doi.org/10.22498/pages.31.2.78

What is controlling $\delta O_2/N_2$ variability in ice-core records?

Romilly Harris Stuart and Amaëlle Landais

O_2 to N_2 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 (CO_2, CH_4, N_2O). Less emphasis has been put on the reconstruction of atmospheric O_2 concentration from air trapped in ice cores, despite its importance in global biogeochemical cycles. This is because the concentration of O_2 in air bubbles is affected by processes associated with pore close-off (Fig. 2). We traditionally express the concentration of O_2 by measuring the ratio of O_2 to N_2 trapped in the ice with reference to today's atmospheric O_2/N_2 (denoted as $\delta O_2/N_2$).

In addition to providing a record of natural variability in atmospheric O_2 concentrations, $\delta O_2/N_2$ records, both from Antarctica and Greenland, are strongly anti-correlated with local insolation intensity at the summer solstice (Fig. 1; e.g. Bender 2002). O_2 in trapped gas is relatively depleted compared to N_2 during periods of high insolation, and vice versa. The strong resemblance between the summer solstice insolation variability and the $\delta O_2/N_2$ variability paved the way for a new dating method, based on the tuning of $\delta O_2/N_2$ curves on 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 O_2 concentration and increases uncertainty when using $\delta O_2/N_2$ as a dating tool.

While this incomplete understanding does not necessarily decrease the usefulness of $\delta O_2/N_2$ 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 O_2/N_2 in the atmosphere from ice-core records, and 2) the processes within the ice sheet that cause O_2 to be depleted in air bubbles during high insolation periods.

Natural variability of O_2/N_2 in the atmosphere

At present, seasonal cycles are apparent in measurements of atmospheric O_2/N_2 from multiple meteorological stations. Biological productivity causes an enrichment of O_2 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 $\delta O_2/N_2$ values.

Over the past 800 kyr, a gradual decreasing trend in $\delta O_2/N_2$, 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 O_2, 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 $\delta O_2/N_2$ measurements on 1.5-million-year-old (Myr) ice from the Alan Hills to propose that the decreasing trend in $\delta O_2/N_2$ may have started around the Mid-Pleistocene Transition (MPT; around 1200–800 kyr BP). They observed comparable mean $\delta O_2/N_2$ values between samples from 1.5 Myr and 800 kyr, thus deviating from the steady decrease in $\delta O_2/N_2$ 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 $\delta O_2/N_2$ 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

