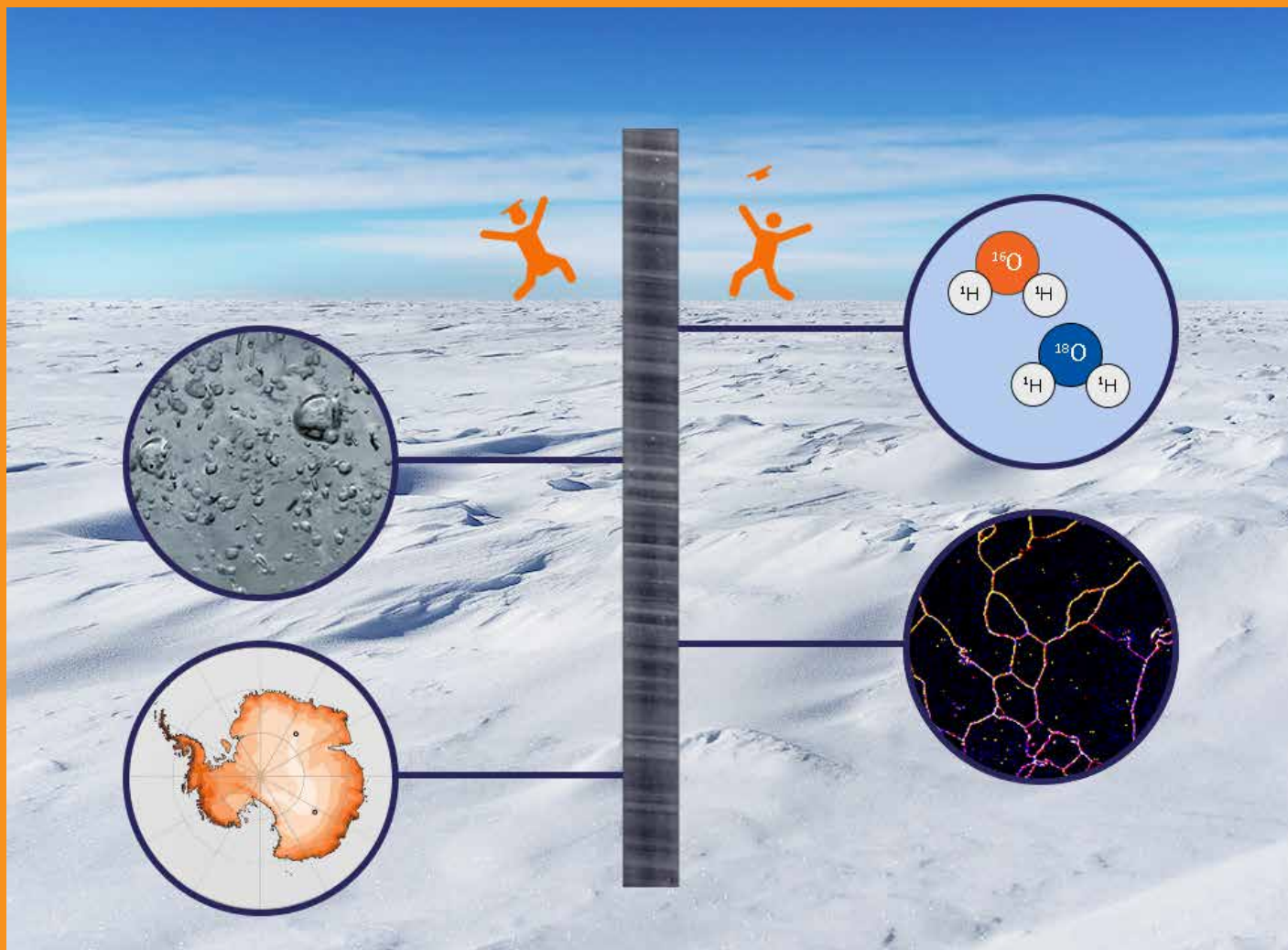# PAST GLOBAL CHANGES
MAGAZINE

YOUNG SCIENTISTS AT THE LEADING EDGE OF ICE-CORE RESEARCH

DEEPICE SERIES EDITORS

Ailsa Chung, Niklas Kappelt, Florian Painer, Lison Soussaintjean and Iván Hernández-Almeida

ICYS SERIES EDITORS

Olivia Williams, Giulia Sinnl, Holly Winton and Iván Hernández-Almeida

PAGES

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News

Goodbye and welcome to SSC and EXCOM members
PAGES says thank you and bids farewell to Zhimin Jian, co-chair and Executive Committee (EXCOM) member, and Emilie Capron, who will be rotating off the Scientific Steering Committee (SSC) at the end of 2023. PAGES thanks Zhimin and Emilie for their dedication and wishes them all the best. PAGES welcomes Natasha Barlow, Yair Rosenthal and Yan Zhao who will join the SSC from January 2024. The PAGES Early-Career Network (ECN) has extended Juliana Nogueira SSC tenure for another year.

Congratulations to Pradeep Srivastava
PAGES would like to congratulate Pradeep Srivastava, PAGES Scientific Steering Committee (SSC) member, who has been appointed as the new International Union For Quaternary Research (INQUA) Vice-President. Pradeep is also president of the local organizing committee of the next INQUA congress that will take place in Lucknow, India, in 2027.

PAGES ATRN working group
The African Tree Ring Network (ATRN) working group focuses on bringing together African tree-ring scientists and advancing the use of tree rings in the tropics, in the areas of paleoecology/paleoclimatology reconstructions, ecology, forestry/agroforestry, hydrology, and archaeology, as a new frontier. Find out more and join ATRN activities: pastglobalchanges.org/atrn

PAGES ACME working group
In May 2023, the Arctic Cryosphere Change and Coastal Marine Ecosystems (ACME) working group successfully applied for a second phase. "The overarching goal for Phase II will be to provide a reconstruction of Arctic coastal ecosystem status under a warmer climate (Holocene thermal maximum, ca. 1–2 K higher than 20th century) using the "good data" criteria refined in ACME Phase I." Details: pastglobalchanges.org/acme

Next PAGES Open Science Meeting and Young Scientists Meeting
PAGES is pleased to announce that the 7th Open Science Meeting (OSM) and 5th Young Scientists Meeting (YSM) will be held in Shanghai, China, in 2025. The confirmed dates for the YSM will be 19–20 May with the OSM running directly afterwards from 21–24 May. PAGES would like to congratulate the Chinese delegation on their successful bid.

PAGES IPO staff update
PAGES communications and project officer, Leigh Martens Winiger, has gone on maternity leave. We congratulate Leigh and her family, and wish them all the best. In the interim, PAGES welcomes Ghislaine Heylen who replaces Leigh until her return. Ghislaine's contact details can be found here: pastglobalchanges.org/about/structure/international-project-office

Apply to be on the Scientific Steering Committee (SSC)
Do you wish to guide PAGES activities and ensure the continuation of a thriving paleosceince network? Then apply to be a part of the SSC. The next deadline is 11 March 2024 (term starting January 2025). Details: pastglobalchanges.org/be-involved/ssc/apply

Deadline for funding support and creation of new working groups
The next deadline to propose a new PAGES working group or to apply for financial support for a workshop/meeting, as well as to submit a Data Steward Scholarship application, is 4 March 2024. Details: pastglobalchanges.org/support

Important news on Swiss GDPR!
The new Swiss Federal Act on Data Protection (FADP) went into effect on 1 September 2023. This means PAGES must ensure compliance with this new data law, and this directly affects PAGES subscribers and members. Please visit the website for all details: pastglobalchanges.org/news/137379

***Past Global Changes Magazine*: request for hard copies**
Past Global Changes Magazine is a free magazine published twice annually and delivered in hard copy format free of charge to those interested. PAGES now requests that for each issue of the magazine, anyone interested in receiving a hard copy must complete the online webform with their postal address details before the deadline. Details: pastglobalchanges.org/news/137348

Upcoming issue of *Past Global Changes Magazine*
The next PAGES Magazine, guest edited by Katrina Kremer, Michael Strupler, Katleen Wils, Renaldo Gastineau and Tatiana Izquierdo Labraca, focuses on (Paleo)-Earthquake and -Tsunami science. The magazine will be published in the first half of 2024.

Calendar

To stay updated on all the latest and upcoming PAGES and paleoscience related activities, check out the calendar on the PAGES website: pastglobalchanges.org/calendar

Featured publications

2k Network
Falster G et al. published an article in *Nature* on "Forced changes in the Pacific Walker circulation over the past millennium"; a new 800-year reconstruction, based on water isotope proxy records from the Iso2k database, of the Pacific Walker circulation. pastglobalchanges.org/publications/137359

2k Network – CoralHydro2k
Walter RM and PAGES CoralHydro2k project members published a paper in *Earth System Science Data* in which they compiled a comprehensive database of curated coral $\delta^{18}O$ and Sr/Ca proxy records to track large-scale regional sea-surface temperature and hydrology signals across various timescales. pastglobalchanges.org/publications/137273

2k Network – Clivash2k
Published in *Earth System Science Data*, Thomas ER et al. synchronized over 100 annual ice-core records of sodium sulfate and sulfur from Antarctica, dating back as far as 2000 years. pastglobalchanges.org/publications/137312

PlioMioVAR
McClymont EL et al., in their paper published in *Reviews of Geophysics*, assessed the spatial and temporal variability of ocean temperatures and ice-volume indicators through the late Pliocene and early Pleistocene (from 3.3 to 2.4 Ma). They find that climate variability evolved in a complex and inconsistent manner, most strongly expressed in northern mid-latitude sea-surface temperature records. pastglobalchanges.org/publications/137325

PALSEA
In their paper published in *Nature*, Saintilan N et al. look at how "widespread retreat of coastal habitat is likely at warming levels above 1.5°C" and conclude that achievement of Paris agreement targets could minimize disruption to coastal ecosystems. pastglobalchanges.org/publications/137367

VICS
In a new paper in *Climate of the Past*, Lücke LJ et al. look at how uncertainties in the solar and volcanic forcing records of the past millennium affect the large-scale temperature response using a two-box impulse response model. pastglobalchanges.org/publications/137268

Cover

An ice core in front of the vast Antarctic ice sheet and areas of ongoing ice-core research: water isotopes for climate reconstructions, air bubbles containing air from the past atmosphere, impurities at grain boundaries and Antarctic climate models. Photo credits: Pascal Bohleber, Ailsa Chung, Qingang Gao, Niklas Kappelt, Amaëlle Landais, U.S. National Ice Core Laboratory.

About this issue

Ice cores have become one of the golden standards in paleoclimate research. Because of the physical nature of their proxy records, their capacity to record past greenhouse (and non-greenhouse) gas concentrations, and their high time-resolution, they have become the focus of multiple PAGES working groups. Two early-career research networks, DEEPICE and ICYS, have contributed and edited this *Past Global Changes Magazine* issue, which contains 26 science highlights on ice cores and new developments in analytical techniques.

Research and training network on understanding Deep icE corE Proxies to Infer past antarctiC climatE dynamic (DEEPICE)

DEEPICE (deepice.cnrs.fr) is an innovative training network for a new generation of 15 early-stage researchers in instrumentation, ice-core analysis, statistic tools and glaciological and climatic modeling. It features 10 research organizations and universities, as well as 11 partner organizations from 11 different countries. The overall objective of DEEPICE is to equip a new generation of scientists with a solid background in ice-core-related climate science with a particular focus on Antarctica, a high level of technical and communication expertise, and a large collaborative network across the academic and non-academic world. The DEEPICE project will develop the necessary tools for the analysis of the Beyond EPICA Oldest Ice, the extraction of which will be completed in 2025.

Figure 1: Entering Little Dome C (Antarctica) precinct on the only road. The camp is visible in the background. Photo credit: Barbante©PNRA/IPEV.

Ice Core Young Scientists (ICYS)

Ice Core Young Scientists (ICYS) (pastglobalchanges.org/icys) is an informal, international network of early-career scientists dedicated to the study of polar and alpine ice cores and ice-core related sciences. Their purpose is to foster personal connections among young scientists from around the world, in order to build a supportive ice-core science community and to inspire future collaborations. ICYS was conceived at the International Partnerships in Ice Core Sciences (IPICS) First Open Science Conference, held in Giens, France, in October 2012. Developed by a small, passionate group of early-career scientists from Europe, Australia and the United States, ICYS exists to foster personal relationships among young ice-core researchers from around the world.

Figure 2: The North Greenland Eemian Ice Drilling (NEEM) camp site, located in northwest Greenland. Photo credit: Tim Burton.

Meet our guest editors

Ailsa Chung
Instituté of Geosciences and the Evironment, Universite Grenoble Alpes, France

Ailsa is doing her PhD in Grenoble on modeling the age of ice in Antarctica by constraining a numerical model with radar observations. She applies the model to predict the age of the ice that might be found at Little Dome C in Antarctica where there are two current ice-core drill sites from the European Beyond EPICA and the Australian Million Year Ice Core projects. When not modeling ice, she can be found climbing and camping in the mountains around Grenoble.

Niklas Kappelt
Department of Geology, Lund University, Sweden

Niklas is a PhD student who is researching a new dating method for ice cores. With a background in chemistry, he previously studied urban air pollution and worked on the development of devices for the removal of pollutants. He transitioned to paleoclimate studies because of his interest in the unique information accessible through ice cores. Dating is a crucial part for the analysis of this data, and his new method is based on cosmogenic radionuclides, which are created in the atmosphere and end up in the ice sheet where they radioactively decay over time.

Florian Painer
Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany

Florian studied geosciences in Graz, Austria. He is interested in the geological past and the dynamics of the Earth system. Currently he is doing a PhD in glaciology and his research is focuses on the microstructure of ice and how ancient air molecules get caged by the ice (i.e. water) molecules. His work has already taken him to the Greenland Ice Sheet. "Ice is a fascinating material to study and key to understanding the Earth's past climate," he said. In his free time, he enjoys hiking in the mountains and being in nature.

Lison Soussaintjean
Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

Lison is a PhD student working on ice-core sciences. Her research focuses on nitrous oxide (N_2O), a potent greenhouse gas and ozone-depleting substance. She analyzes air bubbles in Antarctic ice cores to reconstruct past atmospheric N_2O concentrations, and to understand the production of N_2O in ice using isotope analyses. This study is the result of an international measurement campaign in Switzerland, France, the Netherlands, and the United States. Additionally, Lison has a strong interest in science communication.

Landscape of Finse (Norway) during the DEEPICE Winter School on Snow Sciences in March 2022. Photo credit: Niklas Kappelt.

A European network of young ice-core scientists are developing new methods for the analysis of deep polar ice

Ailsa Chung[1], N. Kappelt[2], F. Painer[3,4] and L. Soussaintjean[5]

Ice cores are unique in that they are the only archives that enable direct measurement of gas composition of the past atmosphere. To date, the longest continuous ice-core record covers the last 800,000 years and was retrieved from the EPICA Dome C ice core (Jouzel et al. 2007). The next challenge is to understand the climatic transition from 41-kyr to 100-kyr glacial cycles which occurred between 1.2 to 0.7 Myr BP, known as the Mid-Pleistocene Transition (MPT) (Gunning et al. p. 58). The aim of the Beyond EPICA–Oldest Ice Core (BE-OIC) project is to drill an ice core as old as 1.5 Myr to obtain a continuous, high-resolution paleoclimatic record, including past greenhouse gas concentrations, which would cover the MPT. The BE-OIC project began in 2019 and drilling is scheduled to reach bedrock in 2026. The BE-OIC drill site (75.29°S, 122.44°E) on the East Antarctic Plateau was chosen for its low snow accumulation rate and topographic conditions, which are conducive to old ice (Chung et al. p. 60).

The oldest ice of the BE-OIC is characterized by very thin layers, which presents a major challenge to study. In preparation for the analysis and interpretation of the core, the DEEPICE Marie Sklodowska-Curie doctoral network was created to train the next generation of ice-core scientists. DEEPICE consists of 15 PhD students working at 10 institutions across Europe with 11 non-academic partner organizations.

This issue presents a selection of current research topics related to the DEEPICE PhD projects. Firstly, water isotope ($\delta^{18}O$ and δD) signals in ice cores are commonly interpreted as a temperature proxy, but they can be altered by surface processes (Ollivier et al. p. 62). Another challenge is to develop new techniques to measure and interpret these signals in the extremely thin layers of the deepest, oldest ice, which are discussed by Malegiannaki et al. (p. 64) and Shaw et al. (p. 66).

Impurities in ice can provide information about climatic changes. For example, mineral dust can tell us about atmospheric circulation changes and organic molecules can be used as tracers of past biospheres. Ongoing methodological developments enable the characterization of single dust particles (Lee et al. p. 68) and increase the number of detectable organic analytes (Notø p. 70). Laser ablation mass spectrometry shows that most impurities are located at grain boundaries between ice crystals (Larkman et al. p. 72). Moreno et al. (p. 74) explore the potential of large area scanning microscopy for the macro-scale analysis of the ice-crystal size.

The interpretation of climate data requires accurate dating, which becomes complicated for the deepest ice. This is why new dating methods using radionuclides (Kappelt et al. p. 76) and the gaseous O_2/N_2

ratio are under development (Harris Stuart et al. p. 78). The latter can also be used to reconstruct the atmospheric O_2 content. Past atmospheric concentrations of nitrous oxide are difficult to reconstruct because this greenhouse gas is produced in the ice. Soussaintjean et al. (p. 80) investigate this process to isolate the atmospheric signal of nitrous oxide.

The analysis and interpretation of gases in ice cores also requires an understanding of how air bubbles transform into air hydrates, which are ice "cages" filled with gas molecules (Painer et al. p. 82). At greater depths, the ice close to the bedrock contains debris and elevated gas concentrations, which could provide novel insights into the history of the ice sheet (Ardoin p. 84).

The developments in ice-core science from the DEEPICE project will enable us to study the only archive that combines continuous high-resolution climate signals with a direct record of the past atmospheric gas composition. A better understanding of past climate will help constrain models of ice-sheet and climate evolution (Gao et al. p. 86). The BE-OIC ice-core data will complement existing paleoclimatic records and assist in unraveling the mystery of the MPT.

The opinions expressed, and arguments employed herein, do not necessarily reflect the official views of the European Agency.

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DEEPICE Marie Sklodowska-Curie doctoral network
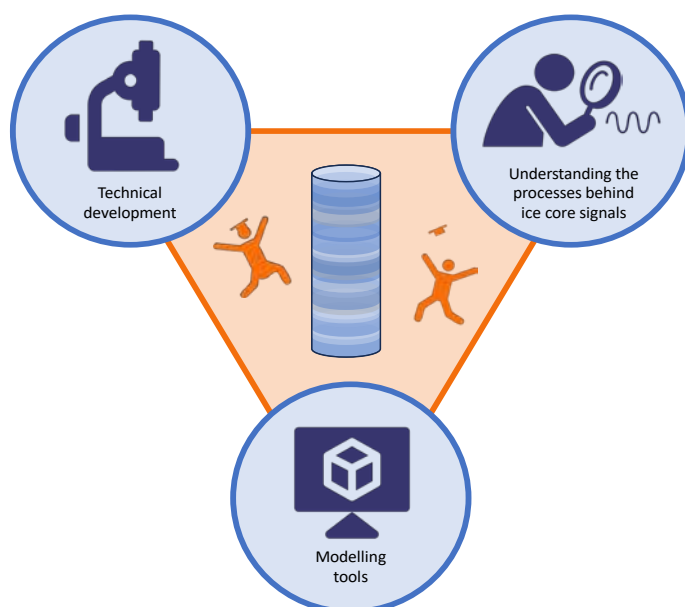Jouzel J et al. (2007) Science 317: 793-796

Figure 1: The three areas that the DEEPICE PhD students are working on to improve ice-core analysis and climate signal interpretation techniques for the BE-OIC project.

On the role of precession in Quaternary glacial cycles

Daniel F.J. Gunning[1], K.H. Nisancioglu[1], E. Capron[2] and R.S.W. van de Wal[3]

An outstanding question of the Quaternary glacial cycles is the gradual emergence of a precession signal. Its absence in the Early Pleistocene may be explained by Northern Hemisphere ice sheets varying out-of-phase with a dynamic Antarctic ice sheet.

The Quaternary glacial cycles and Milankovitch's theory

The Quaternary period (from ~2.6 Ma to present) is renowned for the cyclical growth and decay of large ice sheets in the Northern Hemisphere (NH). An important archive of this climate variability is the oxygen isotope ratio of benthic foraminifera (hereafter benthic $\delta^{18}O$) recovered from deep-sea sediment cores. Temporal variability in benthic $\delta^{18}O$ serves as a proxy for changes in global ice-volume and deep-ocean temperatures. Lisiecki and Raymo (2005) compiled numerous records to produce a globally averaged "stack" of benthic $\delta^{18}O$ for the last 5 Myr BP (LR04) with more positive values indicative of glacial conditions (Fig. 1a). Spectral analysis of this stack demonstrates that glacial cycles have a quasi-regular 100-kyr periodicity for the last ~0.8 Myr BP, together with smaller 23-kyr and 41-kyr cycles (Fig. 1b). Thereafter, shorter cycles begin to emerge with a regular 41-kyr period (Figs. 1c–d). The transition from the "41-kyr world" of the Early Pleistocene (from ~2.6 Ma to ~1.2 Ma) to the "100-kyr world" of the Late Pleistocene (from ~0.8 Ma to present-day) is referred to as the Mid-Pleistocene Transition (MPT).

Since the first $\delta^{18}O$ measurements of marine sediment cores, the importance of changes in the Earth's orbit around the Sun for pacing glacial cycles has been widely acknowledged. In particular, there are oscillations in the eccentricity of the Earth's orbit with periods of 100-kyr and 400-kyr, the obliquity (tilt) of the Earth's rotational axis with periods

of 41-kyr, and the precession of the Earth's rotational axis and orbital path with periods of 19- and 23-kyr. Variations in these three orbital parameters led to a redistribution of solar radiation received at the top of the atmosphere in space and time. Milankovitch (1941) hypothesized that summer insolation at the high northern latitudes was critical for the stability of ice sheets by controlling summer melting. Indeed, spectral analysis of deep-sea sediment and ice-core records support the importance of orbital cycles for Quaternary climate variability (Figs. 1b–d).

The Mid-Pleistocene Transition and precession cycles

On the other hand, Milankovitch's theory cannot explain the MPT based on radiation changes alone, nor the ~100-kyr cycles of the Late Pleistocene. The MPT occurred with no major changes in the variations of Earth's orbital parameters. The ~100-kyr cycles which followed the MPT coincide with variations in the Earth's eccentricity, despite this orbital parameter having a negligible influence on summer-insolation intensity. Theories for the MPT are abundant. They include changes in the dynamics of NH ice sheets (Bintanja and van de Wal 2008) and changes in atmospheric CO_2 concentrations (Raymo et al. 1988). For the 100-kyr glacial cycles of the Late Pleistocene, glacial terminations cluster into intervals of 80- and 120-kyr, and have been explained as a combination of two to three obliquity cycles (Huybers 2007).

Another ongoing question of the Quaternary is the absence of strong precession cycles in the Early Pleistocene. Climatic precession modulates the distance of the Earth relative to the Sun at the solstices and equinoxes, which leads to significant variations in summer-insolation intensity, as exemplified by insolation changes at 65°N during the summer solstice (Figs. 2a–b). Indeed, the conspicuous absence of this precession signal (Fig. 1d) has been referred to as Milankovitch's other unsolved mystery (Raymo and Nisancioglu 2003). Other studies reveal more significant precession variability in the Early Pleistocene (Liautaud et al. 2020), but also demonstrate a strengthening of precession across the Quaternary, as shown in Figures 1b–d. So, what causes the strengthening of these precession cycles?

