for rapid conversion of small volume samples to SF_6gas, 2) vacuum line system for pumping out non-condensable gasses, 3) gas chromatograph for purifying the SF_6gas and 4) micro-volume inlet system for introduction of sample gas to ionization chamber.
Multiple sulfur isotope ratios experimental run products were measured using the new system. Metal phases were separated and sulfur was extracted using Cr(II) reduction method [6]. Preliminary results indicate that S isotope fractionations occur in the pressure range of 3–5 GPa, under high-temperature conditions corresponding to the magma ocean environment. The negative $\delta^{34}S$ of mantle, can hence be explained by sulfur isotope fractionation in a magma ocean environment. Sulfur isotope measurements were also carried out on granitoid samples from the Archean with sulfide sulfur showing positive $\delta^{34}S$ values. Mass independent isotope fractionation, expressed as $\Delta^{33}S$, was also observed, suggesting that sulfur in the mantle alone cannot explain these variations. The incorporation of surface sulfur from sedimentary rocks and seawater is proposed.

Keywords: HPHT experiments, Micro-volume stable isotope measurements, Sulfur isotopes

