

In situ production of N₂O in ice challenges past N₂O reconstructions

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The production of N₂O in glacial ice alters the record of past atmospheric concentrations of N₂O in ice cores. Using isotope analyses of N₂O would help understand the production processes and, thus, isolate the atmospheric signal.

Air bubbles trapped in ice cores represent the only direct paleo-atmospheric archive, and allow for, for example, the reconstruction of past greenhouse gas concentrations. But ice cores are not an inert medium; many chemical and physical processes take place in the ice. Under certain conditions, and for certain compounds, these processes can alter the signal stored in the enclosed air bubbles over time. The measured signals then no longer correspond exactly to the past composition of the atmosphere. Production of CO₂ in Greenland ice cores and N₂O in both Greenland and Antarctic ice cores are prominent examples for such an alteration of the atmospheric signal (Stauffer et al. 2003).

N₂O: A growing climate threat

The study of N₂O is important as it is a potent greenhouse gas that is also involved in the destruction of stratospheric ozone. The atmospheric concentration of N₂O, with a global warming potential 273 times higher than CO₂, has been increasing continuously over the past 150 years, reaching 332 ppb in 2019 (IPCC 2021). Currently, anthropogenic (mainly agricultural) sources contribute 43% of total N₂O emissions, and natural sources from soils and oceans account for 57% (Tian et al. 2020). The main N₂O sink

is photochemical destruction in the stratosphere, and its preindustrial atmospheric lifetime is 123 years (Prather et al. 2015). Warmer climate seems to enhance natural N₂O emissions, resulting in a positive feedback (Schilt et al. 2010a). This effect is difficult to predict because present and past N₂O dynamics are poorly understood (Fischer et al. 2019). Reconstructed atmospheric N₂O concentrations vary substantially on glacial-interglacial timescales (Flückiger et al. 2004; Schilt et al. 2010a). However, significant parts of the 800-kyr atmospheric record of N₂O are missing due to in situ formation of N₂O in glacial ice, rich in mineral dust (Fig. 1).

In situ production of N₂O

Several observations indicate that the N₂O concentrations measured in the ice are affected by a non-atmospheric source. For example, ice cores from different drilling sites show significantly different N₂O values for given time periods (Schilt et al. 2010a, b). Considering the long atmospheric lifetime of N₂O and, as a result, its geographically homogenous atmospheric concentration, this observation is inconsistent with only atmospheric N₂O variations. The non-atmospheric source alters the N₂O records exclusively during glacial periods, when the dust

concentrations are high (Fig. 1). This indicates a production of N₂O from compounds in, or attached to, aeolian dust deposited onto the ice sheet (Schilt et al. 2010a).

For most Antarctic ice cores, the dust-rich sections are almost entirely affected by in situ N₂O production (Schilt et al. 2010a). Comparing different ice cores from Antarctica, the highest N₂O concentrations are found in ice cores with the highest dust levels (Schilt et al. 2010b). In contrast, in situ N₂O production in Greenland ice is not correlated with dust concentrations, and mainly occurs at the beginning and end of the Dansgaard-Oeschger events (Flückiger et al. 2004). Because these climatic transitions are associated with changes in chemical composition of the dust, N₂O production is likely controlled by this factor.

Previous approaches

In situ N₂O production represents a challenge for reconstructing the past atmospheric concentrations of N₂O during glacial periods. To avoid misinterpretation in terms of past climatic variations and derived changes in marine and terrestrial sources, in situ production must be systematically detected.

