Isotope fractionation of Tungsten on geochemical samples using ICP-mass spectrometry

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Recent studies have revealed that natural stable isotope fractionations of many elements heavier than S (e.g., Ca, Fe, Cu, Zn or Tl) are common on the Earth. Among the heavier elements, W is especially important element, because isotopic composition of W can provide us chronological data known as Hf-W isotopic chronometer [1-5]. In the previous works, the mass discrimination effect was internally corrected by normalising a specific W isotopic pair (e.g., $^{186}W/^{183}W = 1.98594$[1]). However, this correction method is not adequate for the stable isotopic study, because not only the mass discrimination effect, but also natural isotopic fractionation of the analyses have been normalized at a same time. It is well recognized that detection of natural variation in isotopic composition of further heavy elements would be very difficult because of their small magnitude of isotopic fractionation mainly due to small relative mass differences [6]. In this study, multiple collector-ICP-mass spectrometry (MC-ICPMS) was used to measure W isotopic ratios. The extension of the capability of ICPMS is to accept external correction technique for a correction of mass discrimination effect (mass fractionation effect inside the mass spectrometer). Here we report the results of high precision W isotopic data for chemical reagents (JMC-22841 and NIST SRM 3163) and series of geochemical samples (JR-1, JR-2 and HSD-USGS), using the MC-ICPMS combined with an external correction technique using Re. The data obtained here revealed that there were no significant variations in W isotopic composition for igneous rocks, whereas W collected from the HSD-WSGS was isotopically fractionated (0.15‰/amu). In this presentation, we would like to discuss the possible mechanism of the W isotopic fractionation found on this deposit sample.

References

[1] C. L. Harper and S. B. Jacobsen (1996) *Geochem. Cosmochem. Acta*, **60**, 1131-1153
[2] A. N. Halliday (2004) *Nature*, **427**, 505-509
[3] A. Scherstén et al. (2004) *Nature*, 427, 234-
[4] 237 Q. Yin et al. (2002) *Nature*, **418**, 949-952
[5] G. Quitté et al. (2002) *J. Geostan. Geoana.*, **26**, 149-16
[6] J. Völkening et al. (1991) *Int. J. mass Spectrom. Ion Processes*, **107**, 36
[7] J. Bigeleisen and M. G. Mayer (1947) *J. Chem. Phys.*, **15**, 261

Multiple sulfur isotope constraints on sulfur cycle in the seafloor hydrothermal systems

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Seafloor hydrothermal system fuels an unusual deep-water ecosystem that depends on the hydrothermal emission of sulfide for its energy source. Understanding chemical and isotopic systematics of such hydrothermal systems may have profound implication into the origin of life and life in the extreme environment.

We will report the first application of non-traditional isotopes of sulfur (^{33}S and ^{36}S) as a tool to decouple combination processes in the sulfur cycle in the modern seafloor hydrothermal system. Our data shows measurable variation (> 5σ analytical precision) in $\Delta^{33}S^{\dagger}$ and $\Delta^{36}S^{\dagger}$ for sulfide minerals from modern seafloor hydrothermal sulfide deposits, suggesting all four sulfur isotope system may provide new insights into sulfur cycle in the seafloor hydrothermal systems.

We will apply thermochemical and isotopic models of seafloor hydrothermal massive sulfide deposits (e.g. Ohmoto et al., 1983, Shanks, 2001), expand the model for multiple sulfur isotope systematics for a biological flow network by Farquhar et al. (2003) into the global-scale oceanic sulfate budget, and model transfer of oceanic sulfate signature into sulfide in the seafloor massive sulfide deposits. We will discuss implication of the new constraints on the sulfur cycle in the hydrothermal systems.

References and notes

† $\Delta^{33}S \equiv \delta'33S-0.515x\delta^{34}S$ and $\Delta^{36}S \equiv \delta'^{36}S-1.9x\delta^{34}S$, where $\delta'^{x}S$ is defined in a logarithmic formula as that used by Hulston and Thode (1965) *J. Geophys. Res.* **70**, 3475-3484.
Ohmoto et al. (1983) *Econ Geol Mono* **5**, 570-604
Shanks (2001) *Rev Mineral Geochem* **43**, 469-525
Farquhar et al. (2003) *Geobiology* **1**, 27-36