A development of SO_2F_2 method to measure sulfate isotopologues

TOSHIKI KATSUTA[1*], YUICHIRO UENO[1,2,3], MAYUKO NAKAGAWA[2], RIHO AOKI[1], NAOHIRO YOSHIDA [2,4]

[1] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo, 152-8551, Japan (*correspondence: katsuta.t.aa@m.titech.ac.jp)

[2] Earth-Life Science Institute (WPI-ELSI), Tokyo Institute of Technology, Meguro, Tokyo, 152-8550, Japan

[3] Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Natsushima-cho, Yokosuka 237-0061, Japan

[4] Department of Chemical Science and Engineering, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8502, Japan

We have developed a method to measure sulfur and oxygen isotopes ratio of sulfate simultaneously as well as measuring S-O clumped isotopologue. Quantitative conversion from barium sulfate ($BaSO_4$) into SO_2F_2 is possible by the reaction with F_2 and $BaSO_4$ at 280˚C for 3 h in a nickel reaction vessel. The product SO_2F_2 was measured on a high-resolution mass spectrometer (MAT253 ULTRA). The overall precision of this method for $\delta^{34}S$, $\Delta^{33}S$, and $\delta^{18}O$ values are ±0.01‰, ±0.02‰ and ±0.04‰, respectively. The reproducibility of the $\Delta^{34}S^{18}O$ value in the entire process from fluorination is ±0.17‰. In order to apply this technique to wide range of natural samples, we have conduted several following tests. First, a natural gypsum was fluorinted directly and compared with the fluorination of $BaSO_4$ made by dissolution of the same gypsum in hydrochloric acid and reprecipitated as barium sulfate. Both the measured $\Delta^{34}S^{18}O$ values are consistent within the analytical uncertainty. Second, two samples of barium sulfate were mixed with SiO_2 of which the $\delta^{18}O$ is 4.4 ‰ in the proportion 3 : 2, and fluorinated to evaluate the effect of impurity. The results showed that the $\delta^{34}S$ did not change, but $\delta^{18}O$ slightly increase about 2 - 3‰ with a decrease of $\Delta^{34}S^{18}O$ value about -0.6‰. This suggests that purification of natural sulfate sample is nessesary, though re-precipitation as $BaSO_4$ allow us to measure variety of natural samples.