Precession counterbalancing and integrated summer insolation

One process that diminishes the precession forcing is a counterbalancing that exists between summer-insolation intensity and the duration of the summer. When the Earth is closest to the Sun during the summer of either hemisphere, there is a prominent increase in insolation intensity. However, due to Kepler's second law, the Earth has a higher orbital velocity when closer to the Sun, and subsequently the length of the summer season becomes shorter. Huybers (2006) demonstrates that the time-integral of the summer-insolation forcing above a critical threshold causes these two effects to largely cancel each other out, which can
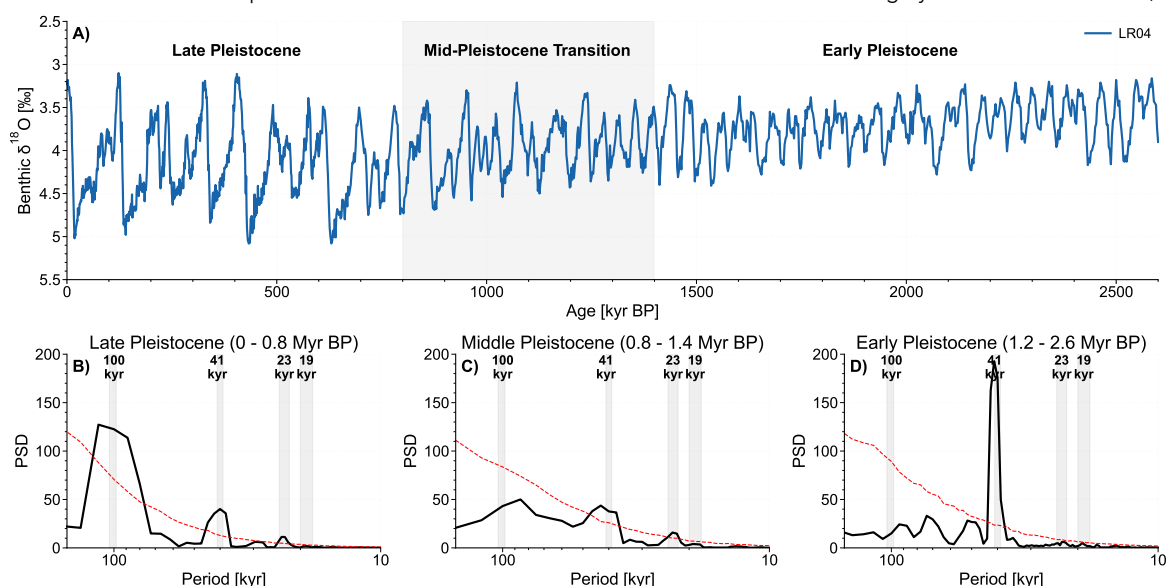

Figure 1: (A) The LR04 benthic $\delta^{18}O$ stack from Lisiecki and Raymo (2005) and the power spectral density (PSD) of the **(B)** Late, **(C)** Middle and **(D)** Early Pleistocene using the multi-taper method from the Pyleoclim python package (Khider et al. 2022). Red lines denote 99% significance level.
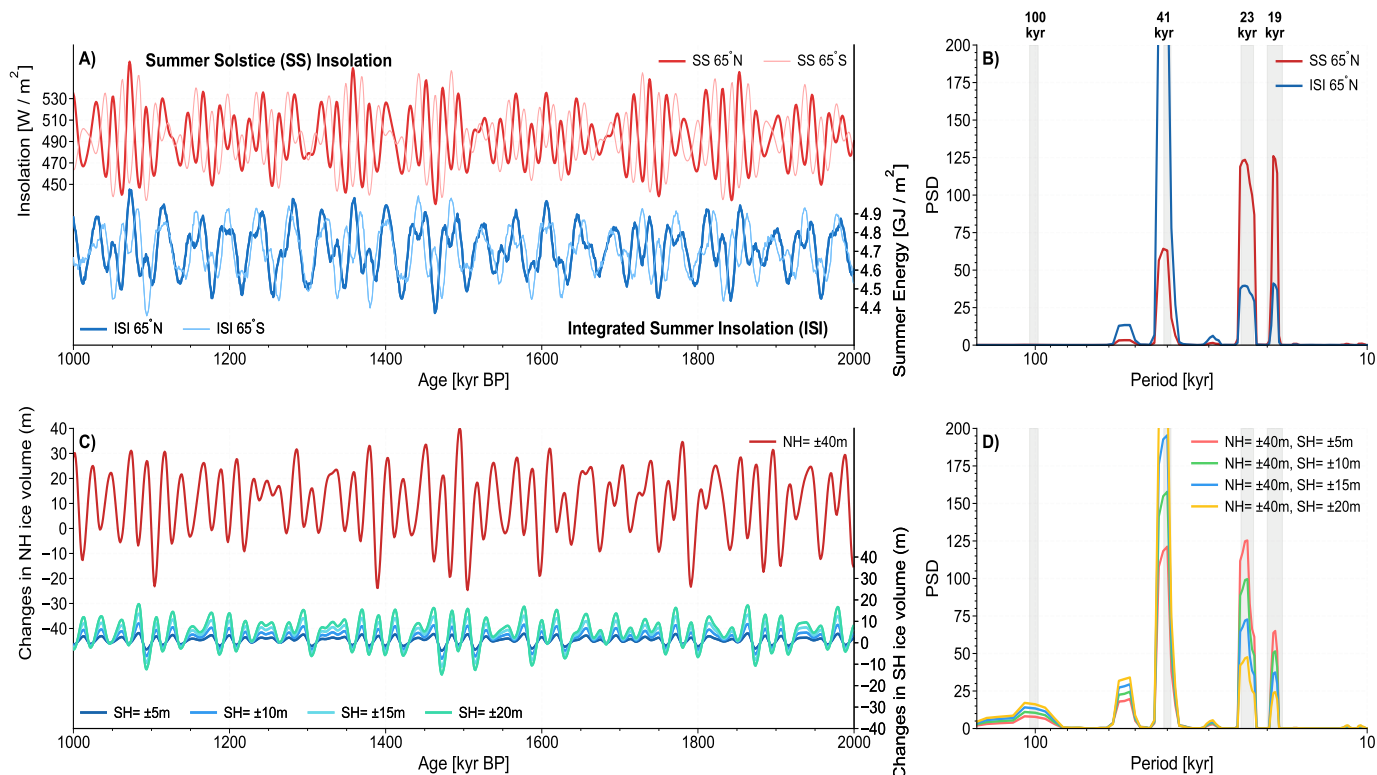
Figure 2: (A) Changes in summer solstice and integrated summer insolation for 65°S and 65°N and **(B)** their respective PSD. **(C)** Modeled variations of a SH and NH ice sheet using a nondimensional ice-volume model (Imbrie and Imbrie 1980) which simulates their lagged response to summer solstice insolation at 65°S and 65°N. **(D)** The model output is scaled for ice-volume variations of up to ±20 m for the SH ice sheet and ±40 m for the NH ice sheet, to illustrate how precession-driven variations of the SH and NH ice sheet can cancel each other in the global record. Panels (C) and (D) replicate plots from Raymo et al. (2006).

significantly reduce the precession variability (as shown in Figs. 2a–b). What then caused the precession signal to become stronger in the Late Pleistocene? Huybers and Tziperman (2008) suggest that a gradual cooling across the Quaternary would shorten the summer melt season and lessen this counterbalancing effect, together with a southward extension of the NH ice sheets into latitudes more sensitive to precession. However, there is the possibility of another contributing factor to the strengthening of precession cycles which lies in Antarctica.

Antarctica and the anti-phased hypothesis
Precession-driven changes in summer insolation are out-of-phase between the hemispheres. With this in mind, Raymo et al. (2006) propose that precession-driven variations of Antarctica and the NH ice sheets may have cancelled each other out in globally averaged proxies of ice volume. This concept can be illustrated by using a simple model of ice-volume change (Imbrie and Imbrie 1980) to simulate variations of both a Southern Hemisphere (SH) and NH ice sheet (Fig. 2c). The nondimensional model simulates the lagged response of each ice sheet to changes in local summer insolation and the output has been scaled to ±40 m of ice volume in the NH and up to ±20 m in the SH. We can see by progressively increasing the variability of the SH ice sheet that these hemispherically out-of-phase precession cycles increasingly interfere with each other, leaving behind a stronger 41-kyr obliquity signal in global ice volume (Fig. 2d). In this way, the notable absence of a precession signal in the Early Pleistocene could be explained by the cancellation of out-of-phase precession cycles between the SH ice

sheet (i.e. Antarctica) and the NH ice sheets. Intrinsic to this hypothesis is the notion that the mass balance of Antarctica is driven by changes in local summer insolation, as proposed by Raymo et al. (2006) for the Early Pleistocene. What then caused the increase in precession variability recorded across the Pleistocene? A gradual cooling across the Quaternary would lead to the development of a marine-based Antarctica with virtually no surface melting, as observed today. Together with the gradual expansion of the NH ice sheets, this stabilisation of Antarctica would decrease the ratio between SH and NH ice-volume variations, enhancing the precession signal observed in global ice volume (as shown in Fig. 2d).

Outlook
Interestingly, a strengthening of precession cycles across the Quaternary, driven either by a reduction in the counterbalancing effect between summer-insolation intensity and duration and/or an increasing imbalance between NH and SH precession cycles, requires a cooling across the Quaternary. However, reconstructions of CO_2 across the MPT have produced conflicting results (Hönisch et al. 2009; Yamamoto et al. 2022). On the other hand, the anti-phased hypothesis predicts that Antarctic temperatures should vary in-phase with local summer insolation in the Early Pleistocene, as has been suggested by ice cores recovered from the Allan Hills Blue Ice Area (Yan et al. 2022). Ultimately, the arrival of the Beyond EPICA Ice Core will prove important to test the anti-phased hypothesis by providing a high-resolution record of changes in CO_2 and local Antarctic temperatures across the MPT.

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Could there be 2-million-year-old ice at North Patch near Dome C, Antarctica?

Ailsa Chung[1], F. Parrenin[1], R. Mulvaney[2] and O. Eisen[3,4]

New modeling combined with radar observations show that North Patch, near Dome C, presents an exciting potential ice-core drilling location where ice up to 2 Myr old may exist with a detectable paleoclimatic signal.

Drilling for old ice in Antarctica

Ice cores offer scientists an invaluable record of the climate of the past. Whether we are studying the composition of the ancient atmosphere in air bubbles or analyzing water isotope ratios ($\delta^{18}O$ and δD) to infer past temperatures, obtaining the oldest ice possible remains a challenge for ice-core research. Currently, the oldest continuous ice core comes from the European Project for Ice Coring in Antarctica (EPICA) at Dome C (EDC), which has given us a climate record from the past 800 kyr (Bazin et al. 2013). The International Partnerships in Ice Core Sciences (IPICS) community set the Oldest Ice challenge of extracting a continuous ice core which covers over 1 Myr (Fischer et al. 2013). An ice-core record of this length would allow us to directly measure past atmospheric greenhouse gas concentrations. It would also help us to understand the change in the periodicity of climate cycles, which occurred between 1.2–0.7 Myr BP, known as the Mid-Pleistocene Transition (Clark et al. 2006). Fischer et al. (2013) determined that a potential Oldest Ice site should

have a low accumulation rate and a relatively thin ice sheet to avoid basal melting, and minimal horizontal ice flow, as basal sliding can cause distortion or even folding of the deepest, oldest ice (Dahl-Jensen et al. 2013).

The European Beyond EPICA consortium selected a site and began drilling in 2021 at a location known as Little Dome C (LDC) on the East Antarctic Plateau, where they hope to find ice up to 1.5 Myr old. The Australian Antarctic Division has also selected a site on LDC for their Million Year Ice Core (MYIC) project. In this article, we look at North Patch (Parrenin et al. 2017), an area approximately 10 km north of EDC. Our preliminary age modeling presents North Patch as an exciting prospect for a new Oldest Ice drill site with ice potentially up to 2 Myr old.

1D numerical age-depth model

Our model determines the age of ice, past accumulation rates and melt rate at a given location. It is a 1D model which means it only considers the vertical flow of ice and takes into account three parameters. The first

parameter is the model's best-fit ice-sheet thickness. From the difference between the best-fit ice thickness and the observed ice thickness, we can infer either a basal melt rate or a layer of stagnant ice (ice with no vertical flow). The second model parameter is the average past snow accumulation rate whose temporal variations can be inferred using the EDC ice-core record (Bazin et al. 2013). The accumulation rate corresponds to an annual snowfall which forms a layer on the surface of the ice sheet. Subsequent snowfall covers and compresses the snow below, slowly turning it into ice. As each layer is compressed further, it becomes thinner and moves deeper, as time goes by. The final parameter in the model accounts for this thinning process.

We provide the model with known age-depth constraints from observations made with radar surveys. We can use radar systems to send a signal deep into the ice sheet, and from the reflections we can detect the internal structure of the ice sheet. The radar images show internal reflection horizons.
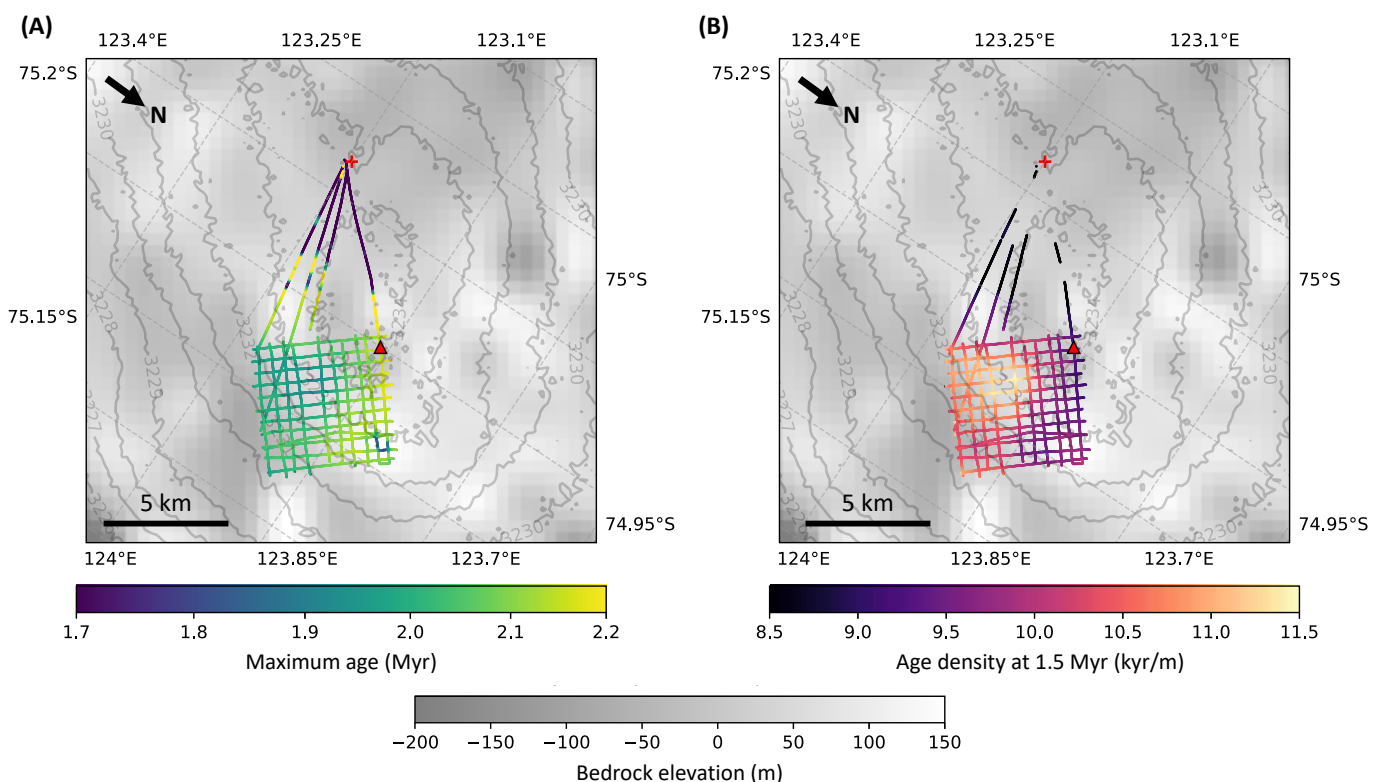

Figure 1: The model was run using 20 horizons traced in DELORES radar data at North Patch. The red cross marks EDC and the red triangle marks a promising North Patch site shown in Figure 2. **(A)** Modeled maximum age of ice at North Patch. **(B)** Modeled age density of 1.5 million-year-old-ice at North Patch.
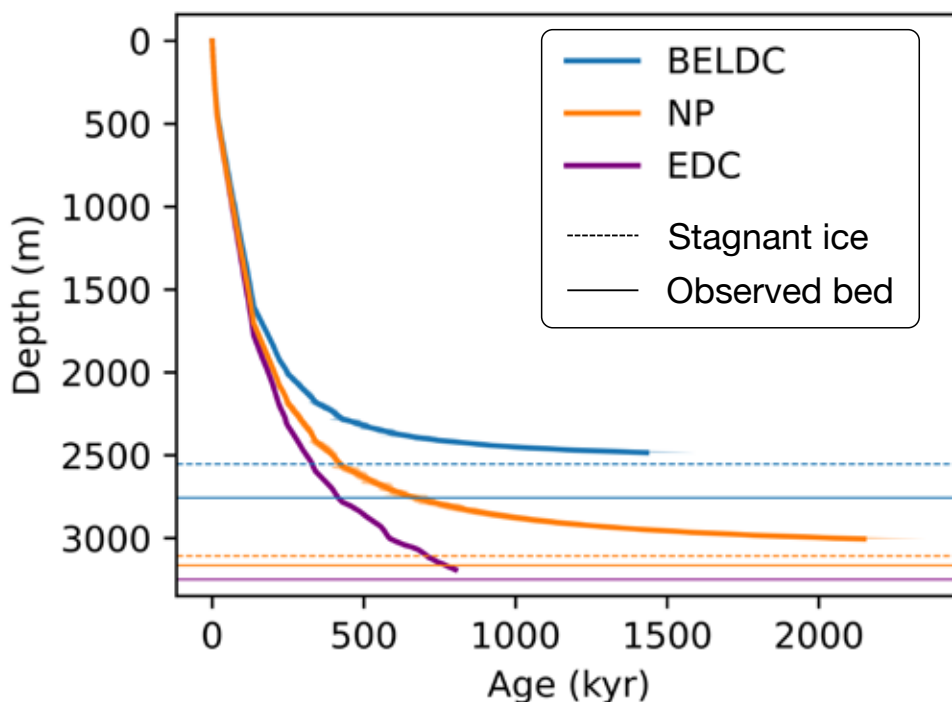
Figure 2: Age-depth profile of EDC (purple) determined experimentally (Bazin et al. 2013), modeled profiles for Beyond Epica LDC (BELDC) – the current ice-core drill site for Beyond EPICA (blue) project (Chung et al. 2023) - and for a promising North Patch site (orange). Dashed lines show the top of the stagnant ice layer, and solid lines show the bedrock depths observed in radar data in colors corresponding to each location.

Since the ice at each horizon was formed from snow which fell at the same time, under the same conditions, the age of the ice along a given horizon is constant. By connecting these radar lines to the EDC age-depth profile, we can determine their ages. Taking into account the three model parameters mentioned above –mechanical ice thickness, average past accumulation rate, and the thinning parameter– the model fits the ages of these isochrones and the surface, and extrapolates down to the bedrock to give us a complete age profile along the radar line.

Modeling at North Patch
At North Patch, the sledge-borne DEep LOoking Radio Echo Sounder (DELORES) was used to collect radar data from 21 lines in a 5x5 km^2 grid (Chung et al. 2023). From these data, 20 isochrones were dated by linking them to EDC with four radar lines (Fig. 1). The isochrones were then used to constrain a 1D numerical model.

The model is able to determine the age of ice at a given depth from the surface. The maximum age of the ice at a given location is either at the bedrock, or if the age density is equal to 20 kyr/m (20,000 annual layers per vertical meter). At this limit, paleoclimate reconstruction becomes impossible as obliquity cycles cannot be distinguished, at least using current experimental techniques (Fischer et al. 2013). Figure 1a shows that the maximum ice age predicted by the 1D model is generally between 2.2 and 1.9 Myr, around 500 kyr older than the expected age at the current Beyond EPICA drill site. The age density for 1.5 Myr-old ice at North Patch is generally between 9 and 11 kyr/m, which is twice as good as what we expect to find at Beyond EPICA (Chung et al. 2023) (Fig. 1b).

Modeling showed that there is very little, if any, basal melting at North Patch. There is also significantly less stagnant ice, which means that the climate record could be analyzed over the entire ice column. This results in thicker annual layers than at LDC, which would give us larger ice samples to analyze.

Potential North Patch drill site comparison
We chose a promising Oldest Ice location at North Patch and compared the age-depth relationship with that of the EDC and Beyond EPICA ice-core sites (Fig. 2).

The EDC ice core gave us a climate record (Fig. 2) which could be analyzed along almost the entire length, as the large ice thickness meant that age density was relatively low (Bazin et al. 2013). However, basal melting meant that the paleoclimatic record older than 800 kyr had been distorted, or completely destroyed (Tison et al. 2015). Modeling suggests that there is no basal melting at the Beyond EPICA drill site on LDC and there could be ice up to 1.5 Myr-old (Fig. 2). However, due to the thinner ice sheet, the oldest ice is likely to have very small annual layer thicknesses (one meter of ice covers over 20 kyr, Chung et al. 2023), so diffusion processes may make it difficult to interpret the paleoclimatic record. The modeling in Chung et al. (2023) shows that an ice core at North Patch could offer a middle ground (Fig. 2). This ice sheet is around 3200 m thick, resulting in lower age density, but there also appears to be little-to-no basal melting, leaving the oldest ice intact.

Outlook
The DELORES radar system is not the highest resolution available, therefore, it would be beneficial to apply newer radar systems

to North Patch in order to confirm the findings in our study. The logistics of constructing a drill site at North Patch would be eased due to its proximity to the French-Italian Concordia station. Despite this, the age modeling suggests that the ice-core age-depth relationship at North Patch would be very different to those of EDC and Beyond EPICA (Fig. 2).

All that remains to be determined is who will choose to exploit this great opportunity to extract the (up to 2 Myr-old) Oldest Ice available at North Patch.

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From precipitation to ice core: On the importance of surface processes for stable water-isotope records in East Antarctica

Inès Ollivier[1,2], H.C. Steen-Larsen[1], M. Casado[2], B. Stenni[3] and A. Landais[2]

Stable water-isotope records from Antarctic ice cores allow the reconstruction of past temperature variability. However, accurate interpretation of the isotopic signal requires comprehensive understanding of the processes leading to its archiving in snow and ice, which can be documented by in situ measurements.

In the history of paleoclimate research, Antarctic ice cores have been largely used to unveil past variability of the Earth's climate. As an example, the EPICA ice core drilled at Dome C in East Antarctica provided the longest record of past atmospheric conditions up to 800,000 years back in time (EPICA community members 2004). Within the ice matrix of the cores, the stable water isotopes are traditionally used as a proxy for past local temperatures. This is based on the observed correlation between the local atmospheric temperature and the surface snow δ^{18}O across spatial transects in Antarctica (see review by Masson-Delmotte et al. 2008 and references therein).

A first challenge to the interpretation of isotopic records of snow and ice is related to the large-scale dynamics of the water cycle that vary through time, but are well constrained in global climate models (e.g. Cauquoin and Werner 2021). Along their trajectory from evaporation to precipitation onto the ice sheet, the air masses reaching the interior of the Antarctic continent are modified by precipitation and sublimation of snow that modulates the isotopic composition of the water vapor. In addition, on the East Antarctic plateau, snow accumulation is the result of a few precipitation events often associated with warm-air intrusions (Genthon et al. 2016). This leads to a discontinuous and temperature-biased recording of the stable water-isotope signal in the accumulating snow.

The ability to infer past temperatures from ice cores is also based on the assumption that the precipitation isotopic composition is preserved from snowfall to deeper burial in the snowpack. However, post-depositional processes taking place at the snow–atmosphere interface have been identified to modify the snow isotopic composition after precipitation. At Dome C, the daily-to-seasonal variations observed in the snow isotopic composition cannot be explained by precipitation only, demonstrating the existence of further processes involved in the formation of the snow isotopic signal (e.g. Casado et al. 2018).

Surface processes

At the ice sheet's surface, the snow is affected by three kinds of physical processes: (i) wind redistribution of the snow; (ii) water-vapor exchanges between the snow and the lower atmosphere; and (iii) diffusion of water vapor within the snow. At very dry and low accumulation sites, such as the East Antarctic Plateau, the snow is exposed for long periods of time before being isolated from the influence of the atmosphere. During these precipitation-free periods, the first two processes mentioned above play a role in the resulting isotopic signal found in the snow.

A large variety of meteorological conditions are encountered on the plateau, but because of its location high up on the ice sheet, and the very small local slope, Dome C is not affected by strong katabatic winds (Genthon et al. 2021). Nevertheless, surface winds are sometimes strong enough to erode and redistribute the snow (Libois et al. 2014), which causes an inhomogeneous distribution of the water isotopes at the surface.
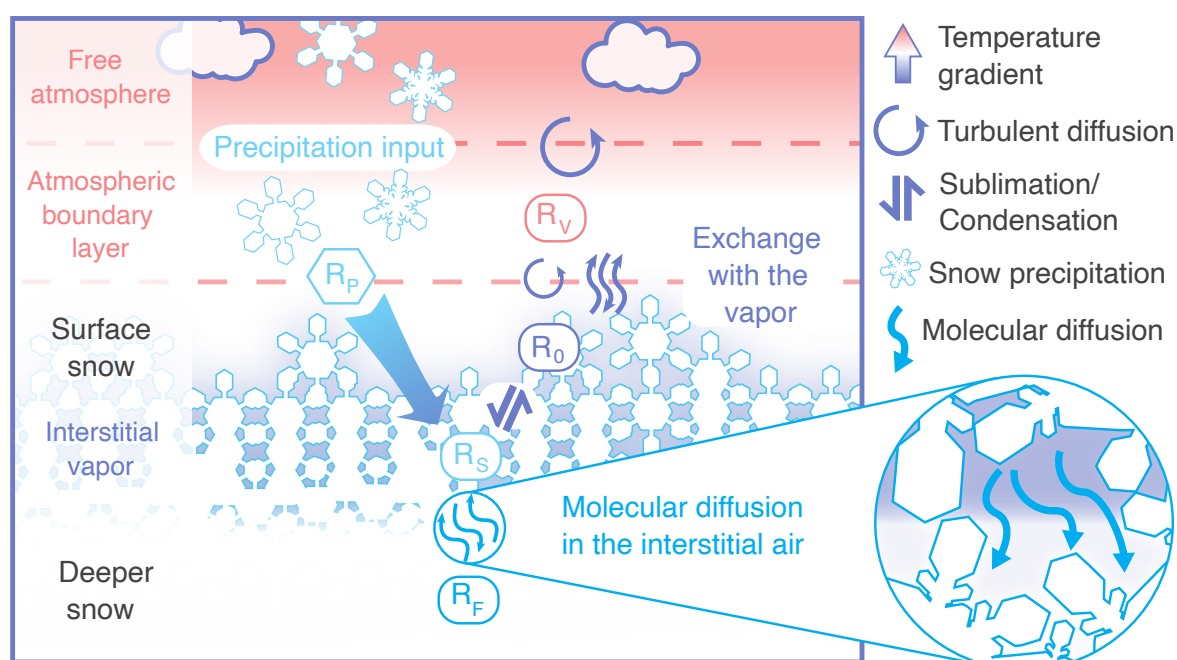

Figure 1: Contribution of the different reservoirs to the isotopic composition of the snow. R stands for the isotopic composition of the vapor (R_V), vapor at equilibrium with snow (R_0), precipitation (R_P), snow (R_S) and firn (R_F). The two water vapor transport mechanisms are mapped: sublimation/condensation at the surface, and molecular diffusion within the snow. Figure modified from Casado et al. (2018).
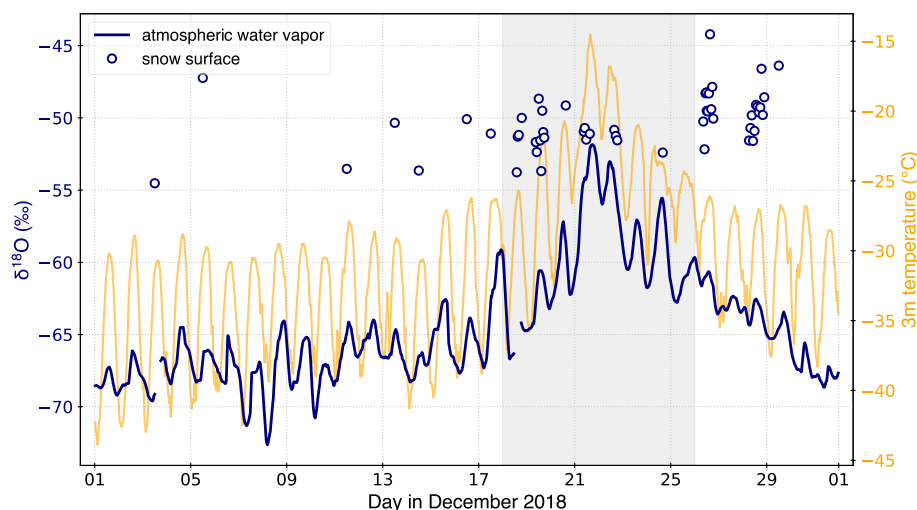
Figure 2: Observed isotopic composition of snow and atmospheric water vapor and local air temperatures at Dome C in December 2018. δ^{18}O was measured using a PICARRO laser spectrometer (atmospheric water-vapor data in Leroy-Dos Santos et al. 2021) and air temperature was measured by a sensor installed at three meters above the ground (data in Genthon et al. 2021). The atmospheric river event is marked by the gray shading.

