Large Δ^{17} O in Atmospheric Methanesulfonate (MSA) Predicted by Δ^{17} O(SO₄²⁻) in Antarctic Atmosphere, Snow, and Ice Cores

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The ¹⁷O-excess (Δ^{17} O) of sulfate (SO₄²⁻) in ice cores offers significant potential for reconstructing past atmospheric oxidant chemistry, as demonstrated in previous study on an Arctic ice core[1]. In Antarctic ice cores, the data from Vostok ice core during the last glacial-interglacial cycle revealed higher Δ^{17} O(nss-SO₄²⁻) values during warm periods (Holocene: 2.8‰ ± 0.6‰; Eemian: 4.8‰ ± 0.1‰) compared to cold periods (Glacial: 2.0‰ ± 0.8‰)[2], interpreted as a shift of sulfate formation from liquid-phase sulfate formation (high Δ^{17} O) to gas-phase reactions (Δ^{17} O = 0‰). However, we have identified a considerable gap between atmospheric and ice core Δ^{17} O(nss-SO₄²⁻) values in Antarctica, which complicates the interpretation [3,4].

Through year-round observations of $\Delta^{17}O(nss-SO_4^{2^-})$ at inland and coastal sites (Dome C and Dumont d'Urville, respectively) in East Antarctica, we identified higher inland $\Delta^{17}O(nss-SO_4^{2^-})$ (2.0‰ ± 0.1‰) than coastal $\Delta^{17}O(nss-SO_4^{2^-})$ during spring-summer, negatively correlating with methanesulfonate (MSA) concentrations [3]. This suggests the possibility of chemical MSA oxidation to $SO_4^{2^-}$, which, in turn, implies MSA may have high $\Delta^{17}O$ value. Further analysis of $\Delta^{17}O(nss-SO_4^{2^-})$ in surface snow along a latitudinal transect in East Antarctica revealed that coastal $\Delta^{17}O(nss-SO_4^{2^-})$ values (1.0 ± 0.5‰) aligned with atmospheric variations, while higher $\Delta^{17}O(nss-SO_4^{2^-})$ values were observed in katabatic (2.7 ± 0.2‰) and inland (3.5 ± 0.3‰) regions. Given the correlation between $\Delta^{17}O(nss-SO_4^{2^-})$ values and MSA/sulfate ratios in Antarctic snow, the post-depositional MSA oxidation to $SO_4^{2^-}$ occurs in the snow. This has important implications for interpreting $\Delta^{17}O(nss-SO_4^{2^-})$ in Antarctic ice cores, particularly regaiding the shift in $\Delta^{17}O(nss-SO_4^{2^-})$ from glacial to interglacial periods, which was previously interpreted as a change in atmospheric sulfate formation but now requires reconsideration.

Overall, the predicted high $\Delta^{17}O(MSA)$ ranging from 8 to 15 ‰ provide a potential tracer for atmospheric chemical processes from dimethyl sulfide (DMS) to MSA that plays a key role in sulfur aerosol formation in the pristine environment both in Arctic and Antarctica. This presentation will also highlight recent advances in MSA isotope measurements using ESI-Orbitrap-MS [5]. Additionally, we have incorporated a $\Delta^{17}O(MSA)$ calculation scheme to the recent updated on DMS chemistry scheme of the GEOS-Chem, and these results will be discussed alongside observational data on $\Delta^{17}O(MSA)$.

Reference:

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