What is controlling δO₂/N₂ variability in ice-core records?
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O₂ to N₂ ratios from air entrapped in ice cores are used as a proxy for insolation, providing a robust dating technique. However, many uncertainties surround the record formation due to limited understanding of the mechanisms driving the insolation signal.

Ice cores are unique archives because they contain bubbles which store samples of the atmosphere over the last several millions of years. In particular, ice cores provide records of greenhouse gas concentration (CO₂, CH₄, N₂O). Less emphasis has been put on the reconstruction of atmospheric O₂ concentration from air trapped in ice cores, despite its importance in global biogeochemical cycles. This is because the concentration of O₂ in air bubbles is affected by processes associated with pore close-off (Fig. 2). We traditionally express the concentration of O₂ by measuring the ratio of O₂ to N₂ trapped in the ice with reference to today’s atmospheric O₂/N₂ (denoted as δO₂/N₂).

In addition to providing a record of natural variability in atmospheric O₂ concentrations, δO₂/N₂ records, both from Antarctica and Greenland, are strongly anti-correlated with local insolation intensity at the summer solstice (Fig. 1; e.g. Bender 2002). O₂ in trapped gas is relatively depleted compared to N₂ during periods of high insolation, and vice versa. The strong resemblance between the summer solstice insolation variability and the δO₂/N₂ variability paved the way for a new dating method, based on the tuning of δO₂/N₂ values versus the well-known curves of past local insolation. However, our understanding of the processes causing the insolation imprint are incomplete, which limits a precise reconstruction of past variability in atmospheric O₂ concentration and increases uncertainty when using δO₂/N₂ as a dating tool.

While this incomplete understanding does not necessarily decrease the usefulness of δO₂/N₂ for ice-core dating, it is important to be able to physically describe the mechanisms. In this article, we present recent and ongoing efforts to understand 1) the natural variability of O₂/N₂ in the atmosphere from ice-core records, and 2) the processes within the ice sheet that cause O₂ to be depleted in air bubbles during high insolation periods.

Natural variability of O₂/N₂ in the atmosphere
At present, seasonal cycles are apparent in measurements of atmospheric O₂/N₂ from multiple meteorological stations. Biological productivity causes an enrichment of O₂ during the summer months (photosynthesis dominated) and a decrease during winter (respiration dominated), with an inverted pattern between hemispheres due to slow inter-hemispheric mixing of air (Keeling et al. 1998). These seasonal effects are not recorded in ice-cores because of air diffusion over several years before the pore closure process. However, the seasonality is a response to productivity in the biosphere, and, thus, we may expect that long-term changes in productivity could influence absolute δO₂/N₂ values.

Over the past 800 kyr, a gradual decreasing trend in δO₂/N₂ first observed in the EPICA Dome C (EDC) record (Bazin et al. 2016; Landais et al. 2012), is apparent in various ice-core records from Antarctica and Greenland (Stopler et al. 2016). This quasi-coherence between records suggests a decrease in atmospheric O₂, posited to be the result of increased rock weathering throughout the Pleistocene (Stopler et al. 2016; Yan et al. 2021). Yan et al. (2021) used discontinuous δO₂/N₂ measurements on 1.5-million-year-old (Myr) ice from the Alan Hills to propose that the decreasing trend in δO₂/N₂ may have started around the Mid-Pleistocene Transition (MPT; around 1200–800 kyr BP). They observed comparable mean δO₂/N₂ values between samples from 1.5 Myr and 800 kyr, thus deviating from the steady decrease in δO₂/N₂ of 8.4‰ per million years (Stopler et al. 2016). This poses interesting questions as to the drivers of the MPT.

Superimposed onto this long-term trend is an orbital-scale cyclicity in δO₂/N₂ records, which closely follows the local insolation curve for a given site. While part of this variability can be attributed to biological or geological causes, the first-order influence
1) Effusion through thin channels

The escape of small molecules, specifically O$_2$ in this case, through narrow channels in the ice lattice. A 3.6 Å threshold is expected given that molecules with larger diameters appear to be unaffected (e.g. N$_2$, Kr, Xe, CO$_2$) (Huber et al. 2006).

2) Molecular diffusion through the ice lattice

Pressure gradients between closed bubbles and neighboring open pores enable smaller molecules (O$_2$, Ar, Ne, He) to permeate through thin ice walls, either by the breaking of hydrogen bonds, or by jumping between stable sites in the ice lattice, where the energy needed to jump depends on the size and mass of the molecule (Ikeda-Fukazawa et al. 2005; Severinghaus and Battle 2006).

Variations in insolation are expected to modify the snow grains’ physical properties that determine the channel structure and ice matrix of the deep firn, and which, in turn, modulate the O$_2$ loss from forming bubbles (Bender 2002; Suwa and Bender 2008). However, we still lack a clear physical explanation that links the fractionation process and the physical mechanism, which results in large uncertainties being associated with the quantitative interpretation of the SO$_2$/N$_2$ records. Moreover, the slope of the linear regression between SO$_2$/N$_2$ and insolation varies between sites, suggesting that additional parameters are influencing SO$_2$/N$_2$ possibly relating to local climate conditions. Any mechanistic explanation would surely include climate parameters (such as accumulation rate or temperature), which have additional influences on the snow properties at the surface, and, thus, the firm properties. A 100-kyr periodicity in the SO$_2$/N$_2$ data from Dome C indicates a glacial-interglacial cycle imprint showing at least a long-term climatic influence (Bazin et al. 2016). Whether this is the result of physical processes or changes in atmospheric composition remains unclear.

Outlook

While many unknowns are associated with the use of SO$_2$/N$_2$ as a proxy for insolation, it provides an excellent ice-core dating tool, especially when considering old ice. The upcoming Beyond EPICA Oldest Ice Core project has the potential to resolve the behavior of atmospheric O$_2$/(SO$_2$/N$_2$) prior to the MPT by providing continuous records from the last 1.5 million years to corroborate the Alan Hills data (Yan et al. 2021).

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