

Sulfur isotopic fractionation in carbonyl sulfide during microbial degradation

KAMEZAKI, Kazuki^{1*}; HATTORI, Shohei¹; OGAWA, Takahiro²; ISHINO, Sakiko¹; TOYODA, Sakae¹; KATO, Hiromi³; KATAYAMA, Yoko²; YOSHIDA, Naohiro¹

¹Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, ²Graduate School of Agriculture, Tokyo University of Agriculture and Technology,, ³Graduate School of Life Sciences, Tohoku University

Carbonyl sulfide (OCS) 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 for Earth of radiation budget and for ozone depletion. OCS, therefore, should be validated for prediction of climate change, but the global OCS budget is imbalanced. 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. Isotopic compositions and isotopic fractionation factors are used to trace the sources and transformations of atmospheric trace gases. Recently, we developed new method measuring sulfur isotopic composition of OCS using fragmentation ions S^+ , and this method can be used to investigate its sources and sinks in the troposphere. In order to determine sulfur isotopic fractionation factors for OCS during degradation via microorganisms, we performed laboratory incubation experiments using OCS-degrading microorganisms.

Bacterium strains, which have OCS degradation activity, were cultured on the slant in a glass tube. After forming the colonies, headspace were replaced with N_2/O_2 (80:20 mixture) and 0.03% of CO_2 , and then approximately 4000 p.p.m.v. of OCS were added to the batch. The concentrations of OCS were measured using gas chromatograph equipped with a flame photometric detector, and headspace gases were collected in the helium purged vials for isotope analysis at the same time of concentration measurements. For isotope analysis, we injected the OCS samples to on-line purification system connected to the gas chromatography-isotope ratios mass spectrometry. The sulfur isotope ratios in OCS were determined by measuring the fragment ions $^{32}S^+$, $^{33}S^+$, and $^{34}S^+$ using triple faraday collector cups. Isotopic fractionation factors were determined by the Rayleigh equation.

The isotopic compositions ($\delta^{33}S$ and $\delta^{34}S$) of OCS were increased during degradation of OCS, indicating that reaction for $OC^{32}S$ was faster than that for $OC^{33}S$ and $OC^{34}S$. On the basis of the concentration of OCS and its isotopic compositions, the Rayleigh isotope fractionation model were applied to determine isotopic fractionation constants ($^x\varepsilon = (\delta^xS - \delta^xS_{initial}) / \ln f$, where x indicates 33 or 34). It is worthy noting that $^{33}\varepsilon$ and $^{34}\varepsilon$ values determined by the experiments shows no significant deviations from mass-dependent relationship, indicating that OCS degradation via microorganisms is not mass-independent fractionation (MIF) process. This result suggests this reaction is not contributed to the MIF signatures observed in sulfur for sulfate aerosol samples and/or Archaean rock records.

At the presentation, the comparisons of variability of $^{33}\varepsilon$ and $^{34}\varepsilon$ values for different strains are presented, and the atmospheric implications for the OCS degradation in the present atmosphere are discussed.

Keywords: Carbonyl sulfide, Isotopic fractionation factor, Microorganism