The surface snow and the atmosphere above also exchange moisture through sublimation of snow or condensation of water vapor onto the surface (Fig. 1). The direction and magnitude of these moisture fluxes are driven by temperature and humidity gradients between the snow and the atmosphere, while wind enhances the mixing process. Although sublimation was previously thought to be a process that did not modify the snow isotopic composition, recent studies have challenged this assumption. Steen-Larsen et al. (2014) first demonstrated the existence of water-vapor exchange between the snow and the atmosphere during summer in Greenland, leading to variations in the isotopic composition of the snow, even in the absence of precipitation bringing fresh snow to the surface. Further measurements confirmed the impact of moisture fluxes on the snow isotopic composition (Wahl et al. 2021).

Diffusion, on the other hand, is a process continuously taking place inside the snowpack. At the grain scale, in the porous space of the snow below the surface, the ice crystals sublimate and the vapor is transported and re-deposited onto other snow grains (Fig. 1). This results in the movement of water molecules driven by temperature and isotopic gradients inside the snowpack, affecting the isotopic composition of the snow and firn after snowfall (Casado et al. 2021; Johnsen et al. 2000).

In situ observations
To provide observational benchmarks for isotope-enabled climate models, and to improve the understanding of post-depositional processes at the surface, measurement campaigns have been carried out for several years at Dome C.

The recent development of laser spectrometry has made it possible to measure the water-vapor isotopic composition in a very dry atmosphere. At Dome C, the analyzer installed on site (PICARRO L2130i) has provided observations of the atmospheric

water-vapor isotopic composition almost continuously since November 2018 (Casado et al. 2016; Leroy-Dos Santos et al. 2021). The results obtained during the summer month of December 2018 are shown in Figure 2. The existence of diurnal cycles in the near-surface vapor isotopic composition (blue line in Fig. 2), following the diurnal cycles exhibited by the atmospheric temperature (orange in Fig. 2), demonstrates the existing link between these two atmospheric parameters. In addition, the analyzer recorded the atmospheric river event (a narrow corridor of intense moisture transport) that occurred between 18 and 26 December. This event led to ambient temperatures up to -15°C, which is much warmer than the average daily mean temperature of -31°C typically observed at this time of the year (Genthon et al. 2021). During this event, the vapor isotopic composition also increased by about 10‰, possibly due to a shift in the source region of the air mass, or less distillation along the trajectory from the source to Dome C.

Besides the atmospheric measurements, samples are regularly taken in the field to monitor the snow isotopic composition. In December 2018, the snow and atmospheric water vapor-isotopic composition at Dome C does not exhibit any clear co-variation (blue dots and blue line in Fig. 2), as observed on the Greenland Ice Sheet during the summer (Steen-Larsen et al. 2014). However, their similar isotopic composition at the peak of the atmospheric river event could suggest isotopic exchange between the two reservoirs. This is supported by the occurrence of sublimation during summer (Genthon et al. 2017), which implies isotopic exchanges between the surface snow and the atmosphere.

Lastly, precipitation samples collected in the field over several years have permitted the establishment of a temporal relationship between the snowfall δ^{18}O and the ambient temperature of 0.49‰/°C. It is significantly lower than the spatial slope of 0.8‰/°C obtained from various datasets of Antarctic snow, and traditionally used for temperature

reconstructions (Masson-Delmotte et al. 2008; Stenni et al. 2016). This further highlights the importance of such measurements for the interpretation of δ^{18}O records in ice cores.

Summary
While water-isotope records from ice cores can provide invaluable information on past climate variability, their quantitative interpretation in terms of temperature has been challenged by recent studies that revealed the impact of several processes at the surface of the ice sheet, modifying the isotopic composition of the snow after precipitation. Research is still ongoing to disentangle and quantify the impact of these different processes, which take place during the archiving of the snow, on the isotopic climate signal found in ice cores. For this reason, field measurements are performed, and provide some of the keys to understanding the dynamics of the water isotopes at the surface of the Antarctic Ice Sheet.

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Challenges of water-isotope measurements on ice cores

Eirini Malegiannaki[1,2], K. M. Peensoo[1], P. Bohleber[2] and V. Gkinis[1]

Due to thinning of ice-core layers, the deepest part of the cores is the hardest to analyze. New micro-destructive and high-resolution instrumental approaches are necessary to retrieve a water-isotope record that accurately represents past climate variations.

Water isotopic composition of ice cores
When water travels from the evaporation to the precipitation site, the different water isotopes ($H_2^{16}O$, $H_2^{18}O$, $HD^{16}O$) modify its isotopic signature, represented by $\delta^{18}O$ and δD. For example, a lighter isotope, such as $H_2^{16}O$, evaporates more easily than a heavy one, such as $H_2^{18}O$, leading to a temperature-dependent fractionation and the establishment of a relationship between water isotopic composition and condensation temperature (Dansgaard 1953).

Ice cores exhibit distinctive layered characteristics where the water-isotopic signature is preserved. Due to the preservation of ice for long time periods in large ice sheets, water-isotope data offers access to a continuous and high-resolution record of past climatic variability. This is shown in the climate records generated during the EPICA (1996–2008) deep-core project which extend up to 800,000 years ago. The ongoing Beyond EPICA (2019–2026) project aims to extend the ice-core record up to 1.5 Myr in order to reconstruct Antarctica's climate history.

However, analyzing deep ice cores poses challenges. Thinning of annual layers in the deeper sections of an ice sheet, and post-depositional processes within the ice core, such as water molecule diffusion within the ice, may result in the smoothing of the water-isotope signal (Johnsen et al. 2000). This challenges the recovery of the original isotopic signal of the deposited precipitation. In addition, there are limitations in the measurement procedures which further increase difficulty in retrieving the original climate signal.

Analytical techniques for water-isotope measurements on ice cores
Advances in sample preparation and signal acquisition techniques have significantly enhanced the capability of obtaining high-resolution water-isotopic data from ice cores. Isotope Ratio Mass Spectrometry (IRMS) is an analytical technique traditionally employed to acquire water-isotope signals that offer high-precision measurements. However, due to the "sticky" nature of the water molecule, and its condensable gas phase, the water should be converted into a chemical form that is compatible with the IRMS, which is a time-consuming process and prone to inaccuracies. Laser-based water-isotope measurement techniques display the potential to tackle the aforementioned issues (Kerstel and Gianfrani 2008), as well as other difficulties related to the expensive and bulky instrumental equipment needed.

Cavity Ring Down Spectroscopy (CRDS) is a sensitive spectroscopic technique that uses laser light and an optical cavity to measure water-isotope ratios. For the measurement, a laser pulse is injected into an optical cavity, and the decay time, or "ring down" time, of the detected light intensity is measured. This decay time is affected by the presence of gas molecules in the cavity, indicating the gas concentration. By coupling specific laser wavelengths with absorption features of the target molecules, CRDS allows for highly sensitive measurements.

CRDS has emerged as a preferred alternative to IRMS, also offering the ability to perform field measurements. Different ice-sample preparation methods enable water-isotope measurements using a CRDS analyzer in either continuous or discrete mode, respectively. However, it is important to note that both approaches require substantial time and sample consumption.

Laser Ablation: a fast micro-destructive sampling method
Laser-matter interaction has been widely used for developing new techniques, including micromachining, laser cutting, sampling, and material development. When a pulsed laser beam is focused on a target surface, a high amount of energy is confined in space and time in the irradiated area, which can cause material ejection in the gas phase, known as Laser Ablation (LA). Ice sampling using LA serves a dual purpose: 1) It provides high-resolution analysis, and 2) it uses the smallest amount of sample possible for analysis, given the micro-destructive nature of the ablation process. In this way, the ice core is not melted and the same sample can be used for other types of analysis while, at the same time, it is possible to obtain high-quality continuous measurements.

LA has already been adopted as a sampling method in elemental concentration studies on ice cores (Della Lunga et al. 2017). Recently, LA sampling allowed for fast two-dimensional imaging of the impurities in ice at very high resolution (just a few tens of micrometers), generating new insights into ice-impurity interactions (Bohleber et al. 2021).

Laser Ablation–Cavity Ring Down Spectroscopy on ice cores
Laser Ablation (LA) and Cavity Ring Down Spectroscopy (CRDS) techniques have recently been used together to enable high-quality water-isotopic measurements on ice cores. The conceptual design of the LA-CRDS system is illustrated in Figure 1.
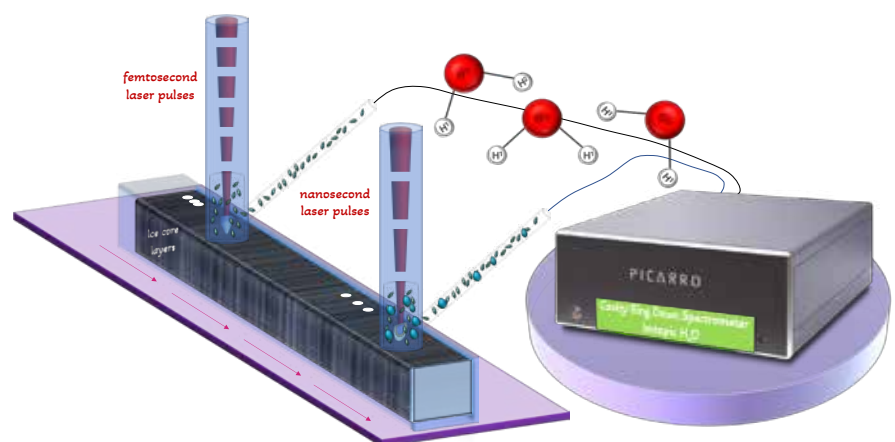

Figure 1: LA on ice-core samples using either nanosecond or femtosecond laser pulses enable material ejection in the gas phase, which is delivered to a CRDS analyzer for water-isotope detection. Placing an ice sample on a motorized stage can enable continuous high-resolution sampling.
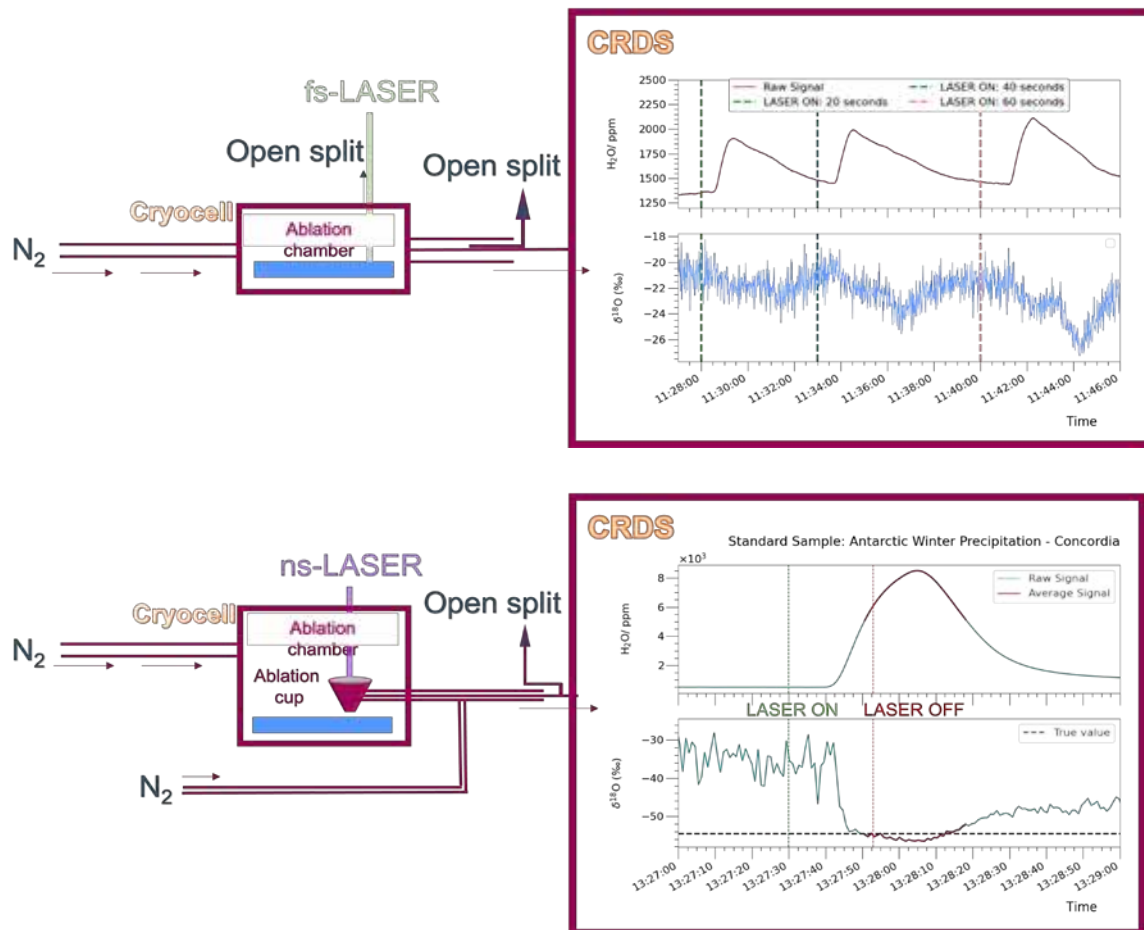
Figure 2: (A) LA-CRDS scheme using femtosecond laser pulses and a cryocell as the ablation chamber (Kerttu and Gkinis 2021). **(B)** LA-CRDS scheme using nanosecond laser pulses and a two-volume cryocell (ablation chamber and ablation cup). Both LA schemes led to ice ablation. The resulting vapor, H_2O, and the corresponding isotopic signal $\delta^{18}O$ detected by the CRDS analyzer, are shown in both cases.

The experimental setup for LA sampling on ice includes essential components such as a focused laser beam, a motorized translational stage for accurate ice movement, an ablation chamber to collect the sampled material, and a transfer line that transports it to the CRDS analyzer. These components work together to enable efficient and reliable analysis of ice samples in a continuous manner.

During sampling, the laser interacts with the ice and creates a mixture of vapor and tiny particles. The laser can produce short pulses, either in the nanosecond or femtosecond range. The amount of time the laser interacts with the ice affects the composition of the mixture. One challenge in measuring water isotopes is that when the ice melts or undergoes incomplete phase changes, it can change the isotopic signature of the material being studied. However, using very short laser pulses in the femtosecond range can help reduce this issue, because the interaction time is shorter than the time it takes for heat to spread in the material.

The compatibility between the vapor produced by the LA sampling process and the gas analyzer, CRDS, led to the inception of the LA-CRDS technique. This innovative design enables fast gas-phase sample collection directly from the ice, facilitating high-quality water-isotopic measurements. The successful implementation of this approach in experimental laboratories has yielded promising results.

Both femtosecond (Fig. 2a; Kerttu 2021) and nanosecond laser pulses (Fig. 2b) have been applied in two distinct experimental configurations coupled with a CRDS analyzer, leading to the detection of the ablated ice (artificial ice samples produced from purified and liquid water from Antarctic winter precipitation) and acquisition of the respective water-isotope signal. These initial results demonstrate the feasibility of ablating ice material with lasers of different pulse durations, and acquiring a water-isotope signal using the CRDS analyzer.

Conclusions

Advances in water-isotope measurement techniques, both on the sampling and the detection side, had already shown a big impact on the retrieval of continuous high-resolution water-isotope records from ice cores. By combining precise analyzers with melting methods, scientists can obtain detailed data.

The introduction of LA, coupled with CRDS analyzers, presents a promising approach for capturing high-resolution isotope signals, especially from the deepest parts of the ice cores. This micro-destructive technique minimizes sample usage while providing valuable insights into laser-ice interaction principles for accurate interpretation of the water-isotope instrumental signal. The synergistic work on diffusion studies (Gkinis et al.

2014; Holme et al. 2018), and the development of high-quality water-isotope measurements, will further enhance the precision of past-temperature estimations.

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How best to recover water-isotope data from ice cores

Fyntan M. Shaw[1], T. Laepple[1,2] and V. Gkinis[3]

Diffusion of water molecules in ice cores attenuates high-frequency variability of the water-isotope records, strongly affecting the interpretation of the deepest, oldest ice. Our ability to partly restore the signal depends on the measurement noise and our knowledge of the diffusion length.

Water-isotope diffusion

Stable water isotopes ($\delta^{18}O$ and δD) stored in ice sheets serve as a valuable proxy of the climate at the time of deposition as snowfall. However, over time, the water isotopes disperse, either between the porous snow and surrounding air at the top of the ice sheet (Whillans and Grootes 1985), or through other processes such as solid-ice-bulk diffusion (Johnsen 1977; Ramseier 1967) or liquid-water veins (Nye 1998) once the snow has been compacted into ice. This process is known as diffusion and attenuates the isotopic signal, primarily over the higher frequencies (shorter timescales), causing a smoothing effect. The degree of attenuation is characterized by the diffusion length, which is the average displacement of water molecules from their initial position within the ice sheet. Since this is a cumulative effect, ice thinning increases the affected timescale as the ice layers descend. Additionally, the very deepest ice close to bedrock is warm, reaching temperatures close to the pressure melting point. This greatly increases the diffusion length due to the non-linear dependence of the ice-diffusivity coefficient on temperature. Consequently, variability on centennial and even millennial timescales can be reduced significantly by diffusion in very old ice. Typical diffusion lengths in the firn range from 0–15 cm (Gkinis et al. 2021; Johnsen et al. 2000), while in the deep ice some estimates suggest values up to 60 cm (Pol et al. 2010). Knowledge of the diffusion length is important, as it enables us to determine on which timescales climate variability is preserved, and even restore some of the attenuated signal.

How diffusion affects the water-isotope signal

To visualize the potential effect of diffusion on the water-isotope signal in deep ice, we produced a virtual water-isotope record with the properties of the Beyond EPICA Oldest Ice Core (BE-OIC) currently being drilled in Antarctica. As an assumed climate record, we use the marine benthic stack (Lisiecki and Raymo 2005, "LR04 stack"), a landmark climate record based on a global collection of $\delta^{18}O$ measurements in benthic foraminifera. This record represents global ice volume and is strongly correlated on glacial-interglacial scales with Antarctic ice-core records. We adjust the age scale of this record to an age-depth model (Chung et al. 2023) of the BE-OIC, and rescale and invert the benthic $\delta^{18}O$ values using the EPICA Dome C $\delta^{18}O$ record (EPICA community members 2004), taking the peak of the Last Interglacial Period and Last Glacial Maximum as reference points.

As an example of the potential effect of diffusion, we zoom into a 25 m section in the deep part of this virtual ice core that represents 11 glacial–interglacial cycles from 1.2 Myr BP to 1.6 Myr BP (Fig. 1a). Simulated diffusion was applied to the record using three different diffusion lengths, demonstrating the potential magnitude of the smoothing effect. While a diffusion length of 10 cm (blue) simply rounds out the sharp peaks and troughs, a diffusion length of 60 cm (red) greatly attenuates the amplitude of even the glacial–interglacial cycles.

To quantify this effect, we calculate the remaining variability of a given frequency as the diffusion length is increased (Fig. 1b). We show the remaining power at decamillennial timescales (light gray, 10 kyr), as well as the dominant frequency driving
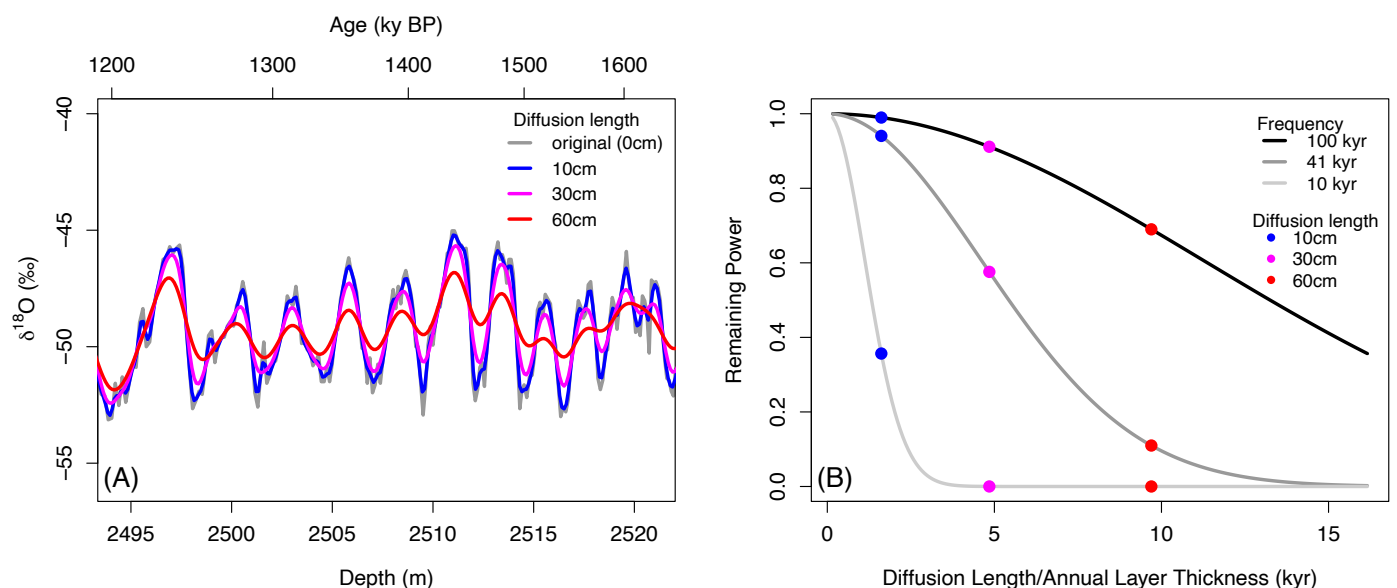

Figure 1: (A) Effect of diffusion length on the simulated deep ice-core record. **(B)** Remaining power at specific timescales against diffusion length in time units, converted from depth units by dividing by the average annual layer thickness across the depth range shown in (A). The three frequencies represent decamillennial variability (light gray, 10 kyr), Earth's obliquity cycle, dominant before the MPT (dark gray, 41 kyr) and Earth's eccentricity cycle, dominant after the MPT (black, 100 kyr). The colored dots represent the diffusion lengths shown in (A).
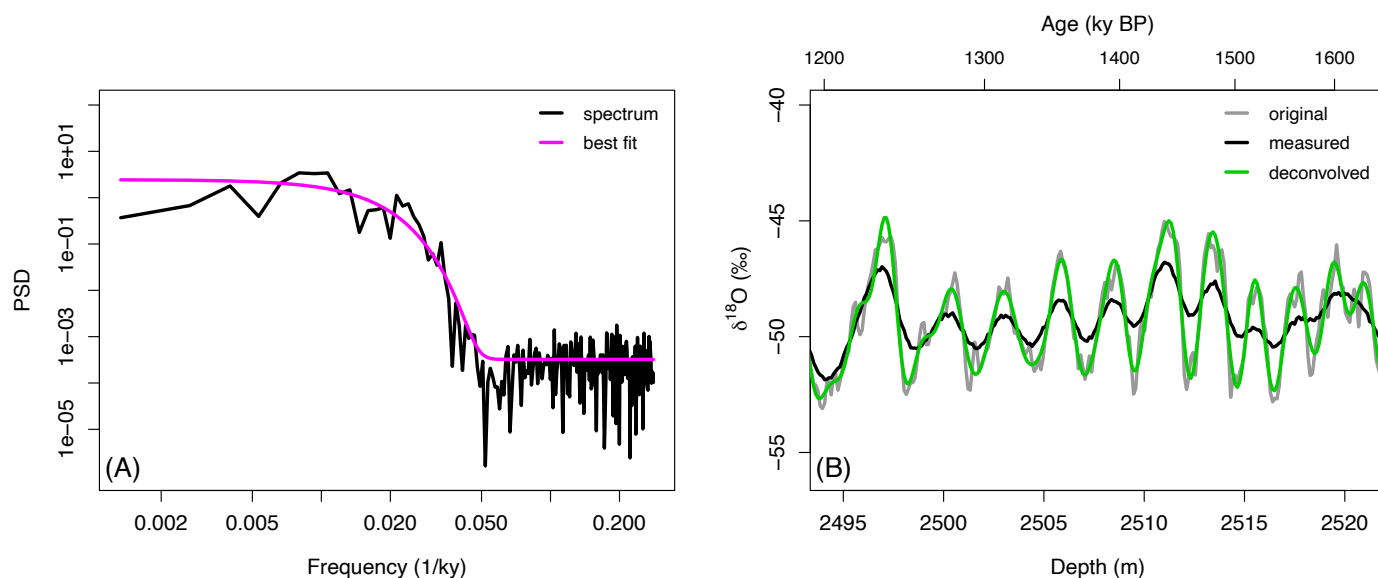
Figure 2: (A) Power spectrum of the diffused virtual isotope record from Figure 1a, assuming 60 cm diffusion and noise (black) and best fit (magenta). **(B)** Time series of the 60 cm diffused record (black) and deconvolved using Wiener deconvolution (green). Also shown is the original record before diffusion (gray). The amplitudes of the original glacial–interglacial cycles are restored, but with negligible sub-millennial variability remaining.

glacial–interglacial variability both before (dark gray, 41 kyr) and after (black, 100 kyr) the Mid-Pleistocene Transition (MPT) (Clark et al. 2006). Significant decamillennial variability only remains for a diffusion length of 10 cm, while on the 100-kyr timescale less than a third of the power is lost, even for a 60 cm diffusion length. The glacial–interglacial cycles in Figure 1a mostly follow a 41-kyr cycle trend, represented by the dark gray curve in Figure 1b. The striking difference in the smoothing of this glacial–interglacial variability for different diffusion lengths is intuitive, once compared with the three diffusion lengths marked on the 41-kyr curve. While approximately 94% of the power remains when diffused with a 10 cm diffusion length, less than 11% survives once the diffusion length is increased to 60 cm.

Recovery of the water-isotope record
For a better reconstruction of past climate evolution, we would like to be able to recover some of the diffused information. To achieve this, we need to know how much variability has been lost at every frequency. Thus, we need to know the diffusion length. It is possible to statistically estimate the diffusion length by analyzing the power spectrum of a water-isotope record. Using the spectral representation of diffusion outlined in Johnsen et al. (2000) enables us to apply a fit to the power spectrum of the water-isotope record to empirically derive the diffusion length (Fig. 2a).

Once a diffusion length has been obtained, we are able to back-diffuse the isotope record through a process called deconvolution. This technique amplifies the variability of the diffused frequencies to the expected initial amplitude, reversing the smoothing process. If water-isotope measurements were taken flawlessly, with perfect precision and no noise introduced by sampling preparation, handling and analytical uncertainty, then it would be possible to almost perfectly reconstruct the signal originally archived in

the upper firn layers. In practice, measurement noise is a significant limiting factor for deconvolution. At the highest, most diffused frequencies, this noise often greatly exceeds the remaining climate signal. Amplifying these frequencies will also blow up the noise, destroying the signal. To resolve this, we can filter out the frequencies with a signal-to-noise ratio (SNR) below one, through the use of a Wiener filter (Wiener 1949). As we are losing the fastest variations, the recovered signal is still smoother than the original, undiffused LR04 stack record (Fig. 2b).

