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Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica

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Abstract. Throughout the year 2001, aerosol samples were collected continuously for 10 to 15 days at the French Antarctic Station Dumont d'Urville (DDU) (66°40' S, l40°0' E, 40 m above mean sea level). The nitrogen and oxygen isotopic ratios of particulate nitrate at DDU exhibit seasonal variations that are among the most extreme observed for nitrate on Earth. In association with concentration measurements, the isotope ratios delineate four distinct periods, broadly consistent with previous studies on Antarctic coastal areas. During austral autumn and early winter (March to mid-July), nitrate concentrations attain a minimum between 10 and 30 ng m^{-3} (referred to as Period 2). Two local maxima in August (55 ng m^{-3}) and November/December (165 ng m^{-3}) are used to assign Period 3 (mid-July to September) and Period 4 (October to December). Period 1 (January to March) is a transition period between the maximum concentration of Period 4 and the background concentration of Period 2. These seasonal changes are reflected in changes of the nitrogen and oxygen isotope ratios. During Period 2, which is characterized by background concentrations, the isotope ratios are in the range of previous measurements at mid-latitudes: $\delta^{18}O_{vsmow}$=(77.2±8.6) ‰ ; $\Delta^{17}O$= (29.8±4.4) ‰ ; $\delta^{15}N_{air}$=(−4.4±5.4) ‰ (mean ± one standard deviation). Period 3 is accompanied by a significant increase of the oxygen isotope ratios and a small increase of the nitrogen isotope ratio to $\delta^{18}O_{vsmow}$= (98.8±13.9) ‰ ; $\Delta^{17}O$=(38.8±4.7) ‰ and $\delta^{15}N_{air}$=(4.3±8.20 ‰). Period 4 is characterized by a minimum $^{15}N/^{14}N$ ratio, only matched by one prior study of Antarctic aerosols, and oxygen isotope ratios similar to Period 2: $\delta^{18}O_{vsmow}$=(77.2±7.7) ‰ ; $\Delta^{17}O$=(31.1±3.2) ‰ ; $\delta^{15}N_{air}$=(−32.7±8.4) ‰ . Finally, during Period 1, isotope ratios reach minimum values for oxygen and intermediate values for nitrogen: $\delta^{18}O_{vsmow}$=63.2±2.5 ‰ ; $\Delta^{17}O$=24.0±1.1 ‰ ; $\delta^{15}N_{air}$=−17.9±4.0 ‰). Based on the measured isotopic composition, known atmospheric transport patterns and the current understanding of kinetics and isotope effects of relevant atmospheric chemical processes, we suggest that elevated tropospheric nitrate levels during Period 3 are most likely the result of nitrate sedimentation from polar stratospheric clouds (PSCs), whereas elevated nitrate levels during Period 4 are likely to result from snow re-emission of

nitrogen oxide species. We are unable to attribute the source of the nitrate during periods 1 and 2 to local production or long-range transport, but note that the oxygen isotopic composition is in agreement with day and night time nitrate chemistry driven by the diurnal solar cycle. A precise quantification is difficult, due to our insufficient knowledge of isotope fractionation during the reactions leading to nitrate formation, among other reasons.

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