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Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling

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Abstract. The nitrogen ($\delta^{15}N$) and triple oxygen ($\delta^{17}O$ and $\delta^{18}O$) isotopic composition of nitrate (NO_3^-) was measured year-round in the atmosphere and snow pits at Dome C, Antarctica (DC, 75.1° S, 123.3° E), and in surface snow on a transect between DC and the coast. Comparison to the isotopic signal in atmospheric NO_3^- shows that snow NO_3^- is significantly enriched in $\delta^{15}N$ by >200 ‰ and depleted in $\delta^{18}O$ by <40 ‰. Post-depositional fractionation in $\Delta^{17}O(NO_3^-)$ is small, potentially allowing reconstruction of past shifts in tropospheric oxidation pathways from ice cores. Assuming a Rayleigh-type process we find fractionation constants ε of −60±15 ‰, 8±2 ‰ and 1±1 ‰, for $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$, respectively. A photolysis model yields an upper limit for the photolytic fractionation constant $^{15}\varepsilon$ of $\delta^{15}N$, consistent with lab and field measurements, and demonstrates a high sensitivity of $^{15}\varepsilon$ to the incident actinic flux spectrum. The photolytic $^{15}\varepsilon$ is process-specific and therefore applies to any snow covered location. Previously published $^{15}\varepsilon$ values are not representative for conditions at the Earth surface, but apply only to the UV lamp used in the reported experiment (Blunier et al., 2005; Jacobi et al., 2006). Depletion of oxygen stable isotopes is attributed to photolysis followed by isotopic exchange with water and hydroxyl radicals. Conversely, ^{15}N enrichment of the NO_3^- fraction in the snow implies ^{15}N depletion of emissions. Indeed, $\delta^{15}N$ in atmospheric NO_3^- shows a strong decrease from background levels (4±7 ‰) to −35 ‰ in spring followed by recovery during summer, consistent with significant snowpack emissions of reactive nitrogen. Field and lab evidence therefore suggest that photolysis is an important process driving fractionation and associated NO_3^- loss from snow. The $\Delta^{17}O$ signature confirms previous coastal measurements that the peak of atmospheric NO_3^- in spring is of stratospheric origin. After sunrise photolysis drives then redistribution of NO_3^- from the snowpack photic zone to the atmosphere and a snow surface skin layer, thereby concentrating NO_3^- at the surface. Little NO_3^- appears to be exported off the EAIS plateau, still snow emissions from as far as 600 km inland can contribute to the coastal NO_3^- budget.

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