



Oxygen isotope dynamics of atmospheric nitrate over the Antarctic plateau: First combined measurements of ozone and nitrate 17O-excess ($\Delta 17\text{O}$)

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Variations in the isotopic composition of atmospheric nitrate (NO_3^-) provide novel indicators for important processes in boundary layer chemistry, often acting as source markers for reactive nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) and providing both qualitative and quantitative constraints on the pathways that determine its fate. Stable isotope ratios of nitrate ($\delta^{15}\text{N}$, $\delta^{17}\text{O}$, $\delta^{18}\text{O}$) offer direct insight into the nature and magnitude of the fluxes associated with different processes, thus providing unique information regarding phenomena that are often difficult to quantify from concentration measurements alone. The unique and distinctive 17O-excess ($\Delta 17\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of ozone (O_3), which is transferred to NO_x via oxidation reactions in the atmosphere, has been found to be a particularly useful isotopic fingerprint in studies of NO_x transformations. Constraining the propagation of 17O-excess within the NO_x cycle is critical in polar areas where there exists the possibility of extending atmospheric interpretations to the glacial/interglacial time scale using deep ice core records of nitrate.

Here we present measurements of the comprehensive isotopic composition of atmospheric nitrate collected at Dome C, Antarctica during December 2011 to January 2012. Sampling was conducted within the framework of the OPAL (Oxidant Production over Antarctic Land and its Export) project, thus providing an opportunity to combine our isotopic observations with a wealth of meteorological and chemical data, including in-situ concentration measurements of the gas-phase precursors involved in nitrate production (NO_x , O_3 , OH , HO_2 , etc.). Furthermore, nitrate isotope analysis has been combined in this study for the first time with parallel observations of the transferrable $\Delta 17\text{O}$ of surface ozone, which was measured concurrently at Dome C using our recently developed analytical approach. This unique dataset has allowed for a direct comparison of observed $\Delta 17\text{O}(\text{NO}_3^-)$ values to those that are calculated solely from local measurements and invoke no assumptions regarding the $\Delta 17\text{O}$ value of ozone and its transfer in the atmosphere. The predicted $\Delta 17\text{O}$ signature for nitrate formed over the Antarctic plateau during OPAL is on the order of $(21 \pm 2) \text{‰}$ when production is assumed to occur only through the $\text{OH} + \text{NO}_2$ pathway, which is expected to be the dominant formation channel during the continuously sunlit summer. This predicted value is much lower than the values measured for nitrate during OPAL, with observed $\Delta 17\text{O}(\text{NO}_3^-)$ varying in the range of 27 - 31 ‰. This discrepancy between expected and observed $\Delta 17\text{O}(\text{NO}_3^-)$ values suggests the existence of an unexpected process that contributes significantly to the atmospheric nitrate budget over Dome C. The relative merits of different potential explanations for this puzzling result will be discussed in the context of oxidation chemistry, air mass transport, and snow/atmosphere exchange.