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

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Sulfur, nitrogen, and oxygen isotopic compositions of atmospheric sulfate (SO\textsubscript{4}^{2−}) and nitrate (NO\textsubscript{3}−) reflect their sources and formation pathways in the atmosphere. We present a year-round observation of multiple isotopic compositions of atmospheric sulfate (SO\textsubscript{4}^{2−}) and nitrate (NO\textsubscript{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 (Δ\textsuperscript{17}O = \textsuperscript{δ17}O − 0.52 × \textsuperscript{δ18}O) of atmospheric SO\textsubscript{4}^{2−} and NO\textsubscript{3}−, we confirmed that Δ\textsuperscript{17}O values of SO\textsubscript{4}^{2−} and NO\textsubscript{3}− reflect sunlight-driven changes in the relative contribution of O\textsubscript{3} oxidation to the oxidation by HO\textsubscript{x}, RO\textsubscript{x}, and H\textsubscript{2}O\textsubscript{2}. In addition, by comparing Δ\textsuperscript{17}O values of SO\textsubscript{4}^{2−} and NO\textsubscript{3}− to ozone mixing ratios, we found that Δ\textsuperscript{17}O values of SO\textsubscript{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 Δ\textsuperscript{17}O values of NO\textsubscript{3}− values. The relatively lower sensitivity of Δ\textsuperscript{17}O values of SO\textsubscript{4}^{2−} to the ozone mixing ratio in spring compared to fall is possibly explained by (i) the increased contribution of SO\textsubscript{2} oxidations by OH and H\textsubscript{2}O\textsubscript{2} caused by NO\textsubscript{x} emission from snowpack and/or (ii) SO\textsubscript{2} oxidation by hypohalous acids (HOX = HOCl + HOBr) in the aqueous phase.

δ\textsuperscript{34}S values of SO\textsubscript{4}^{2−} in summer season show similar values to dimethyl sulfide (DMS), in contrast to \textsuperscript{32}S depletion in winter. This finding shows that the sulfur source of SO\textsubscript{4}^{2−} in coastal Antarctica is not only marine biogenic production. Throughout the year, \textsuperscript{33}S/\textsuperscript{32}S and \textsuperscript{36}S/\textsuperscript{32}S ratios show no significant deviations from mass-dependent law, suggesting there are negligible contributions of mass-independent fractionation in clean coastal Antarctic regions.