Recent progress of in situ sulfur 2- and 4-isotope measurements at Kochi Institute, JAMSTEC

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Secondary Ion Mass Spectrometry with a multiple collector system (MC-SIMS) has capability to perform accurate in situ stable isotope analyses with sub-permil precision and down to a few mm spatial resolution [1]. Sulfur isotope systematics of sediments and sedimentary/igneous rocks provides constraints on the biological activity, the origin of the sulfur reservoirs, the evolution of Earth' s atmosphere, and behaviors of volatile elements in the Earth' s interior. Previously, we reported results of sulfur 2-isotope (34 S/ 32 S) analyses of pyrite, basaltic glass, and barite with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC [2]. Recently, we installed the modified detector slits and achieved capability of the sulfur 4-isotope (34 S/ 32 S) analysis using four Faraday cup (FC) detectors (c.f., [3]). We also explored sulfur 2-isotope analysis using ~2 μ m in diameter primary beam and applied this analytical protocol to the study on the seafloor hydrothermal deposits [4]. In this presentation, we will report the results of test analyses of sulfur 4-isotope analyses and the results of small beam sulfur 2-isotope analyses of fine-grained pyrites in the seafloor hydrothermal deposits.

The sulfur 4-isotope test analyses of the pyrite standard, UWPy-1, were performed using a 20 kV accelerated Cs⁺ primary beam of ~5.4 nA and ~15 μ m in diameter. Four sulfur isotope ion signals were accelerated at 10 kV and detected with 4 FC detectors, simultaneously. The mass resolving power (M/DM) was set at ~2200 for ³²S⁻ and ³⁶S⁻, and ~5000 for ³³S⁻ and ³⁴S⁻, respectively. The typical count rate of the ³²S⁻ signal was 5.8×10⁹ cps. Reproducibility of spot-to-spot analyses was ±0.35‰, ±0.05‰, and ± 0.91‰ (2 SD) for δ ³⁴S, Δ ³³S, and Δ ³⁶S, respectively. These are enough to investigate the sulfur mass independent fractionation signature of Archean sulfide samples.

The sulfur 2-isotope analyses with a small beam were performed using a 20kV Cs⁺ primary beam of ~0.1 nA and ~2 μ m in diameter. Two sulfur isotope ion signals (³²S⁻ and ³⁴S⁻) were accelerated at 10 kV and detected with 2 FC detectors, simultaneously. The mass resolving power was set at ~2200 for ³²S⁻ and ~5000 for ³⁴S⁻, respectively. The typical count rate of the ³²S⁻ signal was ~7×10⁷ cps, and the typical spot-to-spot reproducibility (2 SD) of the δ ³⁴S value was 0.38‰. The seafloor hydrothermal deposit samples frequently contain fine-grained framboidal, colloform, and euhedral pyrites, and we recognized that framboidal pyrites have distinctly lower δ ³⁴S values (down to -38.9‰) than those of other type pyrites, indicating that framboidal pyrites are formed by the bacterial sulfate reduction and other pyrites are grown by separate processes. The present results indicate that the small beam sulfur isotope analysis can be strong tool for better understanding of the origin of the seafloor hydrothermal deposits. The whole dataset and their interpretations of seafloor hydrothermal deposit samples will be reported in the other presentation of this conference [4].

[1] Kita N. T. et al. (2009) Chem. Geol. 264, 43-57.

- [2] Ushikubo T. and Shimizu K. (2017) JpGU abstract #SGC54-04
- [3] Ushikubo T. et al. (2014) Chem Geol. 383, 86-99.
- [4] Nozaki T. et al. (2020) this conference.

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