Development of in situ sulfur 2-isotope analysis technique for studies on sulfur isotope systematics of Earth's deep interior and surface environment

*Takayuki Ushikubo[1], Kenji Shimizu[1]

1. Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology

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 analysis spot size of ~10 μm in diameter [1]. In situ analysis technique with spatial resolution of micrometer range is useful to study multiple processes recorded within complex texture and to show primary signatures from metamorphosed samples. Sulfur isotope systematics of sediments and sedimentary/igneous rocks provides constraints on the biological activity, the evolution of Earth's atmosphere, and behaviors of volatile elements in the Earth's interior. Here, we present results of development of sulfur 2-isotope analyses ($^{34}S/^{32}S$) of pyrite, basaltic glass, and barite with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC.
For all sulfur isotope test analyses, we used (1) a Cs^+ ion beam with a total impact energy of 20 kV, (2) a normal-incident electron gun for charge compensation, (3) the mass resolving power (MRP, M/DM) of ~2200 for $^{32}S^-$ and ~5000 for $^{34}S^-$, respectively, and (4) a secondary-ion accelerating voltage of 10 kV.
Sulfur 2-isotope analyses of pyrite were performed with a 1 nA and 10 μm in diameter Cs^+ ion beam. The secondary ions ($^{32}S^-$ and $^{34}S^-$) were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate of $^{32}S^-$ was 1×10^9 cps. The UWPy-1 pyrite standard ($\delta^{34}S$=16.04±0.18‰)[2] was measured for test analyses. The reproducibility of spot-to-spot analyses was ±0.25‰ (2 SD, n=10). Based on the results of test analyses and the $^{32}S^-$ ion yield, we expect that the reproducibility of sulfur isotope analysis with a 50 pA and ~3 μm in diameter primary beam will be better than ±1‰ (cf. [3]). We consider that in situ sulfur isotope analyses with larger (~10 μm) and smaller (~3 μm) primary beam conditions are suitable to measure $\delta^{34}S$ values of sedimentary pyrites and pyrite grains entrapped in igneous minerals.
Sulfur 2-isotope analyses of basaltic glasses, EPR-G3 ([S]=1269 ppm) and FJ-G2 ([S]=1372 ppm) [4], were performed with a 1.5 nA and 10 μm in diameter Cs^+ ion beam. The secondary ions were detected with a Faraday cup detector for $^{32}S^-$ and an electron multiplier (EM) detector for $^{34}S^-$, simultaneously. A typical count rate of $^{32}S^-$ was 2.7×10^6 cps. Ten fragments of each basaltic glass were mounted in the same epoxy mount to examine homogeneity of sulfur isotope ratios. The reproducibility of sulfur 2-isotope measurements was ±0.52‰ (2 SD, n=20) for EPR-G3 and ±0.60‰ (2 SD, n=21) for FJ-G2, respectively, which are close to statistic errors based on intensities of secondary ions. This indicates that the reproducibility of the present analytical condition is ~0.6‰ and sulfur isotope ratios of both basaltic glasses are homogeneous within analytical uncertainty. We plan (1) to perform sulfur isotope test analyses with higher intensity beam to achieve better analytical uncertainty by MC-SIMS, and (2) to determine sulfur isotope ratios relative to the VCDT value of these basaltic glasses by the fluorination method. We also plan to modify detector slits for sulfur 3-, and 4-isotope analysis with multiple collectors (cf. [2]).
For sulfur 2-isotope test analyses of barite, we used a 1 nA and 10 μm in diameter Cs^+ ion beam and the secondary ions were detected with two Faraday cup detectors (FCs), simultaneously. A typical count rate of $^{32}S^-$ was 2×10^8 cps. We could not determine analytical uncertainty because of absence of appropriate standard barite with homogeneous sulfur isotope ratio. Since the typical internal error of each analysis was ~0.2‰ (2σ), we expect to achieve analytical uncertainty of ~±0.3‰ for sulfur 2-isotope analyses of barite with an appropriate barite standard.

References:
[1] Kita N. T. et al. (2009) Chem. Geol. 264, 43-57.
[2] Ushikubo T. et al. (2014) Chem. Geol. 383, 86-99.
[3] Williford K. H. et al. (2011) GCA 75, 5686-5705.
[4] Shimizu K. et al. (2017) Geochem. J. (in press).

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