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Tracing atmospheric DMS chemistry using the triple oxygen isotope of MSA

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The atmospheric sulfur cycle exerts a central control on Earth's radiative balance by regulating aerosol formation, cloud microphysics, and biogeochemical feedbacks. Within this cycle, oxidation of marine dimethyl sulfide (DMS) represents the dominant natural source of non-sea-salt sulfate and methanesulfonate (MSA), yet the partitioning of sulfur among gas-phase MSA, aqueous MSA, sulfuric acid, and particulate sulfate remains a major uncertainty in climate models. Because these products contribute differently to new particle formation, condensational growth, and cloud condensation nuclei (CCN) abundance, even modest errors in DMS oxidation branching can propagate into substantial biases in radiative forcing. However, the branching mechanisms of DMS oxidation and their climatic implications remain poorly constrained. Conventional concentration-based metrics such as the MSA/SO_4^{2-} ratio are affected by uncertainties in both DMS oxidation chemistry and sulfate source strengths, limiting their ability to uniquely constrain oxidation pathways.

Independent insight into DMS oxidation chemistry can be obtained from the mass-independent oxygen isotopic composition ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$) of MSA. These measurements were enabled by the recent development of an electrospray ionization Orbitrap mass spectrometric method that allows determination of $\Delta^{17}O$ values in intact MSA molecules (Hong et al., 2025 Anal. Chem.). Here we present direct observations of the $\Delta^{17}O$(MSA) values in Antarctic aerosols collected at Syowa Station during 2020–2021. Observed $\Delta^{17}O$(MSA) values exhibit pronounced seasonal variability, with lower values in summer and higher values in winter, indicating seasonally varying oxidation pathways in the Antarctic atmosphere. Comparison with simulations from the GEOS-Chem chemical transport model shows that the default chemical mechanism for DMS chemistry systematically overestimates $\Delta^{17}O$(MSA) values despite reproducing the observed MSA/SO_4^{2-} ratio. Sensitivity experiments indicate that lowering $\Delta^{17}O$(MSA) endmember from the gas-phase MSA production and/or reducing contributions from BrO-involved reactions substantially improve agreement with observations. We will also discuss future directions in which isotope-constrained oxidation chemistry is incorporated into aerosol microphysics and radiative forcing calculations to help close the sulfur budget and reduce uncertainties in climate feedbacks associated with marine sulfur emissions.

[1] Hong et al., (2025) Triple Oxygen Isotope Analysis of Methanesulfonate Using the SO_3^- Fragment in ESI-Orbitrap-MS, *Analytical Chemistry* 97, 27, 14339–14348.