In addition to minimizing the measurement noise, it is also important to obtain an accurate diffusion length, in order to calculate the magnitude of attenuation for each frequency, and to correctly identify at which frequency the SNR drops below one. Deconvolving with an incorrect estimate will either over-amplify lower frequencies if the diffusion length is too large, or amplify the higher noisy frequencies if the diffusion length is too small. Therefore, improvements to diffusion–length estimation methods and models are indispensable for high–quality signal reconstructions of this kind.

Summary
The loss of high–frequency variability in water-isotope records due to diffusion in ice cores poses a significant challenge when attempting to infer past climate. This problem is especially pronounced in deep ice cores where, due to densification and geothermal heat flux, layers are extremely thin and much warmer in the deepest, oldest ice. Statistical methods exist for estimating the diffusion length, which can be used not only to better interpret these smoothed water-isotope records, but also restore variability across certain attenuated timescales. Improved reliability and effectiveness of deconvolution techniques is possible through refining diffusion-length estimation methods, and optimizing measurement processes to minimize the measurement noise. It is also

crucial for obtaining as much information as possible from future deep ice-core projects.

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Where does the mineral dust in Greenland ice come from?

Geunwoo Lee[1], T. Erhardt[1,2] and H. Fischer[1]

The Asian deserts were identified as the primary source of mineral dust in Greenland ice. However, secondary sources may be overlooked when quantifying contributions of different sources in large bulk samples. Single particle studies can help overcome these limitations.

How mineral dust is archived in Greenland ice

Various types of aerosols are produced in different environments on Earth. For example, volcanoes emit aerosols and precursor gases during their eruptions, oceans generate sea-salt aerosols, and deserts produce mineral dust aerosols (Fig. 1). Among these aerosols, mineral dust plays a crucial role in aerosol composition.

The emission of soil-derived dust into the atmosphere occurs when the wind velocity is high enough to disperse the dust. The threshold wind velocity depends on the particle size, mass, and soil moisture content in the source region. In quantitative terms, the flux of dust generated by the wind is nonlinearly dependent on wind speed (Marticorena and Bergametti 1995). Reconstructing the strength of dust emission from measured ice-core concentrations can help us understand climate change in the source regions.

Many of the major dust sources are located in arid regions of the extratropics due to their dry and windy conditions. This restricted location of dust sources implies that dust must be transported over long distances by atmospheric circulation to reach Greenland. The atmospheric lifetime of dust depends on its size, mass, and the degree of washout by precipitation en route. Thus, climatic changes, such as alterations in atmospheric circulation patterns and precipitation, impact the transport efficiency of dust to Greenland. Long-range transported dust is deposited onto the surface of the Greenland Ice Sheet through both wet and dry processes. Size-dependent dry deposition of aerosols always occurs, whereas wet deposition can only occur if a precipitation event happens on the ice sheet. In summary, for efficient dust export to the Greenland Ice Sheet, dry and windy conditions at the source region and little precipitation en route are necessary (which typically implies transport at high altitudes). Ideally, precipitation over the ice sheet should occur at the time the dust plume reaches Greenland.

Different approaches to determine where the mineral dust came from

Various methods have been used to investigate the sources of dust in Greenland ice. Satellite imagery has been used to observe the transport of dust from its sources to Greenland directly. For example, Prospero et al. (2002) used satellite pictures to identify the desert belt extending from North Africa to Eastern Asia as the primary source of dust in the Northern Hemisphere. Since satellite imagery can only be obtained from cloud-free scanned regions and only for the last few decades, it falls short of providing a comprehensive understanding of the influence of past climate on the sources of dust in Greenland ice.

Atmospheric circulation modeling also enables the exploration of dust transport also for past and future conditions. Kahl et al. (1997) modeled back trajectories of air masses from Summit Station, Greenland. They found that approximately 60% of all winter trajectories to Summit, Greenland, were connected to a cluster that allows for aerosol transport from the East Asian desert dust source region, whereas a cluster connected to the North American dust source region was dominant (46%) in summer. However, this approach has limitations in accurately determining the source apportionment when atmospheric conditions are poorly defined in the model. This is especially true for past climate conditions that cannot be validated against meteorological observations, compromising the accuracy of the model's results in such cases.

Direct analysis of the dust deposited onto the Greenland Ice Sheet is another effective way to determine its origin. Mineralogy, elemental composition, and isotopic composition are widely used (often in combination) for source identification. Mineralogy can help identify the type of soil using crystal information. For example,
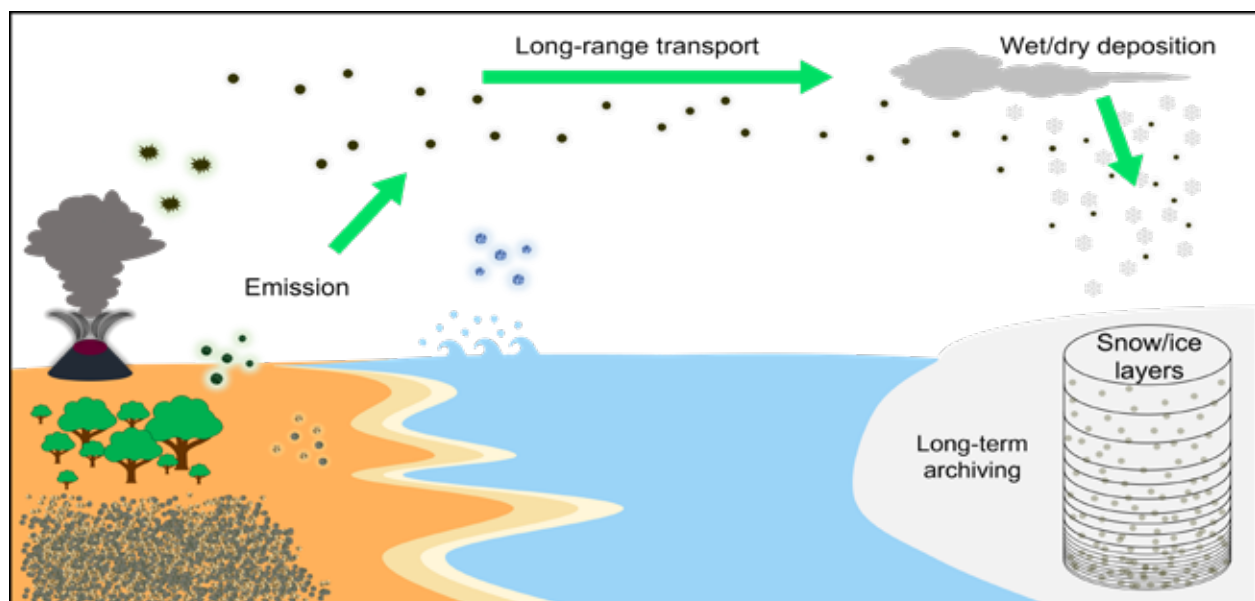

Figure 1: Life cycle of aerosol components archived in ice cores. Aerosol species are emitted from various sources, such as deserts, vegetation, volcanic activities, and oceans, and then transported over long distances by atmospheric circulation. Aerosols (such as dust) are wet- and dry-deposited en route and onto the ice sheet, and preserved in ice layers.
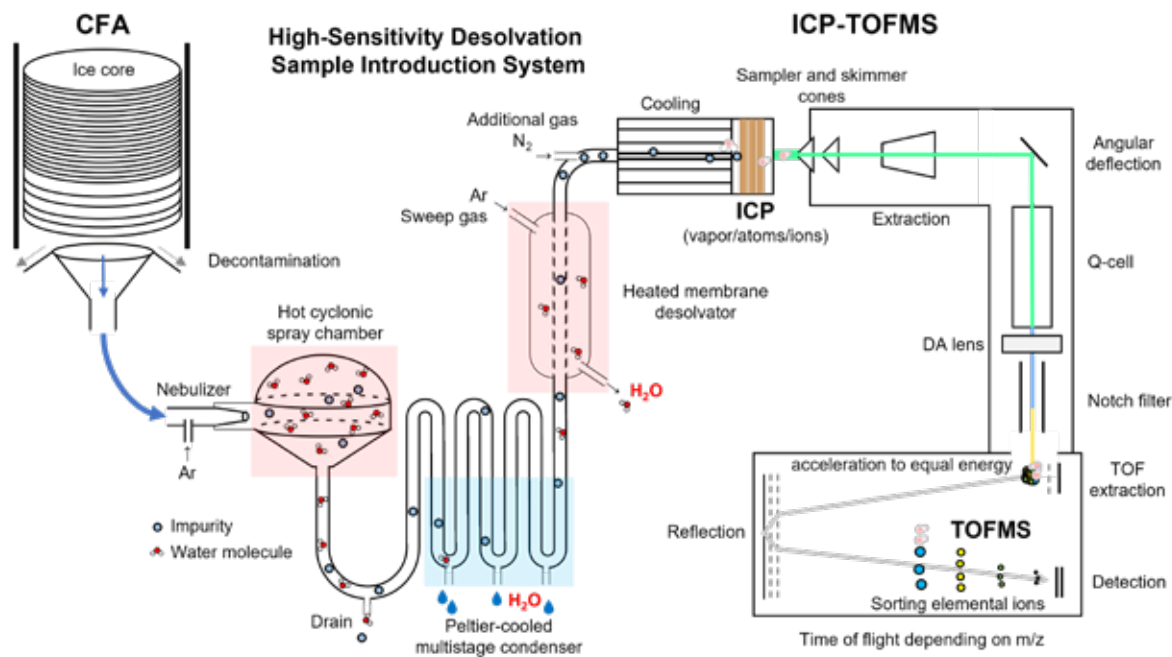
Figure 2: Schematic diagram of CFA-sp-ICP-TOFMS with a high-sensitivity desolvation sample introduction system. The meltwater sample from the CFA flows into the desolvation unit and undergoes a drying process through heating, condensation, and membrane diffusion during sample introduction. The ions reaching the TOFMS can be analyzed over the 23 to 254 mass range, and due to the high time-resolution of sp-ICP-TOFMS, individual dust particles can be detected, in addition to the dissolved background.

Maggi (1997) characterized the mineralogical composition of dust from glacial and interglacial periods in the Greenland Ice Core Project ice core and compared it with dust samples from low- and high-latitude source regions. The results suggest that warm periods are characterized by a higher contribution from chemical weathering in low-latitude source regions compared to more mechanical weathering in mid-latitudes during cold periods.

The elemental and isotopic composition of dust can serve as unique fingerprints for identifying dust sources, and are typically measured using mass spectrometry. Bory et al. (2003) used the mineralogy and isotopic signatures of the dust in snow-surface samples to identify present-day dust sources for Greenland. The mineralogical signatures found in all the dust samples from Greenland snow pits, characterized by low kaolinite to chlorite ratios, provide clear evidence that the sources are dominated by East Asian desert areas. This finding rules out North America and Northern Africa as major sources (Bory et al. 2003). The isotopic signatures of the samples not only agreed with the East Asian origin determined by their mineralogy, but also showed pronounced seasonal variation in sources within Asian inland regions. The Taklamakan Desert contributes substantially to the dust transported to northern Greenland during the maximum dust concentration in spring, while the main source of dust for autumn is shifted to the Tengger and Mu Us deserts (Bory et al. 2003).

However, some recent studies have suggested that the sources of dust may be more complex than previously thought, and may vary in response to abrupt climatic changes, such as Dansgaard-Oeschger events (Han et al. 2018; Újvári et al. 2022).

Single particle analysis: A new approach to dust characterization

Most of the aforementioned chemical methods which describe bulk parameters of large ice samples after melting and pretreatment, like acid digestion, have inherent limitations. This implies that (i) chemical characterization by these methods cannot distinguish between particulate and dissolved dust tracers and (ii) bulk samples average a mixture of many individual dust particles which may originate from different source regions. To overcome these limitations, we follow a new approach that takes advantage of the millisecond time resolution of single-particle inductively coupled plasma time-of-flight mass spectrometry (sp-ICP-TOFMS) (Fig. 2). This novel approach enables the detection and elemental characterization of single dust particles in addition to the dissolved impurities in a meltwater stream provided by the continuous flow analysis (CFA) developed at the University of Bern (Kaufmann et al. 2008). First results on the elemental composition of single dust particles from Greenland meltwater samples support Asian deserts as the main origin of the long-range transported particles to Greenland (Erhardt et al. 2019).

Conclusions and outlook

The origin of dust in Greenland has been determined through various approaches, such as remote sensing, atmospheric circulation modeling, and direct measurements of dust in ice cores. Many previous studies, using diverse approaches, agree that Asian deserts are the primary sources of dust transported to central Greenland. However, we stress the importance of high-resolution single dust particle analysis (Erhardt et al. 2019), in addition to bulk analysis. The sp-ICP-TOFMS enables the investigation of elemental composition of individual dust particles in samples. This allows the precise characterization of the fingerprints of individual soil-derived

aerosols from both source samples and Greenland ice, including the internal variation within each source region and source mixing.

Within the DEEPICE project, we are furthering these studies by improving our analysis system with a desolvation sample introduction, which dries the sample stream before it enters the plasma (Fig. 2). Drying the sample helps to reduce loss of analytes during the introduction, and minimizes spectral interferences caused by the input of water into the system. Furthermore, we are developing automated data analysis routines to characterize different clusters of dust origin. However, diverse methods should be used complementarily to improve our understanding of the origin of dust in Greenland ice under different climatic conditions.

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Organic tracers in ice: Untapped potential for specific biomarkers of past environment

Hanne Ø. Notø

Organic compounds in ice cores are valuable tracers of past terrestrial and marine biospheres. Analytical challenges have previously prevented quantification of these compounds, but recent breakthroughs have allowed us to measure and better understand biogenic processes and past atmospheric circulation.

Organic tracers in the cryosphere

Important paleoclimatic information can be yielded from the analysis of organic impurities in ice cores. Organic compounds contribute up to 90% of total fine aerosol particle mass. Thus, they contain large amounts of information about the sources and transport patterns of aerosols (Kanakidou et al. 2005). Organic particles and microorganisms can be cloud condensation and ice-nucleating particles, which means they can easily end up being deposited as snow. Additionally, wet precipitation is an efficient scavenger of organic particles from the atmosphere. Ice cores serve as an archive of the past atmosphere since they contain traces of organic aerosol particles and dissolved organic matter. Despite this, very few organic compounds have been successfully quantified in ice cores. Biomass burning tracers, such as levoglucosan and vanillic acid, and the sea-ice proxy methanesulfonic acid, are examples of organic compounds which have been successfully quantified in ice cores.

Challenges with quantification of organic compounds in ice

The greatest challenge with quantification of organic compounds in ice cores is their low concentrations. The total organic carbon content in ice cores from Antarctica has been measured in several ice cores to be between 5 and 900 ppb carbon (Federer et al. 2008; Legrand et al. 2013), which results in individual compounds being found at ppb or ppt levels. Most analyses of organic compounds in ice cores, therefore, require preconcentration steps. Ice cores are cut into discrete samples and the exposed outside is removed with a knife before the ice is melted and often preconcentrated. Preconcentration is the process of increasing the concentration of target compounds in a sample, either by collecting the target compounds from the solution, or by evaporating the solvent from the mixture. Preconcentration improves detection, but often part of the target compound is lost in the process. The amount of initial substance preserved after the preconcentration

steps is referred to as the "recovery rate". Preconcentration methods used for organic compounds in ice have reported recovery rates upwards of 80% (King et al. 2019; Müller-Tautges et al. 2014). However, with discrete ice-core samples, the spatial resolution is limited as these methods often require high sample volumes. A measurement of the recovery rate of each compound measured is also necessary for proper quantification. Additionally, the process is labor intensive and the repeated cutting of the ice cores risks sample losses.

Preunkert et al. (2011) found that lab air could be a significant source of organic carbon contamination in their melted ice samples due to the dissolution of atmospheric traces of formic and acetic acids. These authors found a rapid increase in dissolved organic carbon (DOC) in open bottles of ultrapure water left in a clean room and in a "general purpose" room. The general purpose room had a contamination increase two orders of magnitude higher than in the clean room. Even a closed bottle in the general purpose room was found with a 25 ppb carbon DOC increase per hour, but this was much lower than the approximate 3000 ppb carbon DOC increase per hour observed in the open bottle, in the same location. This demonstrates that great care is needed to limit contamination of samples, especially after cutting and melting discrete samples of ice. One way of preventing this issue is by omitting the sample preparation steps altogether. This can be done using continuous methods, rather than discrete samples.

Continuous sampling and measurements of ice cores

Continuous flow analysis (CFA) has become one of the standard methods of ice-core analysis since it was developed in the 1990s (Fuhrer et al. 1993; Sigg et al. 1994). In CFA, sticks of ice are melted from the bottom, and the meltwater is continuously pumped into instruments for analysis. The sample experiences little to no contact with air, and is directly analyzed a few seconds after melting (Fig. 1). The melthead is often shaped so only the innermost section of ice is directed to the most sensitive analyses. The outermost ice is used for analyses less prone to contamination, such as stable water isotopes ($\delta^{18}O$ and δD). CFA reduces several of the issues related to analyzing organic
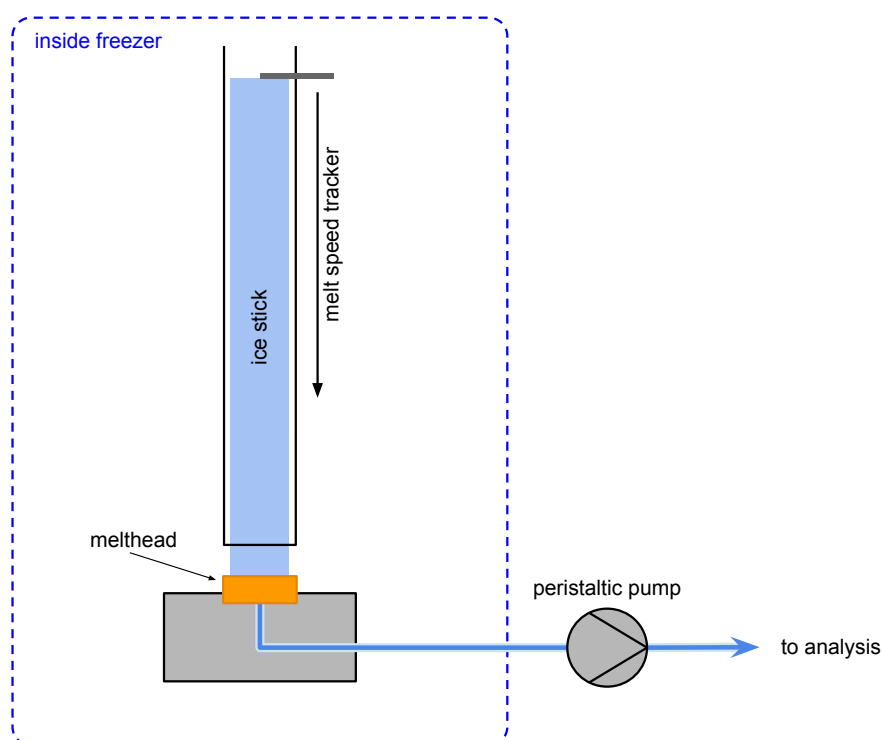

Figure 1: Continuous flow analysis (CFA) melting system. Ice cores are cut into sticks, which are placed on the melthead. The melt speed is regulated through the temperature of the melthead. Peristaltic pumps direct meltwater from the melthead to instruments for analysis.
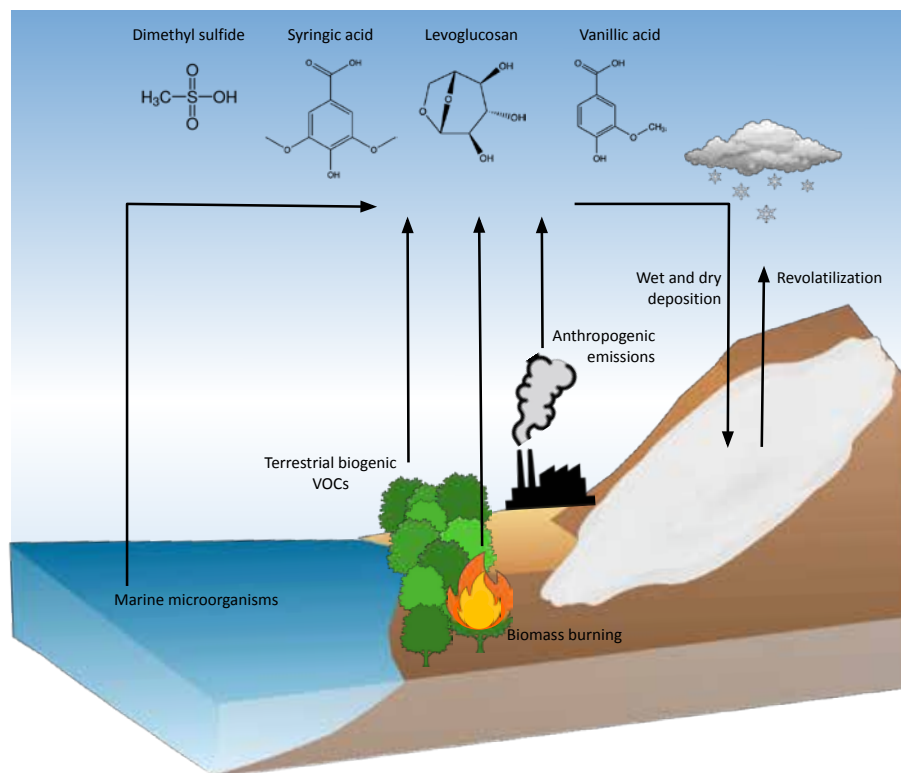
Figure 2: Schematic of transport pathways from sources such as marine microorganisms, terrestrial vegetation, wildfires, and anthropogenic emissions to glaciers and ice sheets. The organic compounds can be deposited as dry or wet deposition, and after deposition, compounds can be chemically or biologically degraded or revolatilized to the atmosphere.

compounds, such as airborne contamination and sample losses from cutting the ice. The drawback is that contamination can stem from the tubing, and signals may be dispersed in the tubing due to diffusion processes (Rasmussen et al. 2005).

The greatest challenge still is that very few methods are able to detect compounds at the low concentrations found in ice cores with high time resolution. Shi et al. (2019) measured discrete surface-snow samples in Antarctica, and observed mean concentrations of vanillic acid and syringic acid of 5.74×10^{-2} pg/mL and 3.84×10^{-2} pg/mL, respectively (1 pg = 10^{-12} g).

Barbaro et al. (2022) recently coupled a CFA melter to a fast liquid chromatography tandem mass spectrometer (FLC-MS/MS). They quantified vanillic and syringic acids, and recently also levoglucosan in alpine ice cores. The method uses two liquid chromatography columns in parallel, allowing one column to be in use while the other is flushed and prepared for the next sample. This results in fast measurements with a spatial resolution of 1 cm. The methods' limit of detection (LOD) was 3.6 pg/mL and 4.8 pg/mL for vanillic acid and syringic acid, respectively (Barbaro et al. 2022). Comparing the LOD of this method to the concentrations found in Antarctic snow shows that current methods involving CFA are not yet able to quantify organic compounds in Antarctica, but can be useful in areas with higher concentrations of organic trace components, such as continental glaciers.

Factors influencing observed organic components in ice
Measurements of organic compounds in ice have given us insight into biomass

burning, sea-ice extent in the Antarctic, and anthropogenic pollution in the past (Fig. 2). Continental glaciers can yield more local information, while ice cores drilled on ice sheets in Antarctica or Greenland can serve as atmospheric background pollution levels.

Shi et al. (2019) found higher levels of levoglucosan and syringic acid near the Antarctic coast compared to further inland. They found no trend with distance from the coast for vanillic acid. Since the compounds have the same sources and similar chemical structures, it is expected that levoglucosan and syringic acid are more sensitive to oxidation and are consequently depleted more rapidly in the atmosphere than vanillic acid. The oxidation of compounds must, therefore, be taken into consideration when interpreting measurements from ice cores. Industrial and fossil-fuel-related emissions have increased the oxidative potential of the atmosphere (Lelieveld and Dentener 2000), which could disproportionally deplete the signal of organic compounds in recent centuries of ice-core chronologies. For older sections of ice, post-depositional effects, such as chemical and microbial degradation, UV-induced degradation in the surface snow, and revolatilization of compounds, must be considered. These post-depositional effects are not currently well understood, but could have differing effects on the levels of organic compounds in different layers of ice.

Conclusion
Organic compounds remain largely unexplored in ice cores, mainly due to difficulties with contamination and not having sensitive-enough methods. Recent developments have allowed continuous measurements of organic biomass burning tracers in alpine ice cores, and high-resolution measurements

of discrete ice samples from Antarctica. Methods are being improved to increase both the number of organic analytes being measured in one core, and the temporal resolution of the ice-core chronology. By analyzing fatty acids, terpenes, phenolic acids, and other components, we gain insight into the terrestrial and marine biospheres of the past, as well as anthropogenic impact on atmospheric chemistry. Developing analysis methods further will allow us to unveil more of these processes, and better understand the biogenic processes and atmospheric circulation in the past.

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Impurities in the ice matrix: Where are they, and why does it matter?

Piers Larkman[1], N. Stoll[2], R. Rhodes[3] and P. Bohleber[1]

The impurities contained in ice impact its physical and chemical properties. To understand this impact, and therefore improve ice-derived climate reconstructions, it is critical to determine the location and nature of impurities in the ice matrix.

The Earth's glaciers and the Antarctic and Greenland ice sheets store a vast amount of information about its climate history. Within the ice, alongside preserved pockets of Earth's past atmospheres and the temperature record detailed in the isotopic ratios of water molecules, impurities provide additional insights into the past. These impurities can be diverse in origin and composition, such as dust particles carried from Patagonia to Antarctica (Basile et al. 1997), ash from Icelandic volcanoes reaching Greenland (Wittmann et al. 2017), and salt aerosols originating from open waters and the surface of sea ice (Rhodes et al. 2017). These impurities are analyzed to investigate past atmospheres' aerosol composition, the physical properties of ice, and many other subjects (Stoll et al. 2021). While analysis of meltwater has proved an excellent approach to extracting such information from ice, melting ice causes the loss of spatial data relating to the location of impurities within the ice matrix.

Precise information regarding the location of these impurities within the ice matrix is crucial (Stoll et al. 2022). Understanding the location of impurities within the ice microstructure helps address questions on how to best exploit highly disturbed and thinned ice, such as that targeted at Little Dome C in Antarctica by the Beyond EPICA Oldest Ice Core project, and translate this proxy data into meaningful climate and environmental data. Both microscale processes, such as ice formation from snow, and macroscale processes, such as ice flow, are linked to how impurities are distributed in ice. These post-depositional effects impact the preservation of impurity-derived climate signals by altering the local concentrations and distribution of impurities within the ice. Ice at the bottom of the Antarctic Ice Sheet has highly thinned layers where many thousands of years of ice and impurities can be packed into a single vertical meter. This concentration of information necessitates further advancements in

analytical techniques to fully exploit this archive. Work done in the DEEPICE project is developing our understanding of these topics, in part through developments of high-resolution analytical techniques to map impurities in ice. Ideally, any analysis of such ice should be micro-destructive or non-destructive to preserve the ice, enabling further analysis and retention of an archive.

