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New joint isotopic analyses of N₂O and NO₃⁻ in Antarctic ice cores for investigating the processes of N₂O in situ production

Content

Nitrous oxide (N₂O) is a trace gas in the atmosphere involved in the destruction of stratospheric ozone through its photodissociation products. It is also a greenhouse gas whose concentration has varied substantially in the past. Direct reconstruction of these past variations is only possible by analyzing the air bubbles archived in ice cores. However, some sections of Antarctic ice cores are affected by *in situ* production of N₂O. As this artifact is not yet quantified, there is no continuous record of atmospheric N₂O so far. Furthermore, ice core information on atmospheric N₂O concentration and its nitrogen and oxygen isotopic composition can be used to reconstruct changes in the terrestrial and marine sources. Existing isotopic data show that the isotopic composition of *in situ* produced N₂O can be very different from that of atmospheric N₂O. The measured isotopic signal and concentration must therefore be systematically corrected for the *in situ* contribution, even if minor, to avoid wrong interpretations regarding the N₂O source attribution.

With the use of isotopic analyses, this study aims at understanding the processes leading to N₂O production in Antarctic ice. The *in situ* production of N₂O occurs specifically during glacial periods, where the dust content is higher compared to interglacials. In addition to being different from the atmospheric signal, the isotopic signature of *in situ* N₂O appears to depend on the accumulation rate. An enrichment in ¹⁵N compared to the atmospheric signature is observed for low accumulation sites, with a δ¹⁵N *in situ* signature in the range of +60‰ for Dome C (EDC) and Vostok, whereas a depletion is observed for higher accumulation sites, with a δ¹⁵N around -10‰ for Dronning Maud Land (EDML).

Based on these observations, nitrate (NO₃⁻) could be a good candidate as a precursor of *in situ* N₂O in ice. Nitrate concentration in ice cores is higher and more variable during glacial periods, following a similar trend to dust levels, and its isotopic composition is also impacted by the accumulation rate through post-depositional processes. The photolysis of nitrate, accentuated in low accumulation sites, induces a high enrichment in ¹⁵N – up to +300‰ during glacial periods in Vostok.

To test the hypothesis of a potential reaction from nitrate substrate in the ice, we carried out joint measurements of nitrogen and oxygen isotopic compositions of N₂O and NO₃⁻ in samples from EDC, EDML, and Talos Dome – a core with low dust content. These new isotopic analyses spanning the Last Glacial Maximum and MIS4 will be used to quantify the N₂O *in situ* contribution using a mass balance approach, and to investigate the correlation between NO₃⁻ and *in situ* N₂O isotopic signatures.

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