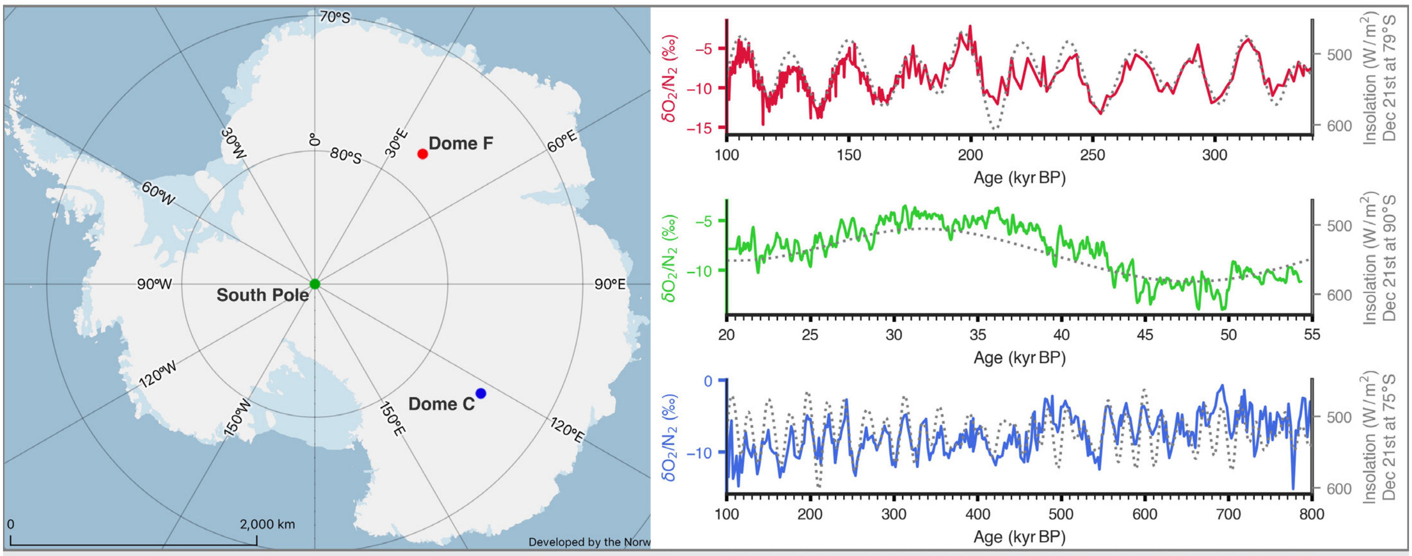

Figure 1: $\delta O_2/N_2$ records covering different time periods from Dome Fuji (Kawamura et al. 2007; Oyabu et al. 2021), South Pole (Severinghaus 2019) and EPICA Dome C (Extier et al. 2018) compared to the summer solstice insolation intensity (dotted line) based on the latitude of the respective ice-core sites. All records are plotted on the respective ice-age scales. The three sites, Dome Fuji (red), South Pole (green), and Dome C (blue) are indicated on the map (Matsuoka et al. 2021).

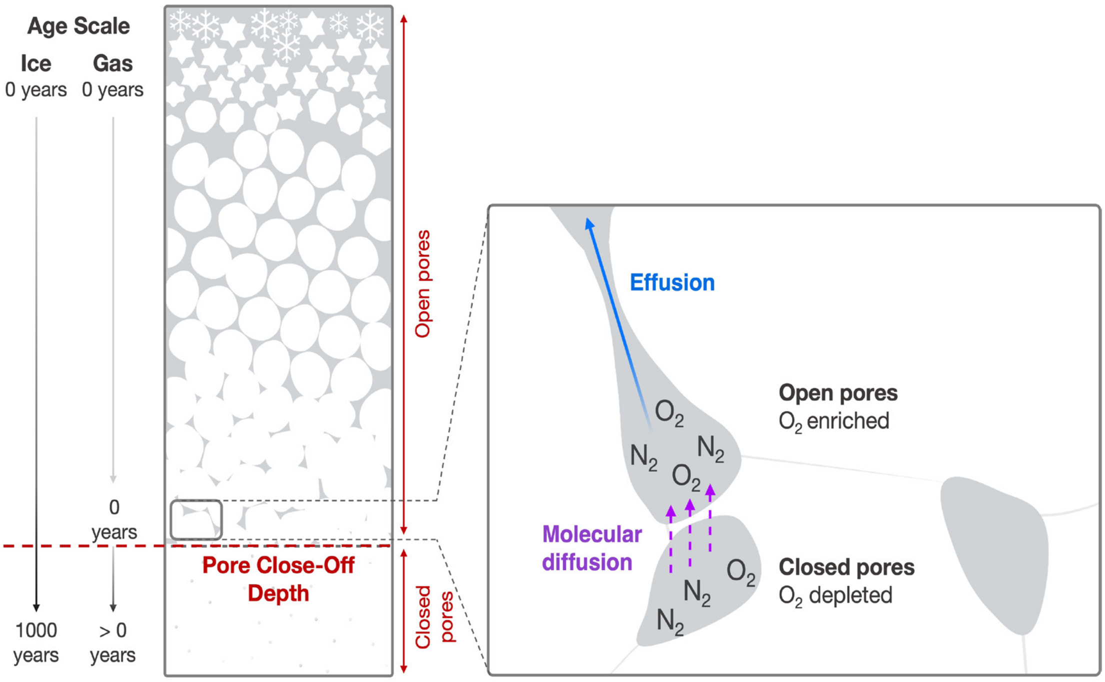

Figure 2: A diagram representing the firn column with an explanation of the two different age scales: the ice-age scale, which tells us when the ice was at the surface; and the gas-age scale, which tells us when the air was trapped in bubbles around the close-off depth. The box illustrates the two proposed mechanisms of gas loss during pore closure using a diagram modified from Severinghaus and Battle (2006).

on this signal is believed to be rather local summer solstice insolation.