Ice structure and impurity locations
A pure ice crystal is a solid arrangement of water molecules in a hexagonal structure. Glacier ice, formed by the metamorphosis of snow, comprises many such crystals. Structural discontinuities between adjacent crystals are known as grain boundaries (Fig. 1). However, glacier ice is not comprised solely of crystals containing pure water. Impurities are also incorporated in the ice and have been shown to exist both within crystals and at their boundaries (Bohleber et al 2021). So, how are the locations of impurities in ice samples determined?

Locating impurities
To enable the analysis of samples in their solid state, and therefore understand the spatial distribution of their impurities, ice samples must be stored and analyzed at stable temperatures of -10°C or lower. Despite this challenge, several techniques have been applied to ice that shed light on the spatial distribution of impurities within the microstructure of ice. These have been discussed in detail in a review by Stoll et al. (2021). These techniques are often coupled with some optical analysis to locate targeted features such as grain boundaries or dust particles in an ice sample. Following is a discussion of three complementary techniques used to understand the spatial distribution of impurities in ice.

Raman spectroscopy uses the change in energy experienced by monochromatic incident photons interacting with a molecule's vibrational modes to determine the chemical structure and, thus, the composition of a target. In ice analysis, Raman spectroscopy is used to determine the mineralogical composition of insoluble minerals throughout the volume of an ice sample. The output is precise information on the mineralogy of a particle at a well-defined location inside the ice, but no information is collected on soluble impurities (Stoll et al. 2022).
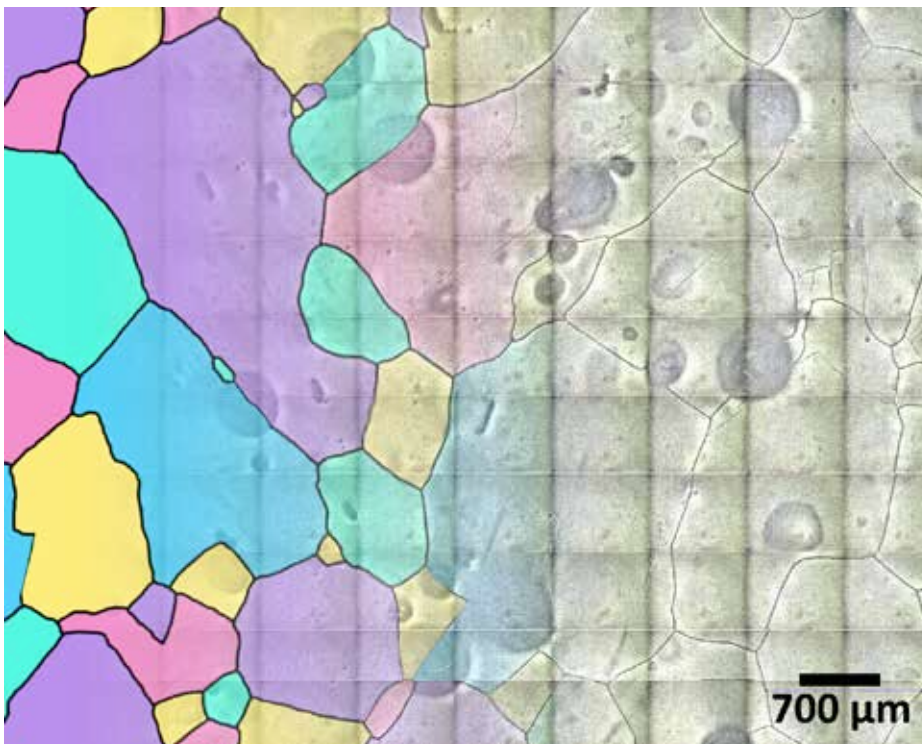

Figure 1: Optical image (right) and illustration (left) of the grain-scale structure of glacier ice collected from Talos Dome, Antarctica. Glacier ice is comprised of crystals (represented in different colors in the cartoon section), which can have different orientations. The intersections of crystals (represented by black lines in the cartoon) are known as grain boundaries. Gray rounded features are air bubbles. Impurities are distributed throughout grain-interior and inter-grain regions, as illustrated in Figure 2, which shows the chemical distribution in the same area. Figure modified from Bohleber et al. (2021).
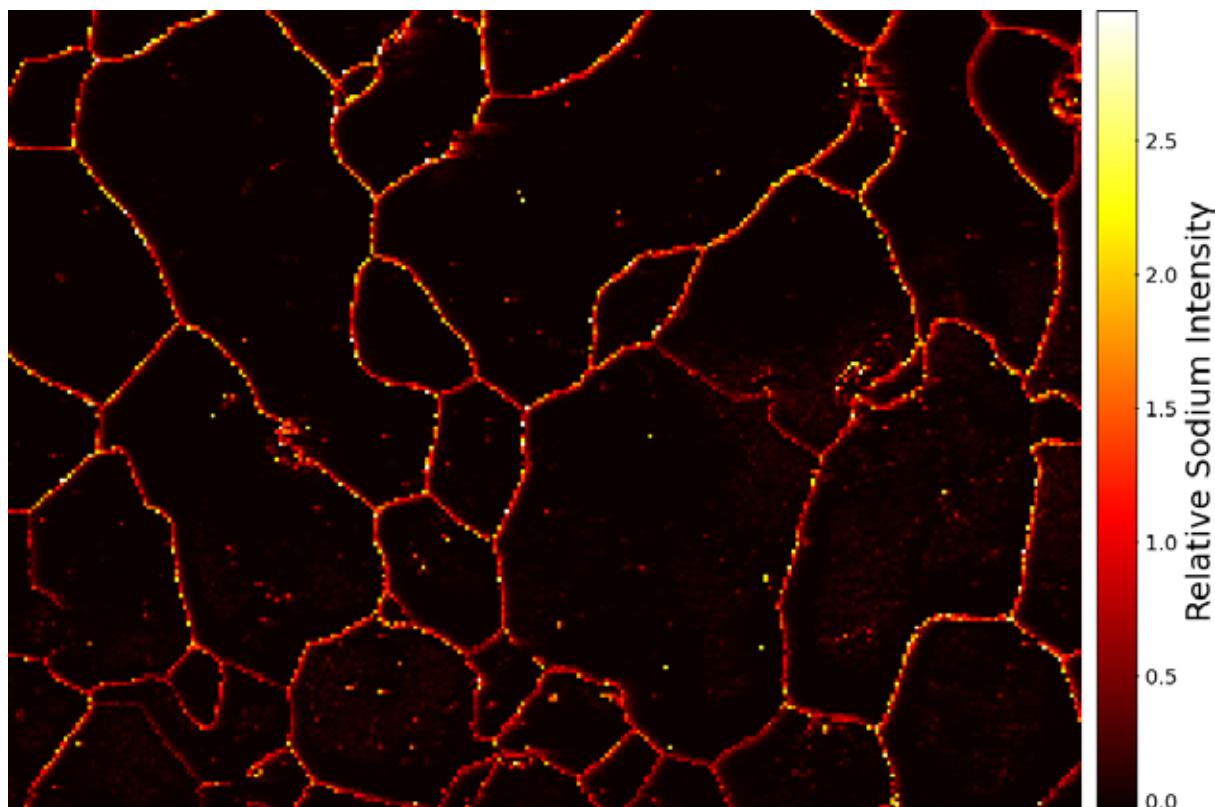
Figure 2: LA-ICP-MS elemental map showing the distribution of sodium on the surface of an ice sample. Note the strong association of sodium with the grain-boundary network, as seen in Figure 1, which shows an optical image of the same area. Figure generated from data presented in Bohleber et al. (2021).

Scanning electron microscopy (SEM) and coupled energy dispersive X-ray spectroscopy (EDS) make use of both the secondary electrons and X-ray radiation emitted from a surface that an incident electron beam has bombarded. When used in tandem, the SEM and EDS techniques can be used to both spatially map the microstructure of ice and gain information on the composition of impurities simultaneously, but without quantifying the concentration of impurities present (Barnes et al. 2002).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) utilizes a brief laser pulse to ablate small volumes of material from a target's surface. This material is aerosolized and transported to a mass spectrometer, where its elemental composition and relative concentration is determined. This process gives information on soluble and insoluble elements present in a target sample. By rapidly firing the laser over an area of a sample, high-resolution two-dimensional elemental maps, usually covering vertical cross-sections, can be generated. Figure 2 displays such data from an ice sample from Talos Dome, Antarctica (Bohleber et al. 2021). This image shows the impurities distribution on an ice sample's surface at a resolution of 35 µm.

These techniques give complementary data on impurities, with the potential for retention of samples due to the non-destructive nature of Raman spectroscopy, joint SEM and EDS analysis, and the micro-destructive nature of LA-ICP-MS. By combining these approaches, a more comprehensive analysis of impurity location in ice can be achieved across different scales, encompassing both detailed particle-level information and broader spatial patterns.

Data processing
The application and improvements of the methods presented here are leading to the production of large amounts of high-quality data. Much like the data collection processes, data-analysis procedures are being adapted to process and interpret these data. Two-dimensional spatial data, such as the chemical LA-ICP-MS image shown in Figure 2, benefits greatly from analysis using automated computer image processing to perform tasks such as isolating the grain boundary network from an image, overlaying optical images over chemical images, and extracting crystal sizes (Binder et al. 2013). After extracting this information, the extensive range of spatial data embedded within these images can give valuable insights into particle compositions and impurity distribution across distinct regions of the ice matrix, allowing for a better understanding of chemical and physical processes occurring within the ice.

Outlook
The ice core due to be extracted from Little Dome C in Antarctica will form a continuous ice record beyond 1.5 million years ago, offering new insights into the past variability of our climate and the history of the Antarctic Ice Sheet. However, analysis of this exceptionally deep and old ice presents distinct challenges. The ice matrix and impurity record at such depths have undergone many changes during their journey down the ice sheet. The ice at the bottom of this core has thinned considerably, containing tens of thousands of years' worth of variability within a single meter, meaning collection and interpretation of high-resolution data is crucial to fully capture the information within the core fully. Furthermore, the nature of this core as a unique archive and limited resource demands careful use. Therefore, any analysis should be high-resolution and non-destructive. Developments to the techniques discussed in this article are well-timed to give insight into the origin, composition, and location of the impurities within the core. This information will form a key part of our understanding of this exceptional climate archive.

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Mapping ice microstructure: Advancements in Large Area Scanning Microscopy techniques

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Microstructure of polar ice cores provides useful information about past climate conditions, improving our understanding of Earth's history and future climate changes. The development of automated imaging systems provides efficient and high-resolution insights into ice-core microstructure and its evolution.

Deep polar ice cores drilled in Greenland and Antarctica have been used to study the Earth's past climate, the evolution of the ice microstructure through an ice sheet, and the processes that control ice flow. As snow accumulates and turns into ice, it begins to deform and flow under the weight of the overlying snow and ice. This process, known as glacial flow, is driven by a combination of gravity and the mechanical properties of the ice itself (Binder et al. 2013; Cuffey and Paterson 2010).

Microstructure analysis of ice cores provides valuable information on the evolution of the ice sheet over time. By studying the size, shape, and orientation of individual ice crystals, we learn about the processes that control ice flow, such as deformation and recrystallization. This information helps us better understand how ice sheets respond to changes in temperature and other environmental conditions.

Over the last few decades, significant advances in computing power and digital imaging techniques have revolutionized the way we study and analyze polar ice cores. These new tools enable us to perform tasks that were once considered unfeasible or extremely time consuming, such as processing and analyzing vast amounts of data or creating continuous high-resolution images of ice-core microstructures.

From still cameras to line scanner
Recent developments in microstructure mapping have seen significant improvements: from the use of traditional still cameras and optical microscopy methods to the use of computer-controlled microscopic imaging systems. Kipfstuhl et al. (2006) provided an overview of the evolution of microstructure mapping, and how the advances in computing power and digital imaging techniques have revolutionized the way we study and analyze polar ice cores.

Early studies, such as Arnaud et al. (1998) and Nishida and Narita (1996), used still cameras to capture images of microstructures in firn and bubbly ice. Optical microscopes were also used to gather statistical data on air bubbles (Bendel et al. 2013) and air hydrates in ice (Kipfstuhl et al. 2001; Lipenkov 2000; Uchida et al. 1994). However, the use of traditional still cameras and optical microscopes had limitations in terms of image quality control and systematic mapping of microstructures.

Kipfstuhl et al. (2006) improved the process of microstructure mapping by setting up and testing a computer-controlled microscopic imaging system. The aim was to streamline and automate the microscopic observation process, resulting in scanning an ice section with dimensions of 5–10 cm x 10 cm, and generating digital images at microscopic resolution within the hour, while drilling operations were still in progress.

While the initial goal of the system was air-bubble and air-hydrate studies, Kipfstuhl et al. (2006) found that after the ice-core surface was exposed to sublimation, the method was also able to record boundaries between the ice crystals (grain boundaries) as well as a wide variety of deformation-induced features.

The microstructure analysis of ice cores dates back to 1960 when studies conducted on Camp Century and Byrd ice cores from Greenland and Antarctica, respectively, focused primarily on average grain sizes and crystal orientations (Faria et al. 2014). Later, comprehensive grain-boundary studies by Kipfstuhl et al. (2006) and Weikusat et al. (2009) led the way to the development of the first Large Area Scanning Microscope (LASM) in industry by Schäfter & Kirchoff GmbH (S+K). Subsequently, Binder et al. (2013) and Binder (2014) introduced a specialized image analysis software capable of extracting and parameterizing grain-boundary networks from LASM images.

The LASM allows for a more efficient analysis of grain boundaries. Unlike the optical microscope that requires XY translation to capture and stitch together 1500
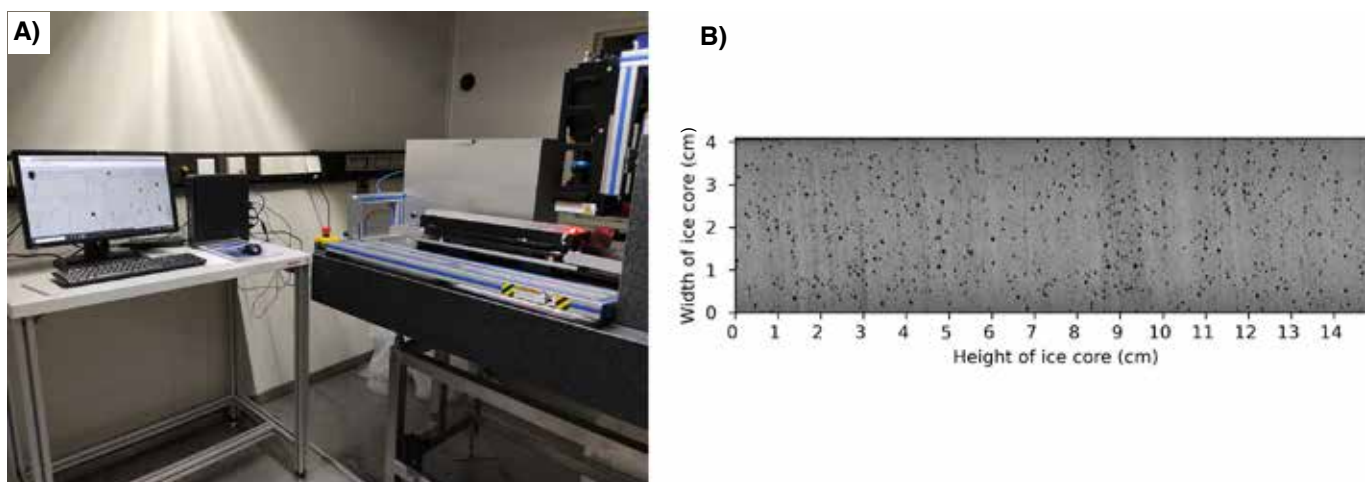

Figure 1: (A) Three-axis xLASM for the analysis of the microstructure of polar ice cores. **(B)** Output example of a full core scanned with xLASM from the NEEM ice core.
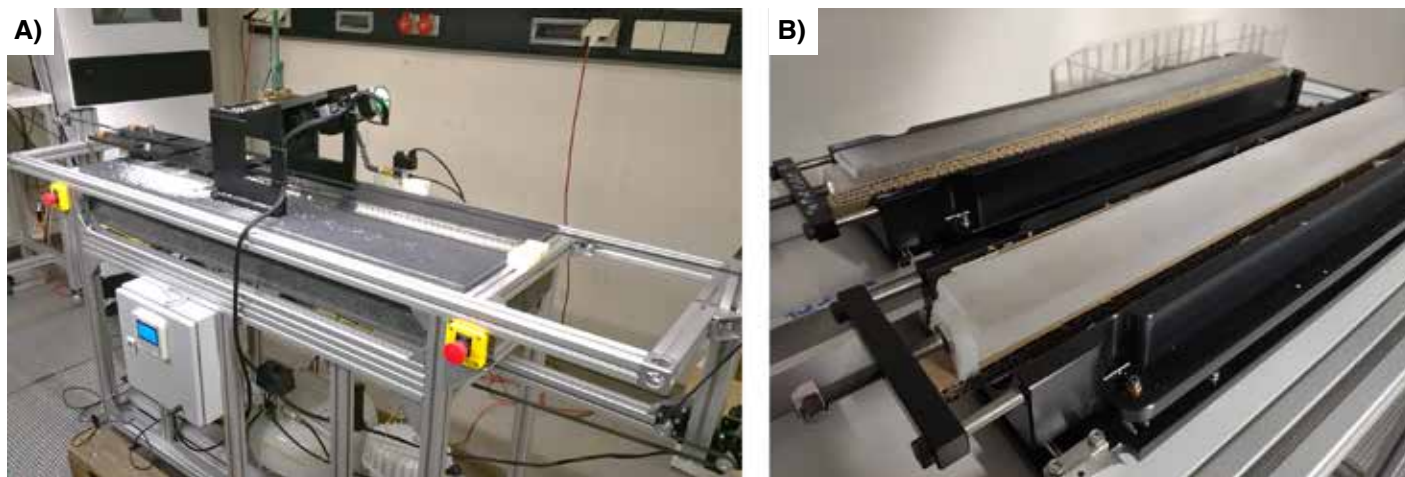
Figure 2: (A) Picture of the automated microtome, which comprises a granite plate, a linear guide for horizontal motion, and a portal housing the surgical blades. **(B)** Photograph of mounted ice cores left to sublimate at -20°C after being microtomed.

micrographs into a map, the LASM utilizes a line scan camera, which captures images line by line, instead of a whole picture at once, and covers a larger area in a single scan (Krischke et al. 2015). Although the LASM does not need thousands of micrographs, there is still a need to stitch tens of images to cover the length of a single core (55 cm). Moreover, both systems require manual focus adjustments due to variations in the ice-sample height (Binder 2014).

The LASM, together with the Image Microstructure Analyzer software developed by Binder et al. (2014), has excellent capabilities for reconstructing the grain boundaries of the ice. This enables a detailed analysis of the spatial arrangements and characteristics of the ice grains. However, the complex sample preparation process and computationally intensive software highlight the need for further enhancements to streamline ice-core microstructure analysis.

Current developments in ice-core microstructure mapping
To address the issues mentioned above, ongoing testing of a second Large Area Scanning Microscope (xLASM) (Fig. 1a), which operates on three axes, aims to scan complete ice cores in a single operation. With a larger mapping area, the need for image alignment and matching is eliminated, significantly reducing computing time. Furthermore, the xLASM enables the automation of the height-focusing process.

The xLASM employs bright-field illumination. A scan of the NEEM ice core, a deep ice-core project in the Greenlandic ice cap, is shown in Figure 1b. This technique utilizes light that interacts with various components of the ice-core surface, such as grain boundaries and other microstructural features, leading to differential absorption, or scattering, of light. The transmitted light is collected by the lens and generates an image of the scanned surface. Bright regions of the sample correspond to areas that absorb or scatter light less, while darker regions correspond to areas that absorb or scatter the light more. The ice-core surface is imaged in reflection

and three consecutive images of 5 µm resolution are produced in 15 minutes.

The development and optimization of the xLASM for continuous observation of crystal size structures requires a precise and smooth ice-core surface to maintain the line scanner focus. To achieve this, we have devised an experimental setup featuring an automated microtome (Fig. 2a). By sampling the entire ice core (Fig. 2b), we can streamline the labor-intensive ice-sample preparation process, minimize inconsistencies during sublimation, scan under different imaging conditions, and eliminate the image stitching procedure.

Outlook
A significant advantage of employing line scan cameras in LASMs is their ability to rapidly capture high-resolution images of ice-core microstructures with excellent contrast. Unlike the standard microscopic method, which is time consuming and computationally intensive, the innovative LASMs developed by S+K can generate high resolution ice-surface images within just 5–10 minutes. Ongoing tests involving the new xLASM, coupled with an automated microtome, enable the sampling of whole ice cores through a new processing framework.

The current setup has been tested in a cold room at -20°C using samples from the NEEM ice core. The process of mounting, microtoming, and scanning ice cores allows for the processing of eight to 10 deep ice cores per day, aiming for more continuous ice microstructure analysis. The main time constraint is the sublimation needed to remove surface artifacts to ensure high quality data. The measurements and continuous observations obtained from the xLASM technology applied to ice cores enable the investigation of ice rheology and its impact on ice deformation. By utilizing this data, it is possible to obtain better insights on folds and disturbances in deep ice layers. This analysis is being conducted on existing ice cores and is anticipated to be applied to future ice cores obtained from the Beyond EPICA Oldest Ice Core project in Antarctica.

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Radionuclide-decay dating in ice cores

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Age estimates using the radioactive decay of radionuclides in ice cores have the potential to verify and extend existing age scales. The method is currently limited by unexplained variations in radionuclide concentrations and the large masses of ice needed for their measurement.

Radionuclide production

Earth is constantly bombarded by a flux of cosmic rays, which consist mainly of protons and alpha particles, traveling near the speed of light. In our atmosphere, they collide with gases and set off a cascade of nuclear reactions that result in the production of a range of radionuclides, including ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, and ^{81}Kr. Because the atmospheric composition is dominated by nitrogen (^{14}N) and oxygen (^{16}O), most reactions produce radionuclides with a relative isotopic mass below 16; heavier radionuclides are much less abundant (Beer et al. 2012; Poluianov et al. 2016).

Radioactive-decay dating is best known from radiocarbon, which is however, not suitable for most ice-core dating due to its comparably short half-life of 5.73 kyr (Beer et al. 2012). Several other radionuclides have much longer half-lives (Fig. 1a), but face two major challenges. Firstly, the low abundance of most radionuclides translates into low concentrations in ice, necessitating large sample masses for their measurement, as shown in Figure 1b. Secondly, the production of all radionuclides varies over time because the cosmic-ray flux on Earth is not constant. It is subject to modulations from the varying magnetic fields of the Sun and the Earth, since protons and alpha particles are charged particles.

The advantage of radionuclide dating is that it can produce absolute age estimates, independent of other age scales and time markers. Therefore, it can also be applied to ice with a disturbed stratigraphy, making it a valuable tool for the dating of deep ice cores.

^{36}Cl/^{10}Be

With a half-life of $t_{1/2}$ = 301 kyr, ^{36}Cl is well suited for dating ice with ages up to 1.5 Myr, which is what the Beyond EPICA Oldest Ice Core project aims to retrieve. For a sample with an age of 1 Myr, about 1 kg of ice is needed (Fig. 1b). Variations in the production signal affect ^{36}Cl and ^{10}Be similarly, so taking the ^{36}Cl/^{10}Be ratio theoretically removes production-related variations and isolates the decay signal (Delmas et al. 2004). However, measurements from the GRIP (Yiou et al. 1997) and Dome Fuji ice cores reveal significant variations of the ^{36}Cl/^{10}Be ratio unrelated to radioactive decay (Fig. 2a; Kanzawa et al. 2021; ca 7450–7350 yr BP). Most likely, these variations are linked to the different chemical and physical properties of the two radionuclides, which may lead to differences in their atmospheric lifetimes, transport pathways and deposition mechanisms (Beer et al. 2012).

At low accumulation sites, ^{36}Cl can be lost from the ice by reacting with acidic species to form volatile hydrogen chloride (HCl) after deposition, further complicating the interpretation of the measured ^{36}Cl/^{10}Be ratio (Delmas et al. 2004). Ice from glacial periods, however, has the potential to be unaffected by this because the glacial atmosphere contains higher concentrations of alkaline dust, which can neutralize acidic species (Röthlisberger et al. 2003; Wolff et al. 2010). Another uncertainty for age estimates is introduced by the accumulation of ^{10}Be at grain boundaries, where it can be adsorbed on to dust particles in deep ice, creating local concentration spikes and disturbing the stratigraphic signal (Baumgartner et al. 1997; Raisbeck et al. 2006).

Nonetheless, the ^{36}Cl/^{10}Be ratio has been successfully used to date the deepest section of ice from the Dye3 and GRIP cores, where the age estimates agreed with other dating methods (Willerslev et al. 2007).

^{26}Al/^{10}Be

The advantage of using ^{26}Al instead of ^{36}Cl is that it quickly attaches to aerosol particles, similar to ^{10}Be. The transport for both radionuclides should, therefore, be identical, leading to less variations in the ^{26}Al/^{10}Be ratio. Indeed, measurements of atmospheric air around the globe yielded the same ^{26}Al/^{10}Be ratio with deviations of no more than 5% and similar values for measurements in firn from several locations in Antarctica (Auer et al. 2009).

The disadvantage of using ^{26}Al is its very low production rate, which is about 300 times lower than that of ^{10}Be, necessitating at least 7–14 kg of ice for a single measurement of 1-Myr-old ice (Auer et al. 2009; Fig. 1b).

