

Seasonal variations of multiple isotopic compositions of atmospheric sulfate and nitrate at coastal Antarctica

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Sulfur, nitroge, and oxygen isotopic compositions of atmospheric sulfate (SO_4^{2-}) and nitrate (NO_3^-) reflect their sources and formation pathways in the atmosphere. We present a year-round observation of multiple isotopic compositions of atmospheric sulfate (SO_4^{2-}) and nitrate (NO_3^-) in aerosol samples collected at Dumont d'Urville (66°40'S, 140°01'E), coastal Antarctica, throughout the year 2011.

Based on the measurements of triple oxygen isotopic compositions ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of atmospheric SO_4^{2-} and NO_3^- , we confirmed that $\Delta^{17}\text{O}$ values of SO_4^{2-} and NO_3^- reflect sunlight-driven changes in the relative contribution of O_3 oxidation to the oxidation by HO_x , RO_x , and H_2O_2 . In addition, by comparing $\Delta^{17}\text{O}$ values of SO_4^{2-} and NO_3^- to ozone mixing ratios, we found that $\Delta^{17}\text{O}$ values of SO_4^{2-} observed in spring (September to November) were lower than in fall (March to May), while there was no significant spring-fall difference in $\Delta^{17}\text{O}$ values of NO_3^- values. The relatively lower sensitivity of $\Delta^{17}\text{O}$ values of SO_4^{2-} to the ozone mixing ratio in spring compared to fall is possibly explained by (i) the increased contribution of SO_2 oxidations by OH and H_2O_2 caused by NO_x emission from snowpack and/or (ii) SO_2 oxidation by hypohalous acids ($\text{HOX} = \text{HOCl} + \text{HOBr}$) in the aqueous phase.

$\delta^{34}\text{S}$ values of SO_4^{2-} in summer season show similar values to dimethyl sulfide (DMS), in contrast to ^{34}S depletion in winter. This finding shows that the sulfur source of SO_4^{2-} in coastal Antarctica is not only marine biogenic production. Throughout the year, $^{33}\text{S}/^{32}\text{S}$ and $^{36}\text{S}/^{32}\text{S}$ ratios show no significant deviations from mass-dependent law, suggesting there are negligible contributions of mass-independent fractionation in clean coastal Antarctic regions.