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Sulfur isotopic analysis of carbonyl sulfide and its application for biogeochemical cycles

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Carbonyl sulfide (OCS or COS) is the most abundant gas containing sulfur in the atmosphere, with an average mixing ratio of 500 p.p.t.v. in the troposphere. OCS is suggested as a sulfur source of the stratospheric sulfate aerosols (SSA) which plays an important role in Earth's radiation budget and ozone depletion. Therefore, OCS budget should be validated for prediction of climate change, but the global OCS budget is imbalance.

Recently we developed a promising new analytical method for measuring the stable sulfur isotopic compositions of OCS using nanomole level samples: the direct isotopic analytical technique of on-line gas chromatography-isotope ratio mass spectrometry (GC-IRMS) using fragmentation ions S^+ (Hattori et al., 2015). The first measurement of the $\delta^{34}S$ value for atmospheric OCS coupled with isotopic fractionation for OCS sink reactions in the stratosphere (Hattori et al., 2011; Schmidt et al., 2012; Hattori et al., 2012) explains the reported $\delta^{34}S$ value for background stratospheric sulfate, suggesting that OCS is a potentially important source for background (nonepisodic or non-volcanic) stratospheric sulfate aerosols.

This new method measuring $\delta^{34}S$ values of OCS can be used to investigate OCS sources and sinks in the troposphere to better understand its cycle. It is known that some microorganisms in soil can degrade OCS, but the mechanism and the contribution to the OCS in the air are still uncertain. In order to determine sulfur isotopic enrichment factor of OCS during degradation via microorganisms, incubation experiments were conducted using strains belonging to the genera *Mycobacterium*, *Williamsia* and *Cupriavidus*, isolated from natural soil environments (Kato et al., 2008). As a result, sulfur isotope ratios of OCS were increased during degradation of OCS, indicating that reaction for $OC^{32}S$ is faster than that for $OC^{33}S$ and $OC^{34}S$. OCS degradation via microorganisms is not mass-independent fractionation (MIF) process, suggesting that this reaction does not contribute to the MIF signatures observed in sulfate aerosol samples and/or Archaean rock records. At the presentation, we report the comparison of $^{34}\varepsilon$ values determined using some strains and the atmospheric implications for the OCS degradation in the present atmosphere are discussed.

Hattori, S., Danielache, S. O., Johnson, M. S., Schmidt, J. A., Kjaergaard, H. G., Toyoda, S., Ueno, Y., Yoshida, N. Ultraviolet absorption cross sections of carbonyl sulfide isotopologues $OC^{32}S$, $OC^{33}S$, $OC^{34}S$ and $O^{13}CS$: isotopic fractionation in photolysis and atmospheric implications, *Atmos. Chem. Phys.*, 11, 10293-10303, 2011.

Schmidt, J. A., Johnson, M. S., Jung, Y., Danielache, S. O., Hattori, S., Yoshida, N., Predictions of the sulfur and carbon kinetic isotope effects in the OH + OCS reaction, *Chem. Phys. Lett.*, 531, 64-69, 2012.

Hattori, S., Schmidt J. A., Mahler D., Danielache, S. O., Johnson M. S., Yoshida N. Isotope Effect in the Carbonyl Sulfide Reaction with $O(^3P)$, *J. Phys. Chem. A*, 116, 3521-3526, 2012.

Hattori, S., Toyoda, A., Toyoda, S., Ishino S., Ueno, Y., Yoshida, N.: Determination of the Sulfur Isotope Ratio in Carbonyl Sulfide using Gas Chromatography/Isotope Ratio Mass Spectrometry on Fragment Ions $^{32}S^+$, $^{33}S^+$, and $^{34}S^+$, *Anal. Chem.*, 87, 477-484, 2015.

Kato, H., Saito, M., Nagahata, Y., Katayama, Y.: Degradation of ambient carbonyl sulfide by *Mycobacterium* spp. in soil. *Microbiol.*, 154(1), 249-255, 2008.