

A new fluorination line for multiple sulfur isotope analysis

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Sulfur and oxygen mass-independent-fractionation (MIF) processes (i.e., $\Delta^{17}\text{O}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$) in atmospheric sulfate provide information on SO_2 oxidation pathways, which constrains the atmospheric conditions, e.g., levels of oxygen, ozone, cloud fraction, etc. [1-2] at the time of sulfate formation. The oxidation processes responsible for the O-MIF are in general well-known [3], yet that for the S-MIF are not unambiguously identified [4-5]. The MIF signals in atmospheric sulfate depend on the relative importance of SO_2 oxidation pathways (e.g., OH oxidation versus photo-oxidation). Simultaneous analysis of S- and O-MIF in a sulfate sample would potentially provide better constraints on the origin(s) of S-MIF. We are developing a new fluorination line complementary to the existing Ag_2SO_4 pyrolysis method, for determination of multiple sulfur and oxygen isotope compositions of sulfate in the same sample. While O_2 produced by the pyrolysis is induced into a MAT-253 mass spectrometer for O-MIF analysis in a continuous flow system, the co-produced SO_2 is collected and converted back to sulfate. An improved and optimized Thode's reducing solution is used to reduce sulfate to H_2S offline. Using CoF_3 , H_2S is then converted to SF_6 , which is purified and collected in a glass vessel and analyzed for multiple sulfur isotope composition by a MAT-253 mass spectrometer using a dual-inlet system. This method will be used to measure sulfate samples created in a large environment chamber, which simulates atmospheric environments similar to those in which S-MIF was discovered. Performance of the new fluorination line and preliminary data from the chamber experiments will be presented at the conference.

[1] H. Bao, *Chem Geol* **395**, 108 (2015). [2] J. Farquhar, B. A. Wing, *Earth Planet. Sc. Lett.* **213**, 1 (2003). [3] J. Savarino, C. C. W. Lee, M. H. Thiemens, *J. Geophys. Res.* **105**, 29079 (Dec 16, 2000). [4] Y. Endo *et al.*, *J. Geophys. Res.* **120**, 2014JD021671 (2015). [5] S. Ono, A. R. Whitehill, J. R. Lyons, *J. Geophys. Res.* **118**, 2444 (2013).