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Triple oxygen isotope signature in methanesulfonate (MSA): method development and atmospheric application

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Dimethyl sulfide (DMS) is the primary natural sulfur source in the marine boundary layer, contributing to the formation of sulfate (SO_4^{2-}) and methanesulfonate (MSA, CH_3SO_3) through DMS chemistry. This process influences Earth's radiation budget, climate, and marine ecosystem by affecting atmospheric aerosol properties, which directly impact solar radiation and cloud properties. Understanding DMS chemistry is crucial for improving atmospheric models.

The mass-independent oxygen isotopic composition (^{17}O-excess, $\Delta^{17}O$) serves as a key tracer for atmospheric reactions. $\Delta^{17}O$ in Arctic ice cores reflects sulfate formation changes after SO_2 emission reductions in 1970 [1]. Recent Antarctic studies suggest MSA oxidation to SO_4^{2-}, with MSA potentially showing high $\Delta^{17}O$ values [2][3]. These findings impact the interpretation of $\Delta^{17}O$(nss-SO_4^{2-}) in Antarctic ice cores, particularly regarding the glacial-to-interglacial $\Delta^{17}O$ shift [4], which needs reevaluation [3].

Our results indicate that MSA's $\Delta^{17}O$ could exceed 10‰, making it a potential tracer for the atmospheric DMS oxidation processes. However, traditional method using gas-source Isotope Ratio Mass Spectrometry (IRMS) are limited by sample size and anaylticlal complexity. Here, we present a newly developed method using ESI-Orbitrap-MS to measure $\Delta^{17}O$ of MSA, achieving high sensitivity with a reproducibility of ±1‰ for 10 nmol MSA samples. This approach provides access to natural atmospheric and ice core samples, enhancing our ability to trace atmospheric DMS chemistry. This presentation also reports first observational results on $\Delta^{17}O$ of MSA in Antarctic aerosol samples.

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