In a pilot study, Auer et al. (2009) measured the ^{26}Al/^{10}Be ratio in the deep, undated section of the EDML ice core (older than 150 kyr) and found that its values varied strongly between samples and were on average 50% higher than in samples from the modern-day atmosphere and Antarctic firn, even though
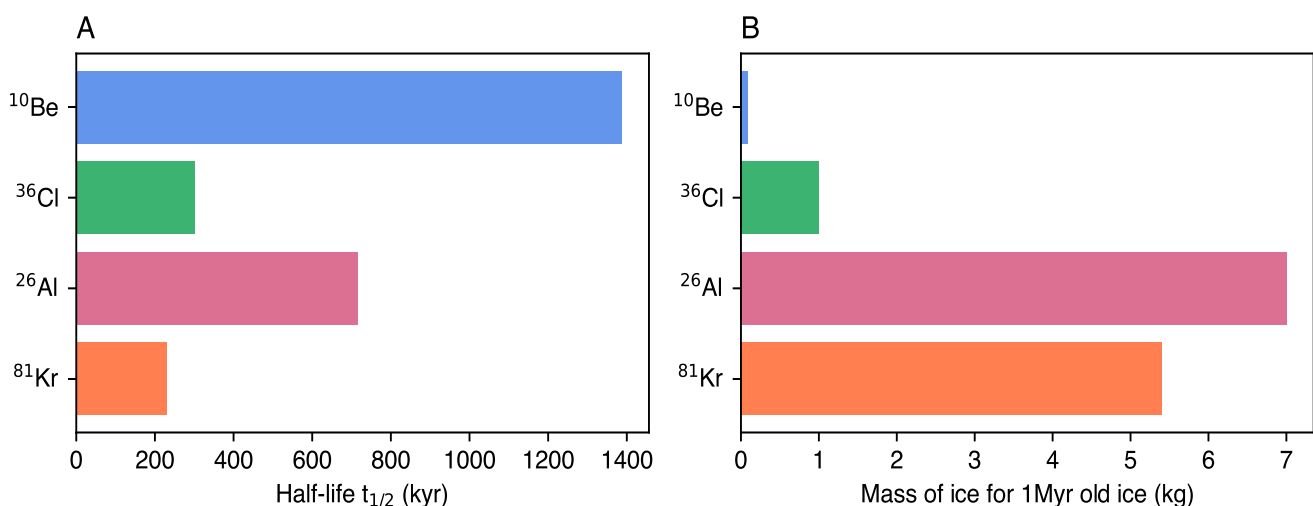

Figure 1: (A) Comparison of the half-lives of different radionuclides and **(B)** the mass of 1-Myr-old ice needed for measuring their respective concentrations.
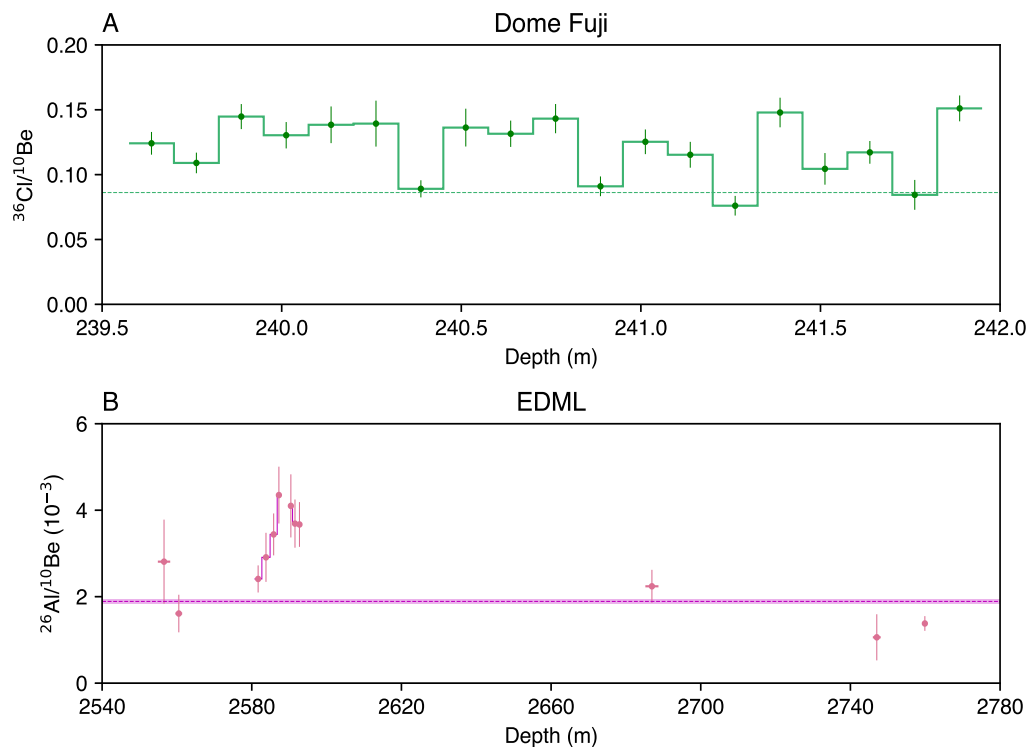
Figure 2: Variations of **(A)** the $^{36}Cl/^{10}Be$ ratio in the Dome Fuji ice core with the theoretical production rate value of 0.0862 shown as a dashed horizontal green line and **(B)** the $^{26}Al/^{10}Be$ ratio in the EDML ice core with the modern-day mean atmosphere value of $1.89 \pm 0.05 \times 10^{-3}$ shown as a horizontal magenta line. Data from Kanzawa et al. (2021) and Auer et al. (2009), respectively. Vertical bars indicate analytical errors.

the decay of ^{26}Al ($t_{1/2} = 717$ kyr) should lead to lower values (Fig. 2b). The authors concluded that recrystallization and high pressure may result in local concentration enhancements at the bottom of the EDML core. However, these alterations and their effects on ^{26}Al and ^{10}Be are not understood, and the $^{26}Al/^{10}Be$ ratio, therefore, appears to suffer from a similar weakness as the $^{36}Cl/^{10}Be$ ratio: although changes in the production signal are theoretically removed, the ratio exhibits unexplained variations.

Using only the two deepest measurements, Auer et al. (2009) arrived at an age estimate of 670 kyr with an uncertainty of almost 40% for the deepest EDML sample, which is approximately the minimum possible uncertainty of $^{26}Al/^{10}Be$ dating with 7 kg of ice, mainly due to the low measurement efficiency.

^{81}Kr

Contrary to the other radionuclides discussed so far, ^{81}Kr is a noble gas, which is largely inert and remains in the atmosphere for most of its lifetime, resulting in a globally well-mixed atmospheric $^{81}Kr/Kr$ ratio.

The approach for taking production variabilities into account is also different for ^{81}Kr. Instead of using a second radionuclide to correct the signal, a reconstruction of geomagnetic field intensities is used to calculate the theoretical $^{81}Kr/Kr$ ratio of the last 2 Myr (Zappala et al. 2020). This introduces uncertainties from the past cosmic-ray flux, the absorption cross sections of krypton, and the half-life of ^{81}Kr, $t_{1/2} = 229 \pm 11$ kyr. Nonetheless, the calculation of the theoretical present-day ratio agrees with measurements of modern air (Zappala et al. 2020).

First measurements of ^{81}Kr in three deep samples of the undated Talos Dome ice-core section yielded age estimates with 9–16% uncertainty, and indicated a disturbed stratigraphy, because the deepest sample had a younger ^{81}Kr age than the second deepest (Crotti et al. 2021).

Due to the low abundance of stable krypton (the target element for ^{81}Kr production in the atmosphere) the production rate of ^{81}Kr is even lower than that of ^{26}Al. Measurements with less than 10 kg of ice became feasible only recently (Crotti et al. 2021) and current improvements aim to reduce the required sample mass to just 1 kg of 1-Myr-old ice (Ritterbusch et al. 2022).

Outlook

Several radionuclides have the potential to assist conventional dating of ice cores, especially in the deepest section, where the stratigraphy may be disturbed.

Two main issues complicate the use of radionuclide dating: uncertainty and required sample mass. For the $^{36}Cl/^{10}Be$ and $^{26}Al/^{10}Be$ ratios, variations occur over time and are not well understood, while ^{81}Kr suffers from uncertainties connected to the calculation of the historic $^{81}Kr/Kr$ ratio and its half-life. Because radioactive decay is used for dating, the required sample mass increases exponentially with age. To measure a radionuclide with consistent precision, the required sample mass doubles for each half-life.

Nonetheless, measurement techniques are constantly improving to reduce the required sample size, making radionuclide dating a more viable solution for dating old ice. Simultaneously, research aimed at a better

understanding of climatic influences and post-depositional effects on the $^{36}Cl/^{10}Be$ and $^{26}Al/^{10}Be$ radionuclide ratios, as well as improved calculations of the historic $^{81}Kr/Kr$ ratio, are expected to reduce the uncertainties of these three radionuclide dating methods.

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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
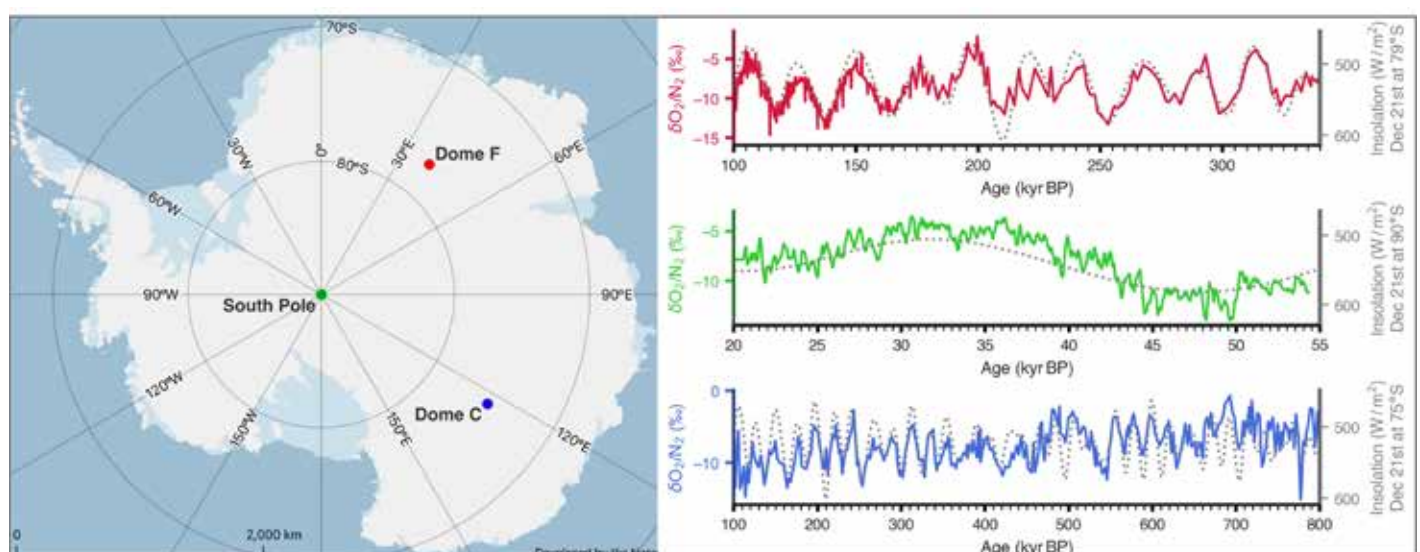

Figure 1: $\delta O_2/N_2$ records covering different time periods from Dome Fuji (Kawamura et al. 2007; Oyabu et al. 2021), South Pole (Severinghaus 2019) and EPICA Dome C (Extier et al. 2018) compared to the summer solstice insolation intensity (dotted line) based on the latitude of the respective 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).
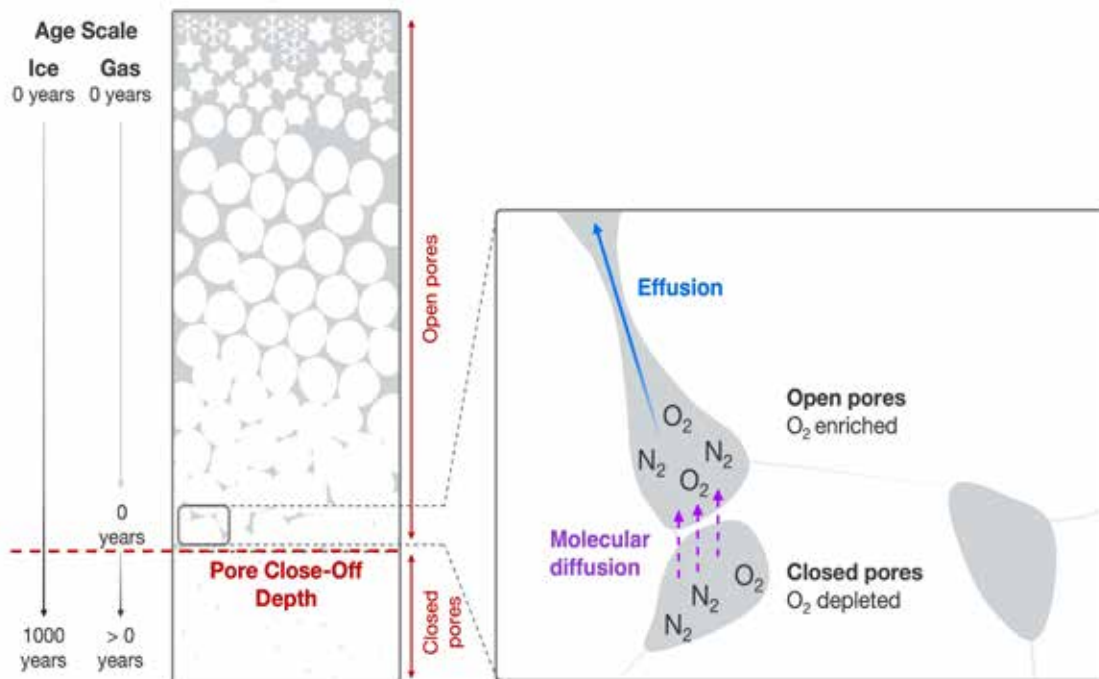
Figure 2: A diagram representing the firn column with an explanation of the two different age scales: the ice-age scale, which tells us when the ice was at the surface; and the gas-age scale, which tells us when the air was trapped in bubbles around the close-off depth. The box illustrates the two proposed 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).

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In situ production of N_2O in ice challenges past N_2O reconstructions

Lison Soussaintjean, J. Schmitt and H. Fischer

The production of N_2O in glacial ice alters the record of past atmospheric concentrations of N_2O in ice cores. Using isotope analyses of N_2O 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_2 in Greenland ice cores and N_2O in both Greenland and Antarctic ice cores are prominent examples for such an alteration of the atmospheric signal (Stauffer et al. 2003).

N_2O: A growing climate threat

The study of N_2O is important as it is a potent greenhouse gas that is also involved in the destruction of stratospheric ozone. The atmospheric concentration of N_2O, with a global warming potential 273 times higher than CO_2, 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 N_2O emissions, and natural sources from soils and oceans account for 57% (Tian et al. 2020). The main N_2O 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_2O emissions, resulting in a positive feedback (Schilt et al. 2010a). This effect is difficult to predict because present and past N_2O dynamics are poorly understood (Fischer et al. 2019). Reconstructed atmospheric N_2O 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_2O are missing due to in situ formation of N_2O in glacial ice, rich in mineral dust (Fig. 1).

In situ production of N_2O

Several observations indicate that the N_2O concentrations measured in the ice are affected by a non-atmospheric source. For example, ice cores from different drilling sites show significantly different N_2O values for given time periods (Schilt et al. 2010a, b). Considering the long atmospheric lifetime of N_2O and, as a result, its geographically homogenous atmospheric concentration, this observation is inconsistent with only atmospheric N_2O variations. The non-atmospheric source alters the N_2O records exclusively during glacial periods, when the dust concentrations are high (Fig. 1). This indicates a production of N_2O 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 N_2O production (Schilt et al. 2010a). Comparing different ice cores from Antarctica, the highest N_2O concentrations are found in ice cores with the highest dust levels (Schilt et al. 2010b). In contrast, in situ N_2O 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_2O production is likely controlled by this factor.

Previous approaches

In situ N_2O production represents a challenge for reconstructing the past atmospheric concentrations of N_2O 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.
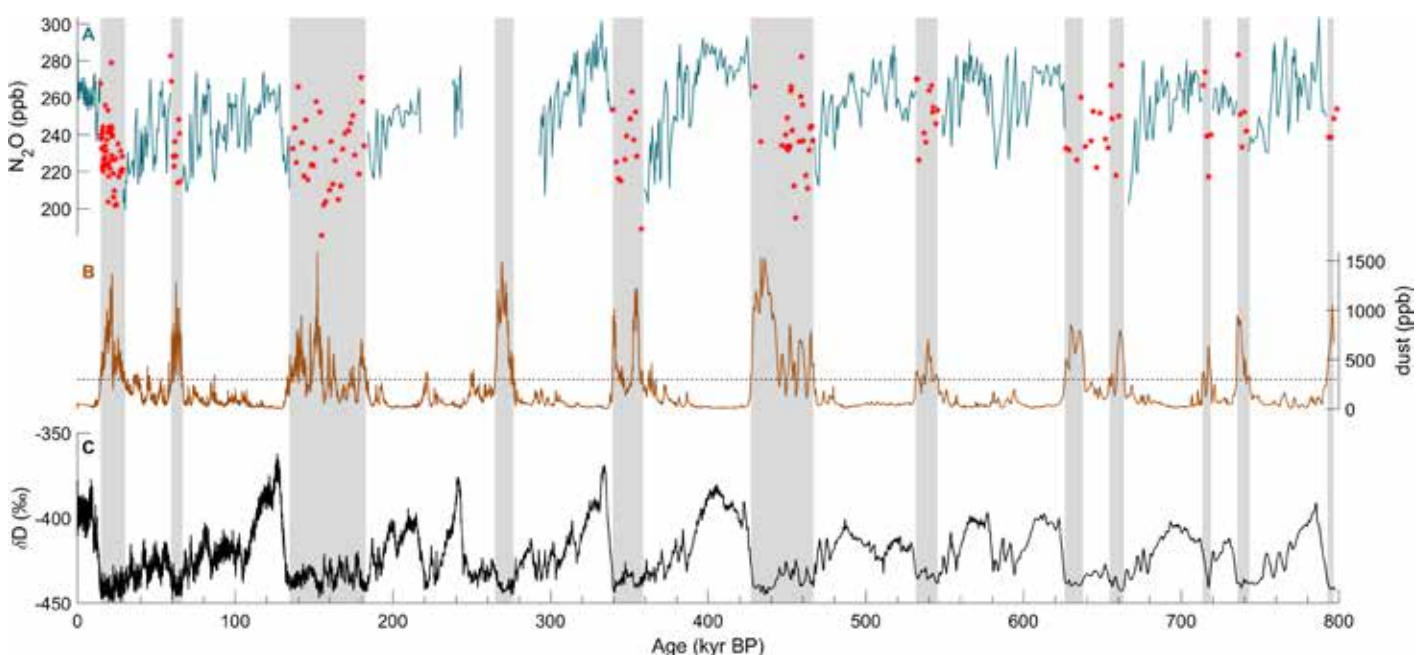

Figure 1: (A) Measured N_2O concentrations from the EDC ice core (Schilt et al. 2010a). Samples likely affected by in situ production are marked by red stars. **(B)** EDC dust concentration measured by laser scattering (Lambert et al. 2008). Gray-shaded areas mark sections with dust concentrations above the threshold of 300 ppb (dashed line). **(C)** EDC δD used as a temperature proxy (Landais and Stenni 2021).
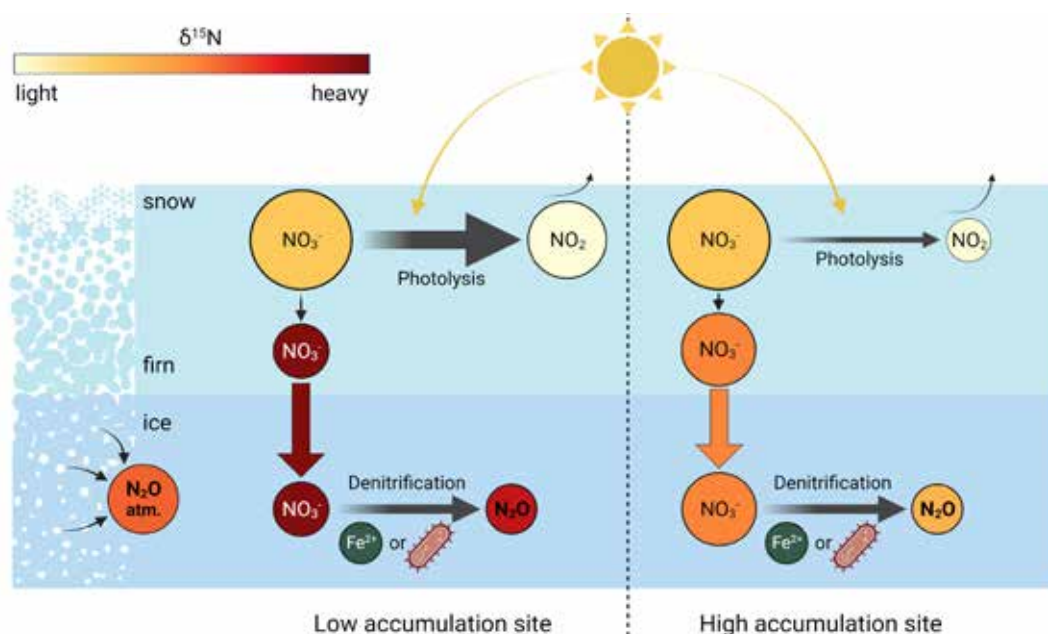
Figure 2: Schematic of the hypothesized process of N_2O in situ production in the ice. Since the snow accumulation rate controls the isotopic fractionation of NO_3^- photolysis, NO_3^- archived in ice has a different nitrogen isotopic signature at low and high accumulation sites. If NO_3^- is the precursor 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 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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Clathrate hydrates of air in polar ice and their importance for climate science

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Ancient air bubbles trapped inside polar ice sheets transform into clathrate hydrates at a certain depth. Not only do they contain the gas molecules used for paleoclimatic reconstructions, but they also serve as a climate proxy themselves.

Clathrate hydrates are solid guest-host compounds, formed by small molecules (guests; e.g. N_2, O_2, CH_4 or CO_2) trapped in a crystalline framework (host) of hydrogen-bonded water molecules (Chazallon and Kuhs 2002). In natural environments, clathrate hydrates occur in deep-sea sediments and permafrost (e.g. as methane hydrates). The first direct observations of clathrate hydrates of air (hereinafter, air hydrates) in polar ice were made in 1982 by Shoji and Langway (1982) in the Dye-3 ice core (Greenland) using an optical microscope. Subsequently, air hydrates have been found in all deep ice cores in Greenland and Antarctica (Uchida et al. 2014).

Air hydrate formation in polar ice

Air bubble inclusions in polar ice sheets are compressed with depth due to the increasing overburden pressure (e.g. Shoji and Langway 1982; Uchida et al. 2014). They transform into air hydrates below a certain depth, where the hydrostatic pressure enters the stability range of the clathrate hydrate at the in situ temperature (Uchida et al. 2011). The conversion occurs over a certain depth range, called the bubble-hydrate transition zone (BHTZ) (Fig. 1a), where bubbles and air hydrates coexist (Uchida et al. 2014). Its upper boundary is determined by the first appearance of a hydrate, the lower boundary by the last appearance of an air bubble.

For air-hydrate crystallization in the BHTZ, their (heterogeneous) nucleation is considered to be the rate-limiting step (Lipenkov 2000). Therefore, the starting depth and extent of the BHTZ varies (several hundred meters) for different ice-core sites in Greenland and Antarctica, owing to site-specific temperature and pressure conditions, as well as the occurrence of nucleation promoting or inhibiting factors (Uchida et al. 2014).

Given that air hydrates are formed from air bubbles, one could conclude that one bubble converts to one hydrate. However, a detailed investigation of the NGRIP (Kipfstuhl et al. 2001) and the Dome Fuji (Ohno et al. 2004) ice cores revealed that the number of total air inclusions (bubbles + hydrates) in the upper part of the BHTZ exceeds the air-bubble concentration above the transition zone.

Moreover, air hydrates in the transition zone show a wide variety of morphologies (Fig. 2a) and a non-uniform spatial distribution compared to air bubbles (Kipfstuhl et al. 2001; Lipenkov 2000; Ohno et al. 2004). The interpretation is that their formation is more complex (e.g. involving impurities; Ohno et al. 2004) than a simple one-to-one conversion and needs to be reinvestigated, including post-formation splintering and recrystallization mechanisms (Kipfstuhl et al. 2001).

Air hydrates and paleoclimate

Air hydrates are the source of at least two different types of information on paleoclimatic conditions. Firstly, they contain most of the air molecules in ice below the BHTZ and, as a result, provide a unique archive to reconstruct changes in past atmospheric gas compositions (Bereiter et al. 2015; Lipenkov 2000; Uchida et al. 2011, 2014). Secondly, some of the air hydrates' geometrical characteristics (mean size and number concentration) correlate with past climatic changes (Lipenkov 2000). This has been shown for the Vostok and Dome Fuji ice core in Antarctica and the GRIP ice core in Greenland, where continuous records of air hydrates exist (Ohno et al. 2004).

In general, ice formed at glacial conditions is characterized by smaller air hydrates and a higher hydrate number concentration compared to ice formed at interglacial conditions (Fig. 1b) (Lipenkov 2000; Salamatin et al. 2003). This is essentially explained by the impact of past temperature and accumulation rate on the physical properties of the firn. For example, smaller ice-crystal grain sizes in colder firn lead to smaller air bubbles in ice. The original climate-dependent geometrical properties of air bubbles are then transferred to air hydrates (Lipenkov 2000).