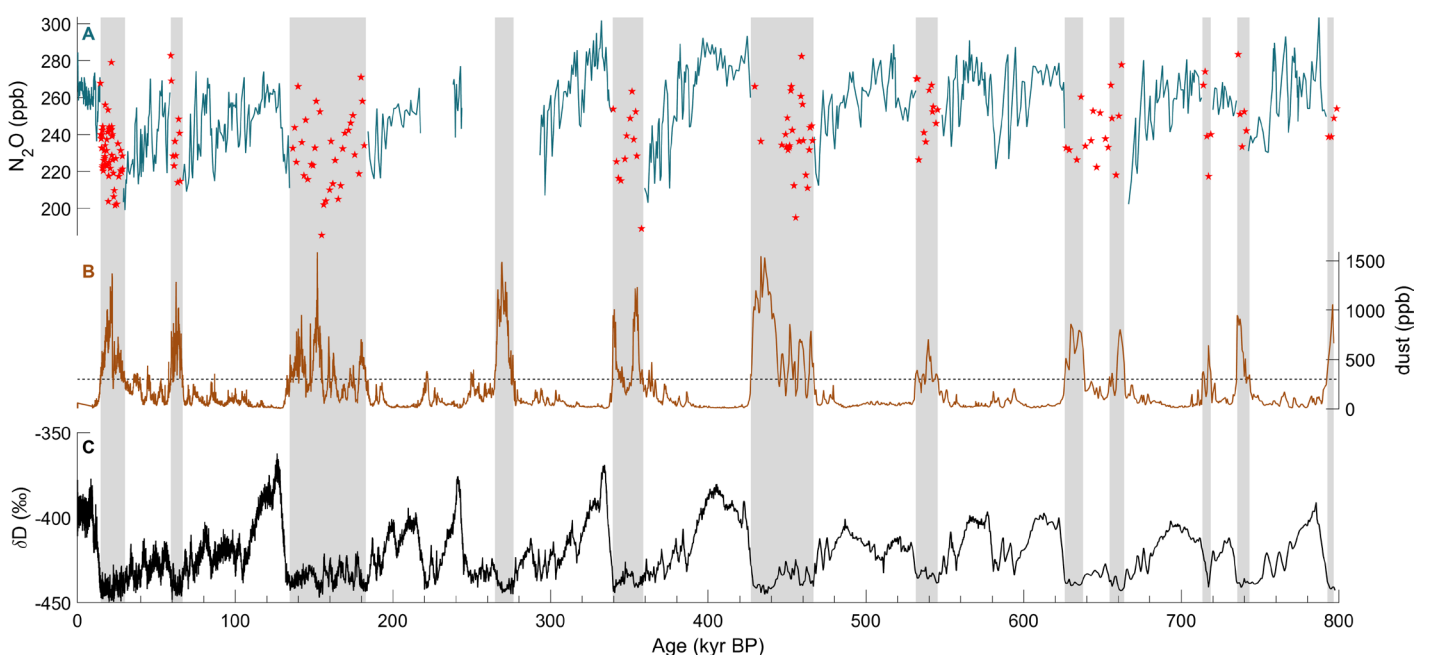


Figure 1: (A) Measured N₂O concentrations from the EDC ice core (Schilt et al. 2010a). Samples likely affected by in situ production are marked by red stars. (B) EDC dust concentration measured by laser scattering (Lambert et al. 2008). Gray-shaded areas mark sections with dust concentrations above the threshold of 300 ppb (dashed line). (C) EDC δD used as a temperature proxy (Landais and Stenni 2021).

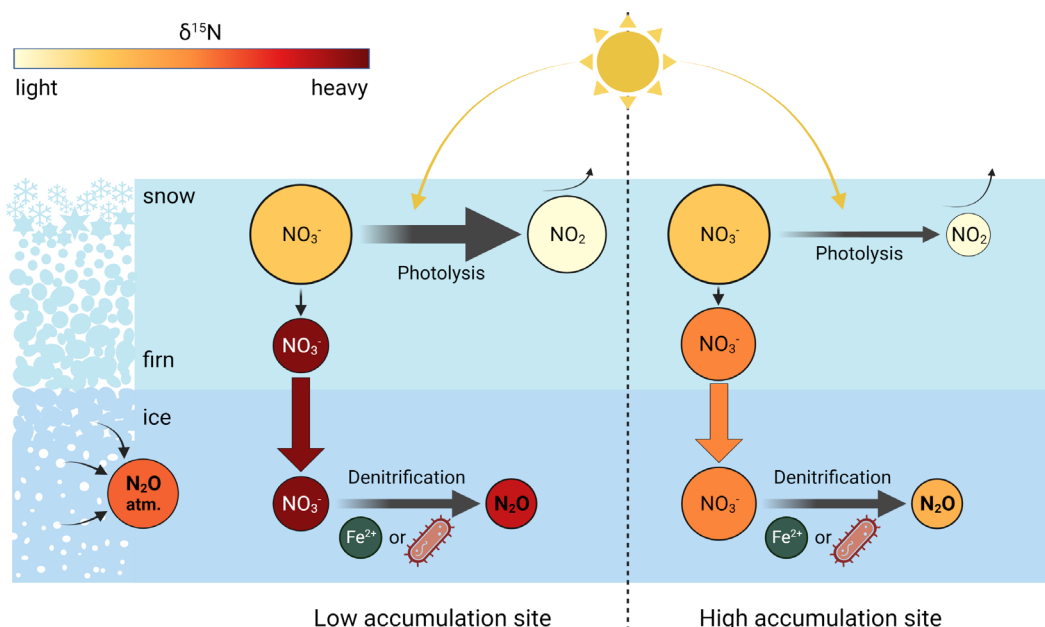


Figure 2: Schematic of the hypothesized process of N_2O in situ production in the ice. Since the snow accumulation rate controls the isotopic fractionation of NO_3^- photolysis, NO_3^- archived in ice has a different nitrogen isotopic signature at low and high accumulation sites. If NO_3^- is the precursor of in situ N_2O , this isotopic difference is transferred to N_2O through denitrification, also associated with fractionation.

