



Empirical sensitivity of $\delta^{15}\text{N}$ in nitrate to current snow accumulation rates in Antarctica : implications for the interpretation of the deep Vostok ice core

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Antarctic deep ice cores provide long term archives of compounds produced in the atmosphere such as nitrate (NO_3^-). At sites with low snow accumulation rates, nitrate undergoes intense surface loss processes after its deposition to the snow. Previous isotopic studies have shown that the subsequent surface recycling has a strong impact on nitrogen stable isotopic ratios in nitrate, expressed as $\delta^{15}\text{N}(\text{NO}_3^-)$ (indeed, values up to +339 ‰ have been observed in the upper firn at Dome C, Antarctica) and that UV-photolysis is an important process responsible for NO_3^- loss from snow. If we assume that photolytic fractionation dominates nitrate mass loss, then photolysis rates j_{-14} and j_{-15} are the main parameters controlling the mass loss and isotopes. Their ratio ϵ and magnitude are in turn determined by a list of parameters including actinic flux spectrum, nitrate absorption cross sections for each isotopologue, quantum yield (if variable with λ). Local snow accumulation rates (that determine NO_3^- exposure time to UV) are expected to drive the strength of the nitrate photolytic loss from snow but the sensitivity to this parameter remains poorly documented. To address this, we have measured the empirical sensitivity of $\delta^{15}\text{N}$ in nitrate to current snow accumulation rates based on the measurement of $\delta^{15}\text{N}(\text{NO}_3^-)$ from 19 shallow (20 and 50 cm) snow pits. Those were collected on the route from the French coastal station Dumont D'Urville to the high Antarctic plateau (Dome C and Vostok) during the austral summers 2007–08 and 2009–10. We assume that UV conditions are the same at each location.

$\delta^{15}\text{N}(\text{NO}_3^-)$ is found to be close to the global mean atmospheric range (–10 to +10 ‰) for sites with snow accumulation rates greater than $150 \text{ kg.m}^{-2}.\text{yr}^{-1}$ (at 2700 m.a.s.l. – corresponding to an accumulation approximately 5 times greater than the current snow accumulation rate at Dome C). However, $\delta^{15}\text{N}(\text{NO}_3^-)$ is highly sensitive to snow accumulation rates lower than $150 \text{ kg.m}^{-2}.\text{yr}^{-1}$, reaching values as high as +360 ‰ at Vostok ($22 \text{ kg.m}^{-2}.\text{yr}^{-1}$). We use a conceptual modeling approach to reproduce the empirical sensitivity of post-depositional fractionation on modern accumulation rates. This study is a first step towards an isotopic atmosphere-snow transfer function which is needed to interpret the deep Vostok ice-core record. Indeed, measurements of $\delta^{15}\text{N}(\text{NO}_3^-)$ in the deep Vostok core reveal values ranging from +89 to +316 ‰ over the last 150,000 years (one and a half climatic cycle). Based on this first study, we attempt to deconvolute effects on $\delta^{15}\text{N}(\text{NO}_3^-)$ due to changes in snow accumulation rates to those due to the UV flux spectrum. We estimate that only a part of the variability in $\delta^{15}\text{N}(\text{NO}_3^-)$ can be explained by changes in snow accumulation rates at Vostok, the remaining being due to changes in the UV flux spectrum.