Determination of the Oxygen Isotope Ratio in Methanesulfonate Using ESI-Orbitrap-MS

Yihang Hong^{1,2,3*}, Shohei Hattori^{1,2,3}, Longchen Zhu^{1,2}, Zhao Wei^{1,2}, Daniel Crocker⁴, Chen Yu^{3,5}, Tengyu Liu^{3,5}, Yu Wei^{1,2}, Hao Yan^{1,2}, Zhenfei Wang^{1,2}, Yongbo Peng^{1,2}, Issaku Kohl⁶, Cajetan Neubauer⁷, & Andreas Hilkert⁸

¹ International Center for Isotope Effects Research (ICIER), Nanjing University, Nanjing 210023, China

² School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

³ Frontiers Science Center for Critical Earth Material Cycling, Nanjing University, Nanjing 210023, China

⁴ Department of Earth and Planetary Sciences, Harvard University, Cambridge MA 02138, United States ⁵ School of Atmospheric Science, Nanjing University, Nanjing 210023, China

⁶ Department of Geology & Geophysics, The University of Utah, Salt Lake City UT 84112, United States

⁷ Institute of Arctic and Alpine Research, University of Colorado, Boulder, Colorado 80303, United States

⁸ Thermo Fisher Scientific (Bremen), Hanna-Kunath Strasse 11, 28199 Bremen, Germany

*Presenting Author Email: yihang.hong@smail.nju.edu.cn

The atmospheric oxidation of dimethyl sulfide (DMS, CH₃SCH₃) to sulfate (SO₄²⁻) and methanesulfonate (MSA, CH₃SO₃⁻) are key processes for the atmospheric sulfur cycle, particularly in pristine regions. To understand the DMS chemistry, oxygen isotope signatures $(\delta^{18}\text{O} \text{ and } \Delta^{17}\text{O})$ are useful to trace the oxidation from DMS to MSA. However, conventional gas-source isotope ratio mass spectrometry (IRMS) is rarely used to measure the natural abundance isotopic compositions of MSA in environmental samples due to the requirement for micro-mole level sample sizes and the complexity of the analytical steps necessary for obtaining oxygen isotope measurements. Here, we present the development of a new method for measuring δ^{18} O and Δ^{17} O values of MSA using Electrospray Ionization Orbitrap Mass Spectrometry (ESI-Orbitrap-MS). To measure δ^{18} O and Δ^{17} O values of MSA on the ESI-Orbitrap-MS, the SO₃⁻ fragment ions from MSA isotopologues, ${}^{32}S^{16}O_{3}^{-}$ (m/z =79.95736), ${}^{32}S^{16}O_2{}^{17}O_2{}^{-}$ (m/z = 80.96158), ${}^{34}S^{16}O_3{}^{-}$ (m/z = 81.95316), and ${}^{32}S^{16}O_2{}^{18}O_2{}^{-}$ (m/z = 81.96161), generated via Higher-energy Collisional Dissociation (HCD), were measured at a mass resolution of 60,000. This approach eliminates interference between ${}^{13}C^{1}H_{3}{}^{32}S^{16}O_{3}{}^{-}$ (m/z = 95.98419) and ${}^{12}C^{1}H_{3}{}^{32}S^{16}O_{2}{}^{17}O^{-}$ (m/z = 95.98506). Based on the dual-inlet system with 4 blocks for reference and 3 blocks for sample measurements, the reference/sample/reference comparison was carried out for 112 minutes (concentration: 25 nmol/L; flow-rate: 4 µL/min) to acquire data for each sample with a reproducibility for δ^{18} O and Δ^{17} O values of MSA better than ±1‰. By cross-calibrating our ESI-Orbitrap-MS measurements with the conventional IRMS method, we obtained a calibration slope that enabled us to estimate $\delta^{18}O(MSA)$ and $\Delta^{17}O(MSA)$ values of the samples with a precision better than ± 1 %. Overall, we developed a new analytical method based on nanomole-level MSA samples, which will be applied to natural atmospheric and/or ice core samples to trace atmospheric DMS oxidation chemistry.