In situ production of N\textsubscript{2}O in ice challenges past N\textsubscript{2}O reconstructions

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The production of N\textsubscript{2}O in glacial ice alters the record of past atmospheric concentrations of N\textsubscript{2}O in ice cores. Using isotope analyses of N\textsubscript{2}O 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 CO\textsubscript{2} in Greenland ice cores and N\textsubscript{2}O in both Greenland and Antarctic ice cores are prominent examples for such an alteration of the atmospheric signal (Stauffer et al. 2003).

N\textsubscript{2}O: A growing climate threat

The study of N\textsubscript{2}O is important as it is a potent greenhouse gas that is also involved in the destruction of stratospheric ozone. The atmospheric concentration of N\textsubscript{2}O, with a global warming potential 273 times higher than CO\textsubscript{2}, has been increasing continuously over the past 150 years, reaching 332 ppb in 2019 (IPCC 2021). Currently, anthropogenic emissions, and natural sources from soils and oceans account for 57% (Tian et al. 2020). The main N\textsubscript{2}O 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 N\textsubscript{2}O emissions, resulting in a positive feedback (Schilt et al. 2010a). This effect is difficult to predict because present and past N\textsubscript{2}O dynamics are poorly understood (Fischer et al. 2019). Reconstructed atmospheric N\textsubscript{2}O 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 N\textsubscript{2}O are missing due to in situ formation of N\textsubscript{2}O in glacial ice, rich in mineral dust (Fig. 1). This can alter the signal stored in the enclosed air bubbles over time. If the measured signals then no longer correspond exactly to the past composition of the atmosphere, production of N\textsubscript{2}O in Greenland ice is not solely on glacial-interglacial timescales (Flückiger et al. 2004; Schilt et al. 2010a). In contrast, in situ N\textsubscript{2}O 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, N\textsubscript{2}O production is likely controlled by this factor.

Previous approaches

In situ N\textsubscript{2}O production represents a challenge for reconstructing the past atmospheric concentrations of N\textsubscript{2}O 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 N\textsubscript{2}O 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).](https://example.com/figure1)
Figure 2: Schematic of the hypothesized process of N\textsubscript{2}O in situ production in the ice. Since the snow accumulation rate controls the isotopic fractionation of N\textsubscript{2}O, photolysis of N\textsubscript{2}O archived in ice has a different nitrogen isotopic signature at low and high accumulation sites. If N\textsubscript{2}O is the precursor of in situ N\textsubscript{2}O, this isotopic difference is transferred to N\textsubscript{2}O through denitrification, also associated with fractionation.

A new process-based quantification method

In the framework of the DEEPICE project, we seek to understand the processes responsible for N\textsubscript{2}O 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\textsubscript{2}O to avoid misinterpretation of atmospheric N\textsubscript{2}O variations; 2) to quantify and predict the amount of in situ production in ice samples; and 3) to correct the N\textsubscript{2}O measurements to isolate the atmospheric N\textsubscript{2}O signal. Since isotopic 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 isotopic analysis of N\textsubscript{2}O and impurities that may be precursors of the N\textsubscript{2}O 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\textsubscript{2}O are nitrification, i.e. conversion of ammonium (NH\textsubscript{4}\textsuperscript{+}) to nitrate (NO\textsubscript{3}\textsuperscript{-}) with N\textsubscript{2}O as a byproduct, and denitrification, i.e. reduction of NO\textsubscript{3}\textsuperscript{-} to N\textsubscript{2}O (Baggs 2011). The amounts of NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} in ice are both more than enough to form the observed amounts of in situ N\textsubscript{2}O. Comparing N\textsubscript{2}O data from different ice cores, we observe that in drilling sites with low snow accumulation rates the in situ fraction of N\textsubscript{2}O has high δ\textsuperscript{15}N values compared to the atmospheric fraction. This is the case in the Vostok (Sowers 2001) and EDC (unpublished data) ice cores. The δ\textsuperscript{15}N value of N\textsubscript{2}O, impacted by post-depositional processes, is also higher with a decreasing accumulation rate. Indeed, NO\textsubscript{3}\textsuperscript{-} photolysis in snow is accentuated in low accumulation sites, inducing high enrichment in δ\textsuperscript{15}N (Fig. 2; Erbland et al. 2013). These similar isotopic enrichments make N\textsubscript{2}O a good candidate as a precursor of in situ N\textsubscript{2}O. To test this hypothesis, we are currently performing joint measurements of the nitrogen and oxygen isotopic compositions of N\textsubscript{2}O and NO\textsubscript{3}\textsuperscript{-}, in the same samples. The in situ fraction of N\textsubscript{2}O and its isotopic composition are calculated using a mass balance approach, with atmospheric values as defined by the almost unaffected 140-kyear record from the Talos Dome ice core (Schilt et al. 2010b). Correlated isotopic signatures of N\textsubscript{2}O and in situ N\textsubscript{2}O 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\textsubscript{3}\textsuperscript{-} is reduced to N\textsubscript{2}O by Fe\textsuperscript{2+} (Samarkin et al. 2010). As the intramolecular distribution of δ\textsuperscript{15}N in the N\textsubscript{2}O molecule (δ\textsuperscript{15}N=δ\textsuperscript{15}N-O or δ\textsuperscript{15}N=δ\textsuperscript{15}N-O) only depends on the production pathway, we plan to measure the position-dependent isotope ratio of nitrogen in N\textsubscript{2}O to distinguish between a biotic or abiotic reaction.

Conclusion

A precise understanding of the processes leading to N\textsubscript{2}O in situ production represents a major step forward in interpreting and completing the N\textsubscript{2}O record, which would complement the existing Antarctic CO\textsubscript{2} and CH\textsubscript{4} records over the last 800 kyear. 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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