Flückiger et al. (2004) used a detection algorithm for Greenland ice that iteratively identifies N_2O values exceeding a threshold of 8 ppb, which is about 3% of the typical glacial atmospheric concentrations, above a smoothing spline calculated through the whole dataset. However, this algorithm is only applicable to high-resolution datasets affected by erratic outliers, and is not valid for sharp rises in atmospheric concentration that could be mistaken for N_2O outliers. The second approach, applied to lower-resolution records from Antarctic ice cores, identifies samples with a dust concentration above 300 ppb (Fig. 1; Spahni et al. 2005). This dust threshold is purely empirical and does not reflect the complexity of the N_2O production. Indeed, if in situ N_2O production in Antarctic ice is roughly proportional to the dust content, samples below this threshold may still be affected (e.g. at 640 kyr BP in Fig. 1). In summary, such detection algorithms help to improve the records, but are heuristic at best, and do not allow us to correct for the in situ contribution. For this, process understanding of the in situ formation is required.

A new process-based quantification method

In the framework of the DEEPICE project, we seek to understand the processes responsible for N_2O production. By identifying the chemical reaction at play, and the specific conditions necessary for its occurrence, we target three objectives: 1) to systematically detect the samples affected by in situ N_2O to avoid misinterpretation of atmospheric N_2O variations; 2) to quantify and predict the amount of in situ production in ice samples; and 3) to correct the N_2O measurements to isolate the atmospheric N_2O signal. Since isotope analysis is a powerful tool to trace sources of a compound, and previous work showed that the in situ fraction has an isotopic signature distinct from the atmospheric fraction (Fischer et al. 2019; Sowers 2001), our approach is based on the isotope

analysis of N_2O and impurities that may be precursors of the N_2O in situ produced (Fig. 2).

Investigating the reaction consists, first of all, in identifying the precursors and reactants. The two main production pathways for N_2O are nitrification, i.e. conversion of ammonium (NH_4^+) to nitrate (NO_3^-) with N_2O as a byproduct, and denitrification, i.e. reduction of NO_3^- to N_2O (Baggs 2011). The amounts of NO_3^- and NH_4^+ in ice are both more than enough to form the observed amounts of in situ N_2O . Comparing N_2O data from different ice cores, we observe that in drilling sites with low snow accumulation rates the in situ fraction of N_2O has high $\delta^{15}N$ values compared to the atmospheric fraction. This is the case in the Vostok (Sowers 2001) and EDC (unpublished data) ice cores. The $\delta^{15}N$ value of NO_3^- , impacted by post-depositional processes, is also higher with a decreasing accumulation rate. Indeed, NO_3^- photolysis in snow is accentuated in low accumulation sites, inducing high enrichment in ^{15}N (Fig. 2; Erbland et al. 2013). These similar isotopic enrichments make NO_3^- a good candidate as a precursor of in situ N_2O . To test this hypothesis, we are currently performing joint measurements of the nitrogen and oxygen isotopic compositions of N_2O and NO_3^- in the same samples. The in situ fraction of N_2O and its isotopic composition are calculated using a mass balance approach, with atmospheric values as defined by the almost unaffected 140-kyr record from the Talos Dome ice core (Schilt et al. 2010b). Correlated isotopic signatures of NO_3^- and in situ N_2O would point to a denitrification reaction.

Our next step is to take a closer look at the production pathway. Denitrification can be performed by bacteria and through abiotic processes (Fig. 2). For example, NO_3^- is reduced to N_2O by Fe^{2+} (Samarkin et al. 2010). As the intramolecular distribution of ^{15}N in the N_2O molecule ($^{15}N-^{14}N-O$ or $^{14}N-^{15}N-O$) only depends on the production pathway,

we plan to measure the position-dependent isotope ratio of nitrogen in N_2O to distinguish between a biotic or abiotic reaction.

Conclusion

A precise understanding of the processes leading to N_2O in situ production represents a major step forward in interpreting and completing the N_2O record, which would complement the existing Antarctic CO_2 and CH_4 records over the last 800 kyr. Knowing the past variations of the three most important greenhouse gases is crucial to understanding the climate system, and, thus, better predict future climate change.

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