After their formation, air hydrates are subject to an evolution with depth: the general trend of number concentration continuously
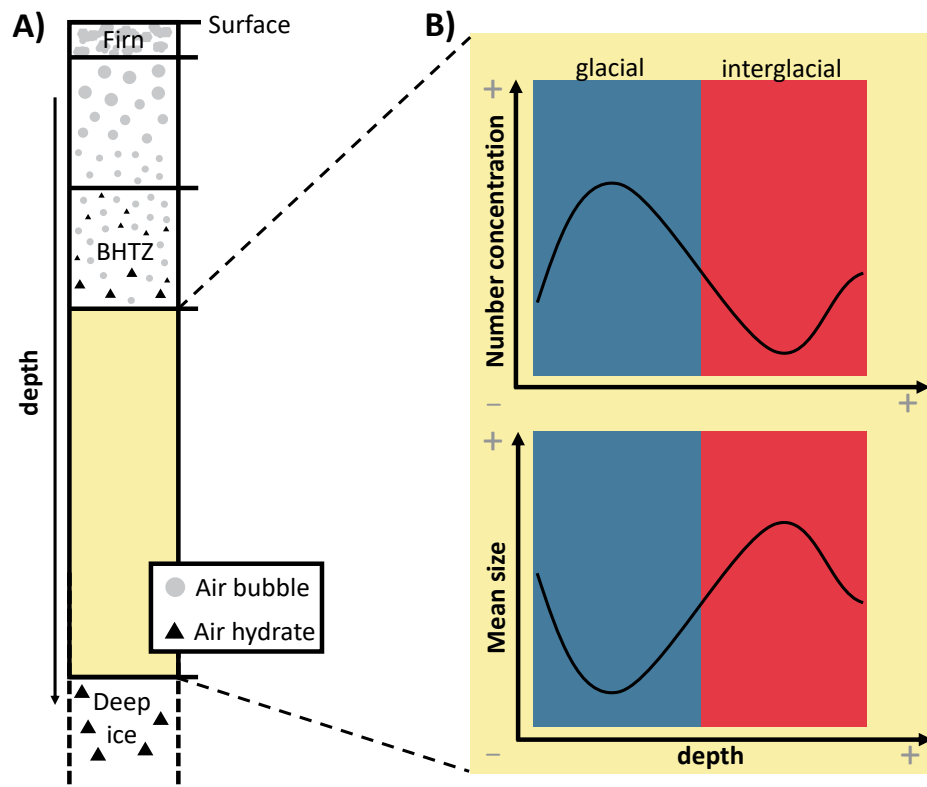

Figure 1: (A) Schematic of an ice core and the occurrence of air bubbles and air hydrates at different depths. **(B)** Climate-dependent variations of the air-hydrate number concentration and mean size for the yellow depth range in A.
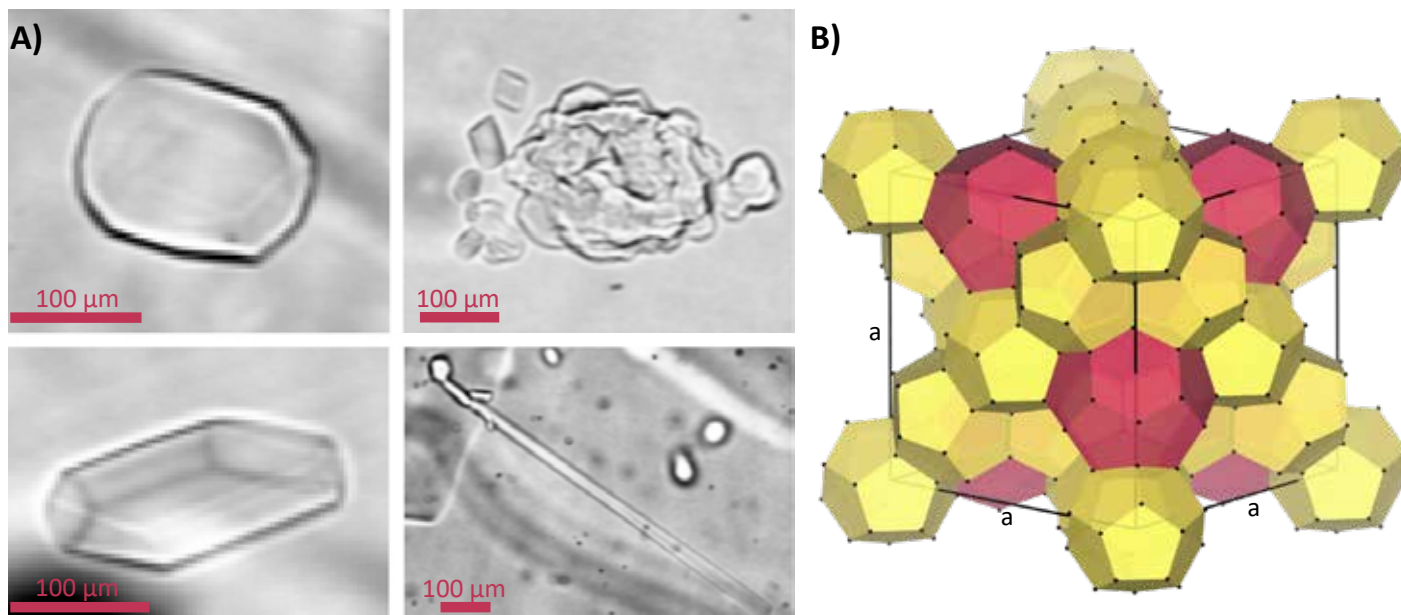
Figure 2: (A) Microphotographs of different air-hydrate morphologies found in the bubble-hydrate transition zone of the EPICA-Dronning-Maud-Land ice core, taken with an optical light microscope (Kipfstuhl 2007). **(B)** Framework structure of the sII clathrate hydrate. The black cube (black line: a ~ 1.7 nm) represents the unit cell and the yellow and magenta polyhedra mark the small and large cages, respectively. The black dots at the polyhedra vertices mark the position of the oxygen atoms of water (dot size not to scale), the edges represent hydrogen bonds. This figure was created using VESTA 3 (Momma and Izumi 2011).

decreases, coupled with an increase in the average size (Uchida et al. 2011). This phenomenon can be caused by a displacement of the hydrates and further fusion, and/or the diffusion of gas molecules and the subsequent growth of larger air-hydrate crystals at the expense of smaller hydrate crystals (a process called Ostwald ripening) (Salamatin et al. 2003; Uchida et al. 2011). This is especially pronounced in the deeper parts of the ice sheet, where it can even alter the original, climate-dependent variation of geometrical properties (Salamatin et al. 2003; Uchida et al. 2011). Increasing depth (and pressure), changes in temperature, and increasing age of the ice are the fundamental parameters behind this phenomenon (Uchida et al. 2011).

Material properties and analytical methods for air-hydrate studies
X-ray diffraction studies on single crystals of natural air hydrates in the Dye-3 ice core revealed the Stackelberg's crystallographic structure II (sII) (Hondoh et al. 1990). It is one of the three main structures found for natural clathrate hydrates. The sII has a cubic unit cell which consists of 16 small cages and eight large cages formed by 136 water molecules (Fig. 2b) (Chazallon and Kuhs 2002). One or two guest molecules can be enclosed in each polyhedral cage, but not all cages need to be occupied. The nature of the guests, temperature, and pressure determine the crystal structure of the host framework and the degree of filling of the cages (Chazallon and Kuhs 2002).

Studying air hydrates in polar ice is challenging because they are thermodynamically unstable under temperature and pressure conditions in the field, or in the cold-laboratories, where samples are processed and inspected. However, the surrounding ice acts as a pressure cell to keep the hydrates metastable for a certain time, which depends on

the ambient temperature conditions (Uchida et al. 1994). Consequently, for the long-term preservation of the record, appropriate storage conditions for the ice cores (≤ -50°C) are necessary (e.g. Bereiter et al. 2015; Uchida et al. 1994).

Optical light microscopy and cryo-Raman spectroscopy are the main non-destructive methods used to analyze air hydrates in polar ice. The microscope is the go-to tool for studying air-hydrate geometric properties. This investigation needs to be made as soon as possible after core retrieval, especially for the study of hydrates of the BHTZ (Kipfstuhl et al. 2001). Cryo-Raman spectroscopy enables the study of the main air-hydrate guest molecules (nitrogen and oxygen). In addition, this method can be used to analyze the various air-hydrate morphologies in 3D (Weikusat et al. 2015).

Outlook
There are still many open questions regarding the formation and evolution of air hydrates in polar ice. In the framework of Beyond EPICA and other Oldest Ice projects, a high analytical resolution and the development of new methodologies and climate proxies (e.g. dating via ^{81}Kr decay or ^{40}Ar/^{38}Ar isotope ratio in entrapped air; Lipenkov et al. 2019) play a key role in analyzing highly thinned, and likely disturbed, deepest and oldest ice in Antarctica. A better understanding of the air-hydrate formation processes and their physicochemical properties is essential for using entrapped air in ice cores as a climate proxy. Certainly, this will improve the evaluation of measured gas concentrations (e.g. O_2/N_2 ratios or CO_2; Bereiter et al. 2015). Equally important are the processes related to their evolution with depth (age) to further develop dating of very old (and disturbed) ice (Lipenkov et al. 2019).

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Investigating the unexplored paleoclimatic information of Greenland Ice Sheet basal materials

Lisa Ardoin

Debris-rich basal ice layer of an ice sheet are shaped by processes at the bedrock which alter the paleoclimatic signal preserved in the ice. Basal layers offer insights on past ice-sheet dynamics and environmental conditions that emerged during ice-free conditions.

Greenland basal layers

Ice cores are a valuable source of information on past climate change because they provide insights into past atmospheric composition and temperature through the analysis of entrapped air and ice properties. In the Greenland Ice Sheet (GrIS) (Fig. 1a), the ice layers are well-defined and arranged in stratigraphic order down to a depth of a few hundred meters above the bedrock. Currently, the oldest continuous paleoclimatic record from the GrIS dates back to approximately 123,000 years ago (Landais et al. 2006). Below this depth, the ice becomes folded but still preserves some of the original paleoclimatic signal (Dahl-Jensen et al. 2013). However, even though basal ice may be less ideal for paleoclimatic research, the deepest part of the ice sheets still hold significant potential for preserving important paleoclimatic information. This is particularly true since silty ice dating back as far as 1 Myr has been retrieved from the deepest sections of the GrIS (Bender et al. 2010; Willerslev et al. 2007; Yau et al. 2016).

The basal ice can be divided into two categories: the so-called silty ice is made up of basal layers which contain debris incorporated from the bedrock (Fig. 1b), contrary to the basal clean ice that is already stratigraphically disturbed, but free of debris (sometimes referred to as "deep ice"). The gases (Fig. 2a) and water-isotopes measurements (Fig. 2b) from silty ice near the bottom of the ice sheet raises concerns about the preservation of paleoclimatic records (Fig. 2; Bender et al. 2010; Souchez et al. 2006; Verbeke et al. 2002).

Alteration of the paleoclimatic signal in basal ice?

The basal ice layers in the GrIS have unique properties that distinguish them from the overlying meteoric ice layers (derived from snow precipitation), including differences in ice texture, debris content, and gas composition (Bender et al. 2010; Goossens et al. 2016; Souchez et al. 2006; Tison et al. 2015). These layers exhibit heterogeneity at different scales, potentially involving a complex history of successive episodes of dynamic instability, melting and refreezing (Goossens et al. 2016), in situ biogeochemical processes, and diffusion from the sediments below.

The basal ice layers exhibit low gas concentrations, between 2 to 80% (Fig. 2a) of a typical meteoric ice concentration (Goossens et al. 2016; Tison et al. 2015). This is due to various processes such as gas rejection during melting/refreezing processes and pressure-expulsion of gas into subglacial cavities at lower local ambient pressures, e.g. downstream from bedrock obstacles.

However, a large accumulation of greenhouse gases in the silty ice are reported (up to 12% and 0.6% of CO_2 and CH_4, respectively), associated with a decrease in the O_2/N_2 ratio down to anoxic conditions (Fig. 2a; Herron et al. 1979; Souchez et al. 2006; Verbeke et al. 2002). This distribution cannot be solely explained by physical processes and requires mediation of microbial activity to account for it, either in the underlying sediments, in the ice itself, or in the soils prior to ice-sheet build up (Herron et al. 1979; Souchez et al. 2006; Verbeke et al. 2002). As the silty ice is at the interface between two contrasted environments (meteoric ice vs. underlying sediments/bedrock), its trapped gas signature may result from the mixing of two endmembers (Souchez et al. 2006). Mechanical ice mixing between a meteoric endmember and a locally derived endmember may explain both the incorporation of debris and changes in gas chemistry, superimposed on diffusion processes generated by potential gradients between contrasting endmember properties (water isotopes, impurities, and gas concentrations). However, the locally derived component must have been affected by microbial processes, resulting in a depletion of O_2 (Souchez et al.
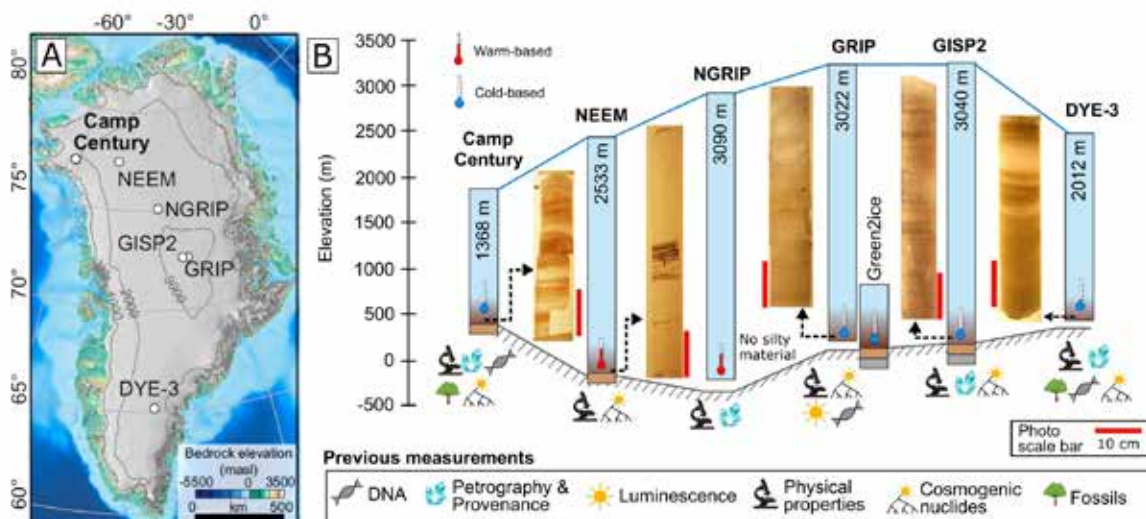

Figure 1: Synthesis of the studied ice cores from Greenland. **(A)** Ice-core locations and ice-surface elevation contours. **(B)** Ice-core thickness above the bedrock elevation (gray line), basal material thickness (exaggerated) and pictures of silty layers. Ice and gas chemistry were measured for all the ice cores. Modified from Christ et al. (2021).
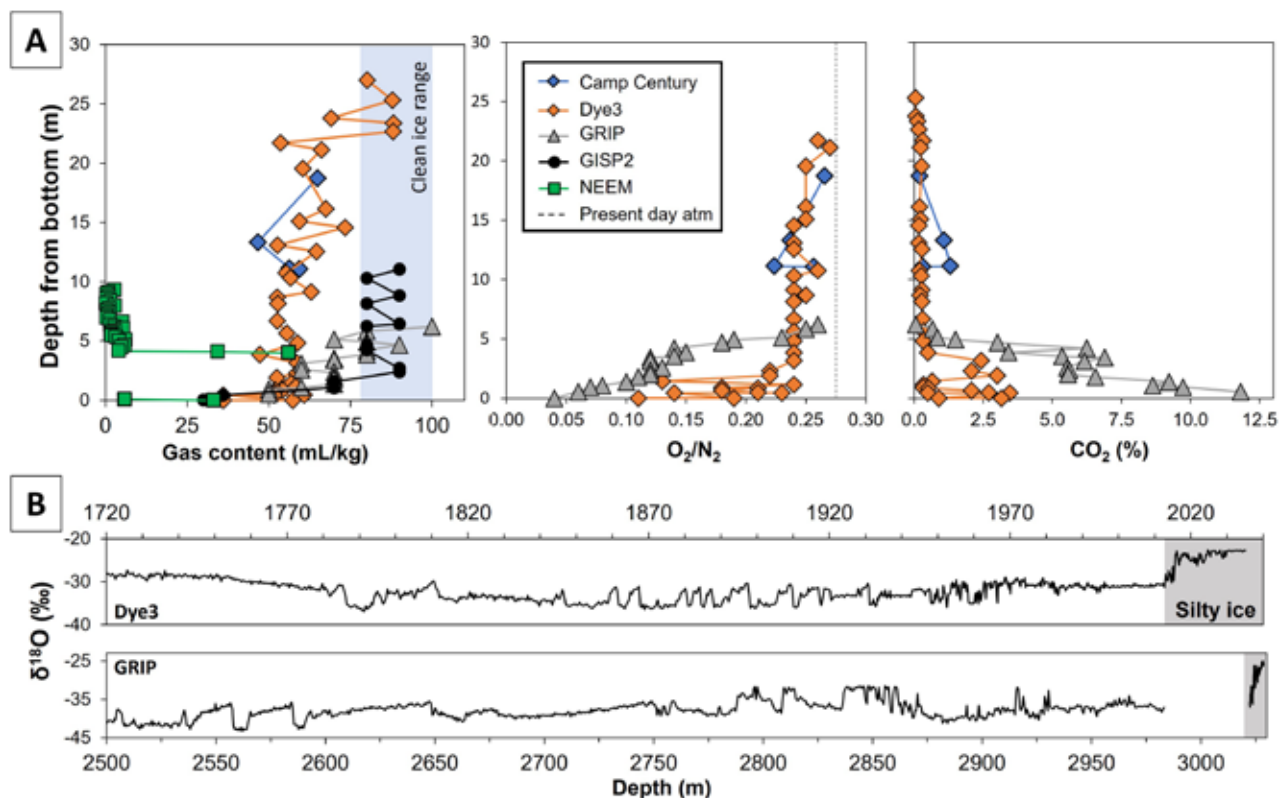
Figure 2: (A) Chemical proxies indicating variations between clean ice containing an atmospheric paleoclimatic signal and the silty layers of the Greenland Ice Sheet. **(B)** Ice $\delta^{18}O$ record for the deepest section of Dye3 and GRIP. Data from Bender et al. (2010), Goossens et al. (2016), Herron et al. (1979), Souchez et al. (2006), Verbeke et al. (2002), and Yau et al. (2016).

2006) and an accumulation of CO_2 and CH_4. This microbial signature may originate from a pre-existing marshy environment (Tison et al. 1998), which was eventually covered by the GrIS and trapped within the ice, or from the ecosystem prevailing in the subglacial environments.

Stable water isotopes ($\delta^{18}O_{ice}$ and δD_{ice}) serve as useful tools for identifying stratigraphic discontinuities in basal ice layers, as they provide a clear paleoclimatic signal, being a proxy of air temperature in both Greenland and Antarctic ice-core records (Dahl-Jensen et al. 2013). Melting and refreezing processes can affect the relationship between $\delta^{18}O_{ice}$ and δD_{ice} (Souchez and Jouzel 1984), a process that could happen close to the bedrock. Therefore, stable water isotopes can shed light on the processes that affected basal ice layers during and after their formation. Another interesting feature observed in some silty ice layers in the GrIS is that their $\delta^{18}O_{ice}$ and δD_{ice} values are higher than those found in the overlying meteoric ice (Fig. 2b). This suggests that these layers may be the remnants of an earlier stage of the ice sheet's growth, possibly from a time when the snow deposition occurred at a lower altitude (Souchez et al. 2006).

Unexplored paleoclimatic information in silty ice

Apart from traditional paleoclimatic proxies, the silty layers of the GrIS are becoming recognized as a valuable source of information on past ice-sheet dynamics. In addition, fossil remains, organic matter, and ancient biomolecules found in these layers provide insights into the types of ecosystems and environmental conditions that existed during periods of ice-free conditions (Fig. 1b). Recent research has demonstrated the potential of these layers to shed light on such key topics (Christ et al. 2021; Willerslev et al. 2007).

Analyses of mineral grains incorporated into the silty ice add constraints on the past waxing and waning (i.e. advance and retreat) of the GrIS. In situ-produced cosmogenic isotopes and the luminescence signal are two complementary methods constraining the past exposure and burial histories of under-ice sediments. The luminescence signal is indeed reset when the sediment is exposed to light. Under the ice cap, it rises because of the radioactive background of the geological environment. Thus, this luminescence signal can be used to date the last burial of the sediments during the last glacial advance. Alternatively, in situ-produced cosmogenic nuclides accumulate in quartz during ice-free conditions and decrease in concentration over time due to radioactive decay under the ice sheet. By coupling both methods, it is thus possible to constrain both the date of the last glacial ice-sheet readvance and the duration of the previous deglaciation (Christ et al. 2021; Schaefer et al. 2016). Additional constraints are provided by directly dating the basal ice, using dating techniques such as the ^{40}Ar accumulation/degassing rate (Bender et al. 2010; Yau 2016) and ^{81}Kr in entrapped air (Buizert et al. 2014).

The ecosystems that occupied Greenland prior to the ice-sheet build-up, and during ice-free intervals, are poorly known because much of the fossil evidence is hidden below the kilometer-thick ice sheet. Terrestrial plant macrofossils, ancient molecules (DNA and lipid biomarkers, including their carbon and hydrogen isotopic composition) hold promises to unravel prevailing climatic conditions during ice-free intervals (Willerslev et al. 2007).

Despite stratigraphic disturbance and metamorphism effects, the basal layers of the GrIS, therefore, offer a unique opportunity to extend our knowledge about the history of the ice sheet and its (in)stability in a changing climate. The European Research Council Green2Ice synergy project will investigate this opportunity in the years to come (shorturl.at/kDFLN).

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Exploring the origin of Antarctic precipitation for an improved climatic interpretation of ice-core records

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To refine moisture-source and site-temperature reconstructions inferred from measurements from ice cores, we must understand moisture provenance from which Antarctic precipitation originates. Here, we discuss our current understanding of Antarctic precipitation origins and some recent modeling developments.

Why study Antarctic precipitation?

Antarctic precipitation is crucial to many aspects of the climate system. Firstly, Antarctic snowfall influences sea level through freshwater storage and ice-dynamic discharge. For instance, increased Antarctic snowfall might have mitigated global mean sea-level rise by ~10 mm during the 20th century (Medley and Thomas 2018). Secondly, enhanced atmospheric heat transport associated with increased Antarctic precipitation could promote polar amplification (Hahn et al. 2021). In addition, deep ice cores drilled in Antarctica enable us to understand how the Antarctic and global climates varied over hundreds of thousands of years. Water isotope ($\delta^{18}O$ and δD) measurements from these ice cores have been used to infer past surface climate changes (e.g. Jouzel et al. 2007). By obtaining information about evaporation conditions of the precipitation, such as relative humidity and wind speed, we can tackle some key uncertainties in the interpretation of these isotopic measurements from ice cores.

How do we investigate Antarctic precipitation and its origin?

Because of its importance, continental and regional variations in Antarctic precipitation have been studied from daily to inter-annual timescales for many decades. For example, daily snowfall has been measured using a wooden platform at EPICA Dome Concordia (Dome C) since 2006 (Schlosser et al. 2016). Similarly, individual site measurements, which use snow stakes across Antarctica, allow observations of precipitation changes across the continent (Lenaerts et al. 2019). Invaluable larger-scale satellite measurements of precipitation over Antarctica have been available since the launch of CloudSat in 2006, though these measurements remain subject to calibration uncertainties (Palerme et al. 2014).

Complementary to observations, atmospheric general circulation models, which are sometimes run using data assimilation techniques, have provided precipitation and other relevant climate data for Antarctica.

The European Centre for Medium-Range Weather Forecasts (ECMWF) combined numerous observations and a weather forecast model to produce the ECMWF Reanalysis v5 (ERA5, Hersbach et al. 2020). Based on the ERA5 dataset (1979–2022), average precipitation over the Antarctic Ice Sheet is ~175 mm/yr, and it decreases from coastal regions towards the Antarctic interior (Fig. 1a). Using multiple model simulations, Frieler et al. (2015) quantified the impact of a thermodynamic factor, i.e. the higher water holding capacity of a warmer atmosphere, on Antarctic precipitation. They found that, at the continental scale, Antarctic accumulation increases with temperature at a rate of ~5 %/K.

Combining ice-core data and reanalyses, Medley and Thomas (2018) investigated the Southern Annular Mode (SAM), which is the primary mode of atmospheric circulation variability in the southern mid-to-high latitudes. They found that SAM exerts regionally different controls over precipitation across
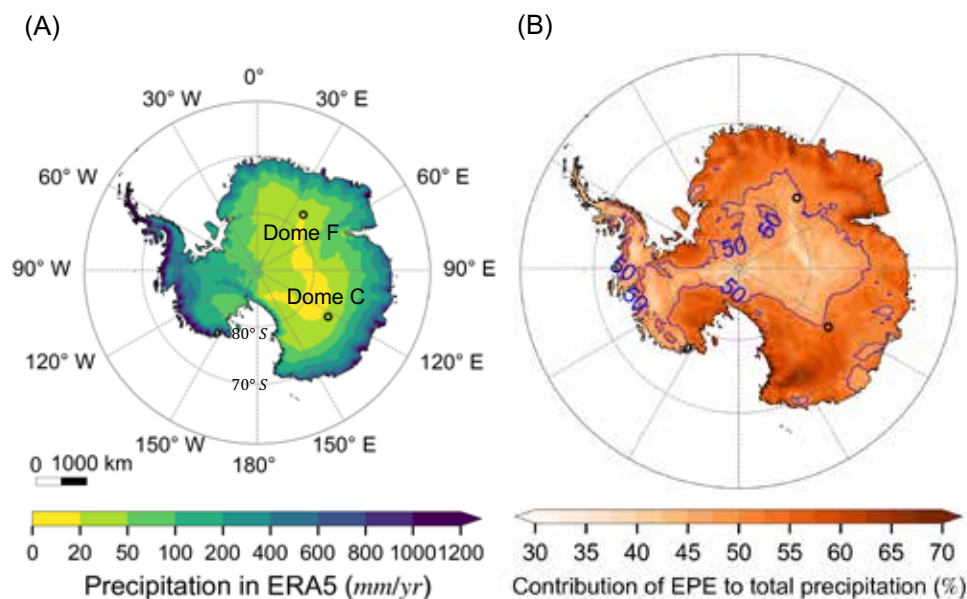
Figure 1: (A) Annual mean precipitation over Antarctica from the ERA5 reanalysis (1979–2022, Hersbach et al. 2020). **(B)** Contribution of extreme precipitation events (EPE) to total precipitation amount in the ERA5. Here EPE is defined as the top 10% heavy precipitation days following Turner et al. (2019). To help visual interpretation, blue lines show contours of 50% EPE contribution.
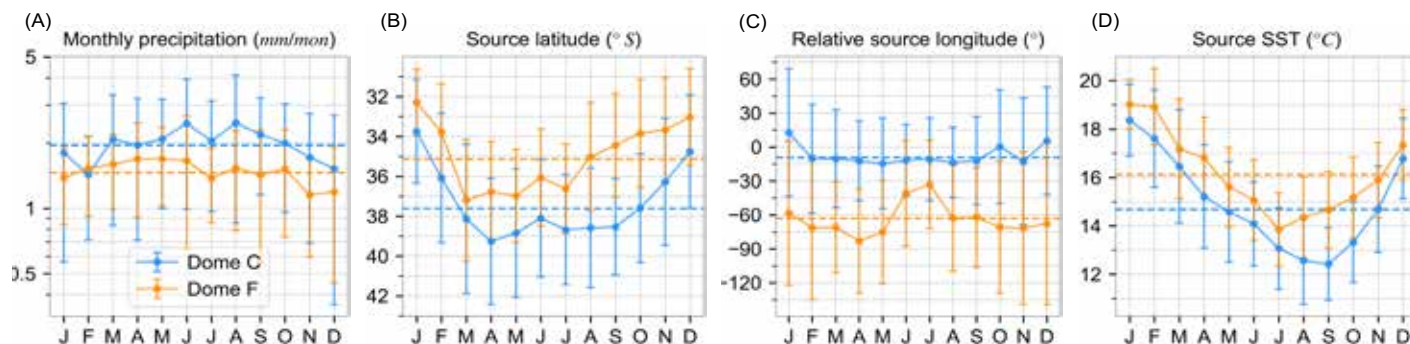
Figure 2: (A) Monthly mean precipitation at Dome C and Dome F. Panels show the **(B)** source latitude, **(C)** relative source longitude, and **(D)** source SST of monthly mean precipitation which originates from the open ocean. Data are from a preindustrial simulation using the atmospheric model ECHAM6. Moisture source information of precipitation at Dome C and Dome F is derived from our water-tracing diagnostics implemented in ECHAM6. Horizontal dashed lines represent annual mean values.