Insolation-driven $\delta O_2/N_2$ due to physical processes within the ice

Insolation-driven variations in $\delta O_2/N_2$ ice-core records are classically interpreted as being the result of a loss of O_2 molecules from bubbles as they seal off from the atmosphere (Fig. 2; e.g. Severinghaus and Battle 2006). The formation of air bubbles occurs at about 60–120 m below the ice-sheet surface when the unconsolidated and porous snow constituting the upper part of the ice sheet has become as dense as ice. At this depth, called the close-off depth, the gases can be over 1000 years younger than the surrounding ice, resulting in separate timescales for the ice and the entrapped gases (Fig. 2). Even though $\delta O_2/N_2$ is measured in the air bubbles, $\delta O_2/N_2$ variations more strongly correlate with insolation variations when set to the ice-age scale than when set on a gas scale (Bender 2002). This observation suggests that the link between insolation and $\delta O_2/N_2$ in air bubbles is related to physical properties of the snow, as discussed below.

Insolation intensity modifies the properties of the snow near the ice-sheet's surface, such that strong insolation drives snow grain growth. These near-surface modifications in snow properties persist during the snow densification process from the surface down to the close-off depth (Fig. 2), and then determine the amount of O_2 lost during the pore closure process. So, by some mechanism, more O_2 escapes from the closing air bubble when the surrounding ice experienced strong insolation when near the surface, and vice versa. This preferential loss of O_2 is called fractionation. The route by which the O_2 escapes remains up for debate, but two possible processes are:

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 $\delta O_2/N_2$ records. Moreover, the slope of the linear regression between $\delta O_2/N_2$ and insolation varies between sites, suggesting that additional parameters are influencing $\delta O_2/N_2$ 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 firn properties. A 100-kyr periodicity in the $\delta O_2/N_2$ 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 $\delta O_2/N_2$ 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 (O_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).

AFFILIATION

Laboratoire des Sciences du Climat et de l'Environnement, CNRS-CEA-UVSQ-UPS, IPSL, Gif-sur-Yvette, France

CONTACT

Romilly Harris Stuart: romilly.harris-stuart@lsce.ipsl.fr

REFERENCES

Bazin L et al. (2016) Clim Past 12: 729-748

Bender M (2002) Earth Planet Sci Lett 204: 275-289

Extier T et al. (2018) Quat Sci Rev 185: 244-257

Huber C et al. (2006) Earth Planet Sci Lett 243: 61-73

Ikeda-Fukazawa T et al. (2005) Earth Planet Sci Lett 229: 183-192

Kawamura K et al. (2007) Nature 448: 912-917

Keeling RF et al. (1998) Global Biogeochem Cycles 12(1): 141-163

Landais A et al. (2012) Clim Past 8: 191-203

Matsuoka K et al. (2021) Env Modelling and Software 140: 105015

Oyabu I et al. (2021) The Cryosphere 15: 5529-5555

Severinghaus J (2019) South Pole (SPICECORE) ^{15}N, ^{18}O, O_2/N_2 and Ar/N_2. USAP Data Center

Severinghaus J, Battle M (2006) Earth Planet Sci Lett 244: 474-500

Stopler D et al. (2016) Science 353(6306): 427-1430

Suwa M, Bender M (2008) Quat Sci Rev 27: 1093-1106

Yan Y et al. (2021) Sci Adv 7: 3-11