



## Comprehensive isotopic composition of nitrate in Antarctic snow and atmospheric aerosol samples: Towards interpretation of the polar ice core record

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Nitrate ( $\text{NO}_3^-$ ) is the final product of the oxidation of atmospheric reactive nitrogen ( $\text{NO}_x$ ) and is one of the most abundant ions present in polar ice and snow. Stable isotope ratios of  $\text{NO}_3^-$  obtained from deep ice cores may serve as useful proxies for paleo-atmospheric conditions, such as  $\text{NO}_x$  removal pathways and the role of ozone ( $\text{O}_3$ ) in overall oxidation activity. However, strong post-depositional processing (photolysis of  $\text{NO}_3^-$  and desorption/evaporation of  $\text{HNO}_3$ ) has been shown to complicate the interpretation of long-term ice core records of nitrate. Analysis of  $\text{NO}_3^-$  obtained from a deep Antarctic ice core suggests that nitrogen stable isotopes are strongly impacted by surface processing, while the oxygen signal seems to be at least partially preserved. A primary goal of this study is to establish the atmosphere/surface snow transfer of the  $\text{NO}_3^-$  isotopic signal, particularly the  $\Delta^{17}\text{O}$  anomaly, which reflects the relative importance of different  $\text{NO}_3^-$  formation mechanisms.

Here we report measurements of the nitrogen ( $\delta^{15}\text{N}$ ) and triple oxygen ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) isotopic composition of  $\text{NO}_3^-$  and use them to infer the origin and fate of  $\text{NO}_x$  and  $\text{NO}_3^-$  in the Antarctic atmosphere and surface snow on a seasonal basis. Surface snow ("skin layer," first 3-4 mm) and aerosol samples were collected at Dome C, Antarctica ( $75^\circ 06'\text{S}$ ,  $123^\circ 21'\text{E}$ , altitude 3233 m a.s.l.) throughout 2009. Preliminary results indicate that the seasonal variations in the oxygen isotopic composition of  $\text{NO}_3^-$  in the skin layer closely follow those of atmospheric  $\text{NO}_3^-$ , suggesting that the upper-most snow layer acts as an integrator of the atmospheric signal. In the winter, the  $\Delta^{17}\text{O}$  ( $\text{NO}_3^-$ ) of both surface snow and aerosols reach maximum values (40-45 per mil), reflecting an increased interaction of  $\text{NO}_x$  with stratospheric ozone ( $\text{O}_3$ ), which possesses a strongly positive oxygen isotope anomaly. The lowest  $\Delta^{17}\text{O}$  ( $\text{NO}_3^-$ ) values (25-30 per mil) for surface snow and aerosols are observed in the late spring and early summer when  $\text{O}_3$  concentrations are at a seasonal low and atmospheric  $\text{NO}_3^-$  production occurs predominantly through reaction of  $\text{NO}_x$  with the hydroxyl radical (OH). Conversely, skin layer  $\delta^{15}\text{N}$  ( $\text{NO}_3^-$ ) values are consistently enriched by 10-20 per mil over the atmospheric signal throughout most of the year. This observation indicates fractionation of  $\text{NO}_3^-$  isotopes during post-depositional processing, which is known to preferentially remove lighter isotopologues from the snowpack; however, the persistence of this offset through the winter months cannot be explained at the present time. For both the  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$ , an approximate equilibrium between the atmosphere and skin layer is achieved in the late spring/early summer, when atmospheric  $\text{NO}_3^-$  concentrations reach their annual maxima ( $> 100 \text{ ng m}^{-3}$ ). This strongly suggests that  $\text{NO}_3^-$  removal and subsequent recycling is very intense and most likely composed of more than one cycle (i.e., removal, atmospheric processing, redeposition or possibly export). Information on these cycles is critical to the development of a conceptual view of  $\text{NO}_3^-$  recycling at the snow surface on the Antarctic plateau.