Antarctica through modified moisture fluxes. Using a regional climate model, Turner et al. (2019) found that extreme precipitation events (EPE) contribute significantly to the amount and variability of Antarctic precipitation (Fig. 1b). It appeals for the study of dynamic drivers of EPE to project its future changes and impacts on Antarctic climate.

Alongside these thermodynamic and dynamic controls, it is valuable to understand how the evaporative sources, and changes in these source properties, impact Antarctic precipitation. Water sources of Antarctic precipitation have thus been investigated using three different techniques.

Firstly, water isotope fractionation models can be applied to infer source temperature during evaporation processes based on deuterium excess data in Antarctic surface snow (Stenni et al. 2010). The deuterium excess is defined as the difference between the abundance of deuterium and ^{18}O in water isotopes: $d = \delta D – 8\delta^{18}O$. This method relies on multiple assumptions, such as idealized moisture transport trajectories. Secondly, Lagrangian trajectory diagnostics can attribute moisture sources by identifying humidity changes along the transport of air parcels (Sodemann and Stohl 2009). However, even using 20-day backward trajectories instead of five-day trajectories as commonly used, moisture sources can be identified for only ~90% of total precipitation. Thirdly, atmospheric general circulation models simulate the global water cycle and are, thus, suitable for moisture-source attribution. A technique called "water tracing" in atmospheric models tracks moisture evaporated from prescribed regions until it precipitates. Traditionally, the globe is divided into multiple complementary regions, and then the contribution of each region to total precipitation at any location can be quantified. While the traditional approach has some downsides, such as being computationally expensive, recent progress in modeling developments has helped alleviate these issues, as discussed below.

Modeling advances in identifying moisture sources

Fiorella et al. (2021) developed a new and improved method for using water tracers in atmospheric models. This new method involves complex mathematical transformations throughout the water cycle, in addition to traditional water tracing. These new tracers allow for more precise inferences of environmental conditions during evaporation, transport, and condensation, making it possible to infer mass-weighted mean evaporation surface temperature and other parameters. This new approach is also much less computationally expensive.

Following on from this, we further developed and implemented this water-tracing approach in the state-of-the-art atmospheric model ECHAM6. We are also implementing the same water-tracing diagnostics in the Hadley Centre Global Environment Model version 3 (HadGEM3). Our water tracers provide abundant new information on moisture-source locations and evaporation-related properties of precipitation across Antarctica.

Figure 2 shows monthly precipitation and its evaporative source conditions at Dome C and Dome Fuji (Dome F). We find that annual mean oceanic-sourced precipitation has a source latitude of 37.6°S at Dome C and 35.1°S at Dome F (Fig. 2b). The source latitude reaches the most northern locations during December and January at both sites, and the most southern locations between March and May. Source sea-surface temperature (SST) of annual mean oceanic-source precipitation is approximately 14.7°C at Dome C and 16.1°C at Dome F (Fig. 2d). Note that annual mean oceanic-source precipitation is from more equatorward (by 2.5° in latitude) and warmer (by 1.4°C) waters at Dome F than at Dome C. Annual cycles of source SST are different from annual cycles of source latitude despite predominant meridional temperature gradients, mainly because of seasonal variations of SST at mid-latitudes. That is, at both sites, the source SST of monthly precipitation peaks in Austral summer (December to February) and is at its minimum in Austral winter (July to September). Although both sites receive moisture primarily from the west, the moisture source is located much further west for Dome F (~60°) than for Dome C (~10°).

Based on our moisture-source diagnostics, EPE derives its moisture from more northern regions by 3.0° and 3.7° than the rest of precipitation at Dome C and Dome F, respectively. The different moisture sources reflect distinct dynamic controls, which might imprint on water-isotope records.

Our current research aims to apply the water tracers to the study of paleoclimate. Indeed, measured water isotopes from Antarctic ice cores and the derived parameter deuterium excess have been interpreted for evaporation-source and precipitation-site temperature, based on simple water-isotope models (Landais et al. 2021). However, it is very challenging to quantify with atmospheric models the uncertainties associated with this method due to a lack of moisture-source information. Thanks to our new quantitative information on moisture sources, we will be able to refine uncertainty estimates attached to ice-core-based past temperature reconstructions from ice cores. In particular, future research will apply these new modeling tools to constrain local surface-temperature reconstructions from the ice core currently drilled at Little Dome C in the framework of the Beyond EPICA Oldest Ice Core project.

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Meet our guest editors

Holly Winton
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Holly is an ice-core and aerosol scientist with interests in biogeochemistry, sea ice, dust and climate-relevant aerosol. She is currently working on novel proxies of marine primary production in Antarctica and the Southern Ocean to understand the interactions between phytoplankton and climate on a range of timescales.

Giulia Sinnl
Copenhagen University, Denmark

A physicist on loan to paleoclimatology, Giulia completed her PhD on the timescales of Greenland ice cores, under the supervision of Prof. Sune Rasmussen. Her research has focused on improving our interpretation of the Earth's past climate by adjusting the chronological alignments between paleo-archives, using tools such as annual-layer counting or measuring cosmogenic radionuclides.

Olivia Williams
Oregon State University, Corvallis, USA

Olivia is a paleo-climatologist and stable isotope geochemist currently completing a PhD with Dr. Christo Buizert at Oregon State University. Her project focuses on noble gas ratios as a proxy for previous melting in Greenland ice cores. By improving our understanding of melt in past warm periods, she hopes this project will be useful for understanding the cryosphere of today. .

Lana Cohen (Victoria University of Wellington, New Zealand) examines storm layers in a snow pit on Roosevelt Island, Antarctica, 2010. Photo credit: Bradley Markle.

Ice Core Young Scientists spotlight new developments in ice-core science

V. Holly L. Winton[1], G. Sinnl[2] and O. L. Williams[3]

This special issue highlights recent advances in ice-core paleoclimatology led by early-career researchers (ECRs) and reflects the efforts of the Ice Core Young Scientists (ICYS; pastglobalchanges.org/icys) workshop in October 2022 in Crans-Montana, Switzerland (pastglobalchanges.org/calendar/26967). These articles are dedicated to promoting ECR research at the frontiers of ice-core science, and they recognize the recent surge of development in novel ice-core proxies, ice-core dating, and modeling techniques over the last decade. This endeavor is divided into areas at the heart of our field today: interpretation of ice-core proxies such as impurities, water isotopes, and gases; paleo-chronological constraints; and data integration with models to reconstruct paleoclimate scenarios.

The first set of articles feature novel environmental proxies based on ice-core impurities, with a focus on analytical techniques and applications. Increasing observations of climate-relevant aerosols, and assessing their impact on the climate system, is a pressing need, particularly over the Southern Ocean where the unique and poorly observed aerosol properties limit the ability of global climate models to correctly simulate the radiative budget. Novel analytical techniques show great promise for characterizing the size, shape, and composition of ice-core impurities, providing crucial data for radiative transfer models. New insights into the radiative properties of aerosols are highlighted by

Lomax-Vogt et al. (p. 90), who describe the recent advances in ice-core single-particle analysis, while Cremonesi and Ravasio (p. 92) review innovative ice-core optical techniques. Burgay (p. 94) explores the potential of non-target screening of ice-core organic compounds as a previously untapped archive of atmospheric composition.

Trapped bubbles of ancient air are one of the most unique components of the ice-core record (Fig.1a). These gases provide a direct window to study the atmosphere of the past. Among recent advances, Shackleton (p. 96) shows how noble gas ratios in the ice-core record are used to reconstruct past mean ocean temperatures. Interpretation of the gas record in older ice samples presents a challenge, especially where the stratigraphic order has been disturbed. Current efforts to extract paleoclimatic information are described by Yan (p. 98) who reviews the use of blue ice areas – where very old ice has flowed to the surface – to record changes in million-year-old greenhouse gases.

Water isotopes are a fundamental component of ice-core temperature reconstructions. Yet accurate calibration of this traditional paleothermometer is hindered by diffusion, precipitation intermittency, and wind redistribution processes, as Casado and Orsi discuss (p. 100). Davidge (p. 102) explains recent developments in clumped water-isotope analysis, which provides more detailed information about the path of a

water parcel from evaporation at the source, to precipitation on the ice sheet.

Robust age models provide the foundation to interpret the relatively high-resolution paleoclimate records from ice cores (Fig. 1b). Bouchet et al. (p. 104) showcase how Antarctic glaciological models for older ice are tuned using dating constraints from orbital parameters, the geomagnetic field, and volcanic eruptions. Fang et al. (p. 106) describe how radiocarbon in shallow Alpine ice cores can be used to resolve detailed climate records over the Holocene. Soteres et al. (p. 108) describe surface exposure dating of ^{10}Be, a cosmogenic nuclide, on Patagonian glaciers to date millennial-scale climate shifts that resemble signals seen in both Greenland and Antarctic ice cores.

Integrating ice-core data with models is crucial to reliably forecast anthropogenic global warming. Slattery and Sime (p. 110) assess the effectiveness of ice-core data in statistical tools to pinpoint the timing of abrupt changes from Greenland glacial records.

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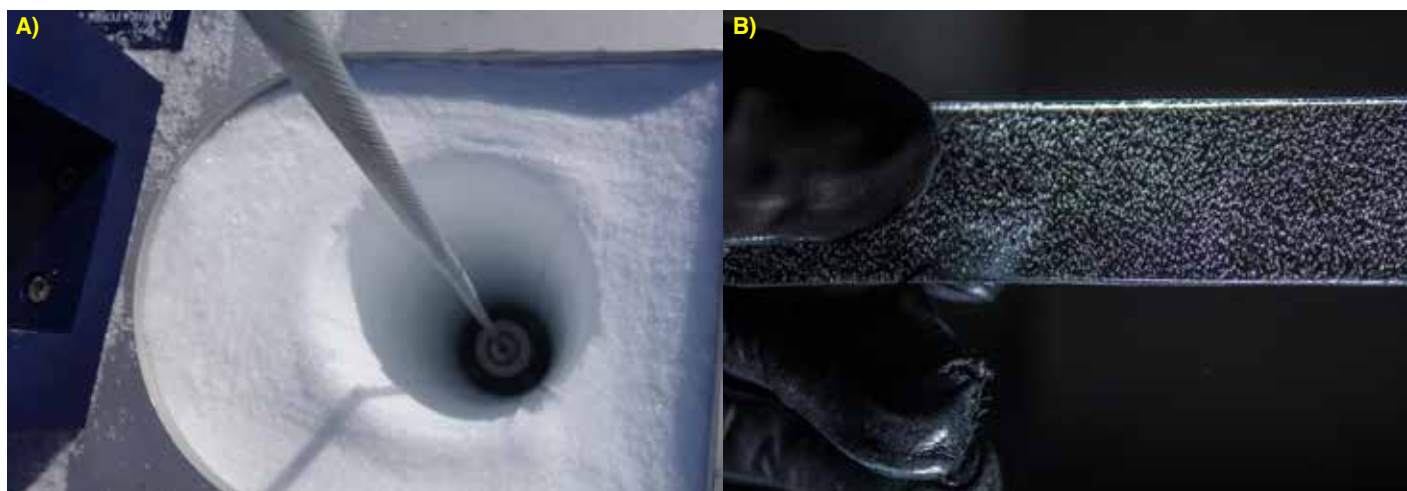V. Holly L. Winton: holly.winton@vuw.ac.nz

Figure 1: (A) Looking back through time down an ice-core borehole. Photo credit: LSCE, GLACCIOS. **(B)** Visible air bubbles in an ice core recovered from Talos Dome. Photo credits: A. Grisart and J-W. Yang.

Analytical challenges and advancements in measuring individual mineral nanoparticles and microparticles entrapped in ice cores

Madeleine Lomax-Vogt[1,2], S. Kutuzov[1,3], P. Gabrielli[4] and J. W. Olesik[1,3]

Ice cores provide a record of atmospheric particles that could have affected past climate. Single-particle inductively coupled plasma time-of-flight mass spectrometry can measure size distributions, number concentrations, and elemental chemical composition of many thousands of individual insoluble nanoparticles and microparticles.

Particles in Earth's atmosphere and climate

Atmospheric particles include sulfates, nitrates, black/organic carbon, sea salt, and mineral or other water-insoluble particles with diverse natural and anthropogenic sources (e.g. volcanic eruptions, desert dust, biomass burning, fossil-fuel combustion, sea spray). Compared to other climate forcings like carbon dioxide (CO_2) and methane, atmospheric particles are irregularly distributed in the atmosphere, reflecting diverse sources, short lifetimes, and complex atmospheric transport conditions (Raes et al. 2000).

The chemical (e.g. mineralogy/elemental composition) and physical (e.g. size, solubility, density) properties of individual mineral atmospheric particles affect climate directly through absorption and scattering of solar radiation, and indirectly through changes in cloud and ice formation and structure (Haywood and Boucher 2000). Bioavailable iron-bearing particles can fertilize the ocean, creating algal blooms, thus, reducing the global CO_2 concentration (Martin 1990). Particles with diameters <2.5 μm ("fine particulates") containing toxic metals have negative impacts on human health (Shiraiwa et al. 2017).

Most particles in the atmosphere and entrapped in ice cores (by number concentration) are classified within the Aitken mode size range (10 to 100 nm, nanoparticles), with a smaller but significant number within the accumulation mode size range (100 to 1000 nm, fine microparticles) (Seinfeld and Pandis 2006; see conceptual model particle size distributions in Fig. 1). However, particles within the Aitken mode contribute very little to the total mass (and volume) of particles, while most of the total mass (and volume) is in coarser particles. Glaciers are excellent archives of the Earth's climate over hundreds of thousands of years, including deposited insoluble mineral atmospheric nanoparticles and microparticles. The physical and chemical characteristics of particles are indicative of the past atmosphere and can offer insight into how the Earth's climate changed over time. Measuring particles entrapped in remote Antarctic ice can also provide a benchmark of comparison to the modern, anthropogenically affected atmosphere.

Here, we first discuss analytical techniques traditionally used to measure the particles entrapped in glacial ice cores. While useful, these methods cannot measure the elemental chemical composition of thousands of individual nanoparticles and fine microparticles. We then highlight single-particle inductively coupled plasma time-of-flight mass spectrometry (spICP-TOFMS) as a tool for measuring hundreds of thousands of individual mineral nanoparticles and microparticles.

Traditional techniques used to measure mineral atmospheric particles entrapped in glacial ice

Several analytical techniques, including Coulter Counter and Abakus, bulk analysis by inductively coupled plasma-sector field-mass spectrometry (ICP-SFMS), and transmission or scanning electron microscopy (TEM or SEM) with energy dispersive X-ray spectrometry (EDXS), are used to measure atmospheric particles in melted glacial ice.

Coulter Counters and Abakus are widely used to measure size distributions and number concentrations of accumulation and coarse mode insoluble particles larger than 500 nm (Fig. 1; Delmonte et al. 2002; Folden Simonsen et al. 2018) independent of the elemental-chemical composition of particles.

Bulk analysis by ICP-SFMS determines average elemental concentrations in an acidified sample (McConnell et al. 2018; Uglietti et al. 2014). It is impossible to differentiate between contributions from chemically digested insoluble mineral particles, water-soluble particles, and dissolved ions in the sample. Bulk analysis cannot measure particle-number concentrations, size distributions, or individual particle compositions. Measuring low-abundance trace elements (e.g. Ir, Pt) is challenging and requires ultra-clean techniques in order to avoid contamination (Gabrielli et al. 2004).

SEM/TEM-EDXS determines the shape, size, and elemental chemical composition/mineralogy of individual particles. SEM/TEM-EDXS is a time-consuming technique which requires locating and scanning each individual particle. The time required to measure a statistically significant population
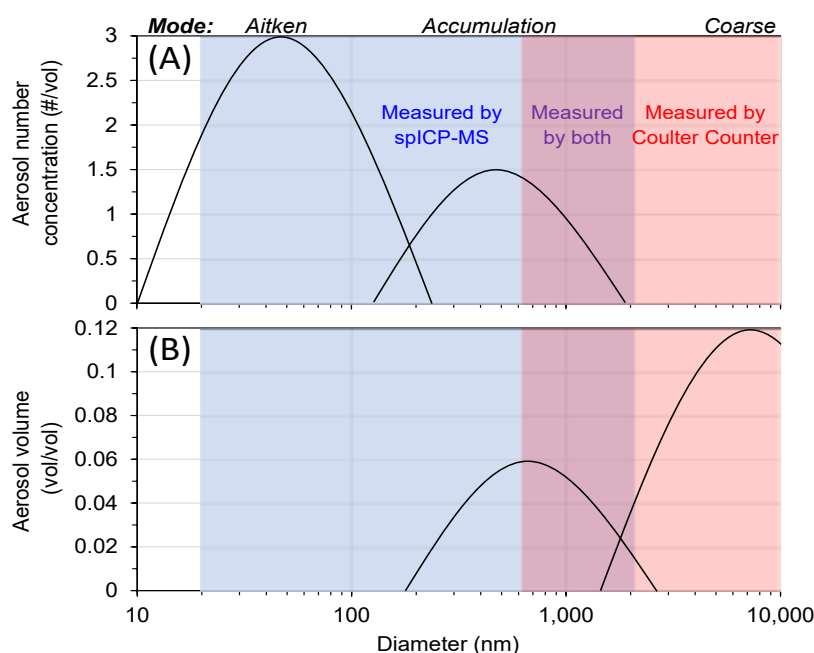

Figure 1: Theoretical lognormal size distributions of aerosol particles measured by spICP-MS displayed as **(A)** a function of number concentration and **(B)** volume/mass. Figure adapted from Seinfeld and Pandis 2006.
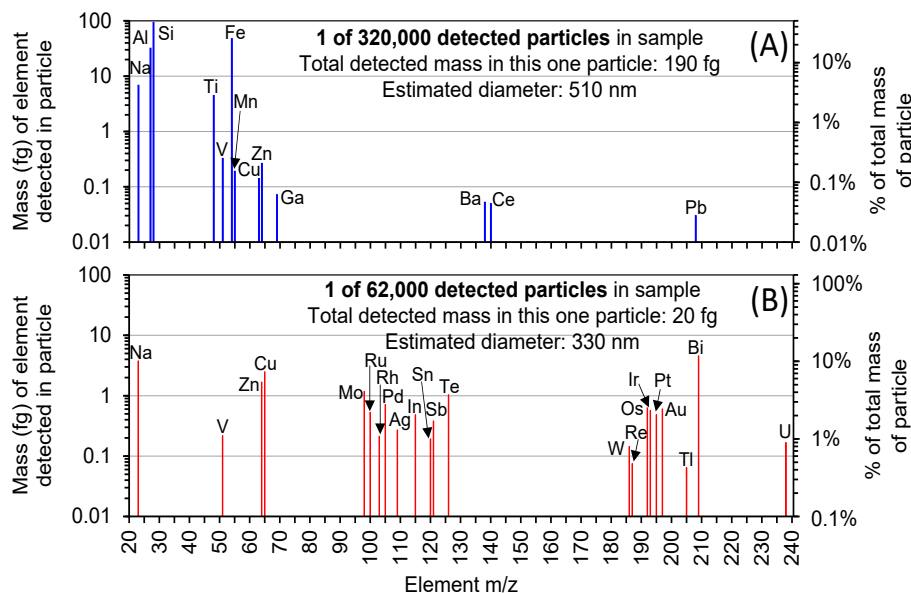
Figure 2: Amount (mass, femtograms -fg-) of each element detected in an individual particle from **(A)** 17 kyr BP and **(B)** 11 kyr BP Taylor Glacier samples. 560,000 particles/mL were detected in the 17 kyr BP sample. 110,000 particles/mL were detected in the 11 kyr BP sample (m/z=mass/charge ratio of ion detected by mass spectrometer; used to identify each element from a characteristic isotope).

(i.e. thousands or hundreds of thousands) of particles in a sample is prohibitively long. A limited number of studies have used TEM/SEM-EDXS to measure mineral nanoparticles and microparticles, with most focusing on common particles containing elements present at major or minor abundances in the Earth's crust (Ellis et al. 2015).

Techniques to measure elemental composition and size of thousands of individual particles
Single particle mass spectrometry (SPMS) has been used since the 1990s to measure particles in the modern atmosphere in real-time (Noble and Prather 2000). In the only reported use of SPMS to measure particles in ice cores (Osman et al. 2017), long sampling times (>1 hour) and more than 100 mL of liquid sample were required, which can be a limitation in analyzing ice cores with small sample volume. Furthermore, SPMS typically does not quantify the amount of each element in a particle. Instead, the amount of each element is reported as a percentage of the total ion current detected.

Single-particle inductively coupled plasma-mass spectrometry (spICP-MS) is becoming widely used to measure engineered nanoparticles in the environment, biological samples, and food (Montaño et al. 2016). The particle suspension is nebulized and introduced into the ICP ion source. Unlike bulk ICP-MS which measures the average concentration of elements over a few seconds, spICP-MS measures the ion signal with a time resolution as short as 10 µs. While spICP-MS using a quadrupole or sector field MS can only measure one element per particle, spICP-TOFMS measures a complete elemental mass spectrum (up to 70 elements excluding O, H, N, F, and the noble gases) every 30 µs. Each particle produces a discrete burst of signal ~500 µs long ("particle event"); instrument software identifies mass spectra due to a particle

event. The relationship between ion-signal intensity and the mass of each detected element is calibrated using solutions so that the amount (femtograms -fg- =10^{-15} grams) of each detected element can be quantitated. From the amounts of each detected element, the percentage of each element in the particle can be estimated. There was only one previous publication (Erhardt et al. 2019) that used spICP-TOFMS to measure particles in an ice core to our knowledge.

Measuring insoluble mineral particles by spICP-TOFMS
spICP-TOFMS is uniquely capable of quickly (in ~30 minutes) measuring the estimated mass equivalent size distribution, number concentration, and elemental chemical composition of more than 100,000 individual insoluble mineral nanoparticles and microparticles using only one milliliter of melted ice.

The mass-equivalent particle diameter is estimated for each particle using the total mass (in femtograms) of all detected element(s) and an estimated density (i.e. average crustal density, 2.7 g cm^{-3}). The shape of the particle cannot be determined by spICP-TOFMS. spICP-TOFMS can detect particles as small as ~20 nm (that are too small to be measured by a Coulter Counter; Fig. 1).

Figure 2 shows examples of mass spectra produced from two individual insoluble-mineral particles detected in Taylor Glacier ice samples by spICP-TOFMS. The top spectrum is from a common particle composed mainly of elements (e.g. Na, Al, Si, Fe, Zn, etc.) at major or minor concentrations in the Earth's crust (Fig. 2a). The bottom particle contains ultra-low amounts (<10 fg) of uncommon elements such as Os, Au, Pt, Ir, and Tl (Fig. 2b). It would be difficult to measure these particles by bulk ICP-MS because the signal each element produces would be a very small

fraction of the background signal integrated over several seconds.

Potential minerals and mineral groups can be inferred for each particle by comparing the ratio of the amounts of detected elements to known mineral elemental ratios. Common minerals (e.g. quartz, ilmenite, kaolinite) can be differentiated from particles with unusual compositions that would be undetectable by bulk ICP-SFMS, or challenging to find by SEM/TEM-EDXS. These particles can act as markers of very rare environmental events (i.e. micrometeorites; volcanic tephra from eruptions).

Conclusions and perspectives
Glacial ice cores contain crucial information about the size, number concentration, and elemental chemical composition of hundreds of thousands of insoluble mineral particles over Earth's climatic and environmental history that were unmeasurable using conventional techniques. Measuring additional ice-core samples from the glacial–interglacial transition by spICP-TOFMS will give us a better understanding of the impact of mineral particles on past climate, and answer questions about how particle mineralogy, size, and number concentration changed over the glacial–interglacial timescale.

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Inspecting the radiative properties of insoluble impurities stored in ice cores

Llorenç Cremonesi and Claudia Ravasio*

In addition to air bubbles and ions, ice cores contain insoluble particles, mainly mineral dust. These particles provide a temporal record of the atmospheric aerosol content of the past, which is key to understanding Earth's energy balance.

In an era of rapid, global, and significant climatic changes, the scientific community is devoting great efforts to the study of the current and past major drivers of these changes. Fully understanding these changes also means studying their trends, determining their periodicity, and possibly assessing the extent to which they can be dealt with or mitigated. In this context, atmospheric aerosols have attracted much attention in the literature, as they have a significant impact on the climate system (Kok et al. 2023). Cloud cover depends primarily on the ability of water molecules to condense or crystallize around condensation nuclei, i.e. aerosols. Cloud cover is a determining factor in planetary albedo and is highly dependent on the aerosol species that populate the atmosphere. In addition, aerosols themselves contribute to the Earth's energy balance by scattering and absorbing solar and terrestrial radiation, thus cooling or warming the climate (Forster et al. 2021). While direct measurements in the atmosphere and remote sensing can be used for information about the present time, measurements of impurities in ice cores can be relied upon to obtain valuable information about the past.

Overview

In the framework of studying the Earth's energy balance and climate, the optical properties of impurities in ice cores give us insight into the radiative properties of aerosol particles, and provide data that can be used for radiative transfer models. Light scattering, absorption, and albedo depend on many characteristics of the particles, including their size, shape, and composition, and are challenging to retrieve without direct measurements. Nonetheless, radiative transfer models still use the spherical shape approximation, which contributes to the uncertainties in the estimate of the impact of aerosols on the Earth's energy balance. This requires some further steps toward the integrated measurement of as many parameters as possible, on an experimental basis. A continuous flow analysis (CFA) system is currently being developed in the EuroCold laboratory in Milan, oriented toward the light-scattering characterization of particles in polar and Alpine cores using single-particle extinction and scattering, an optical particle sizer, and digital holography microscopy. The aim is to characterize dust records and contribute to the monitoring of

the fast evolution of climate, which is having a detrimental impact on glaciers, among other consequences.

What to look for with optical-based instruments, in a nutshell

A powerful system for studying ice cores is the CFA of different chemical and microphysical compounds. Significant temporal resolution can be achieved by slowly melting cores from one end to pump meltwater into in-line instruments (Bigler et al. 2011; Erhardt et al. 2019). Here we provide a snapshot of what can be observed with optical-based instruments, i.e. light scattering within the optical spectrum. The radiative properties of a particle can be predominantly traced back to its extinction cross-section (C_{ext}), which has the units of a surface area. This is the area that effectively interacts with solar light, or any other incoming radiation. Similar definitions exist for the fraction of light that is scattered and absorbed and give the scattering and the absorption cross-sections, respectively. These optical cross-sections are determined by the conservation of radiative energy and may have little to do with the geometric cross-section of the particle, which is another parameter that may be of interest in its own right. From the scattering and the extinction cross-sections, we can assess the single-scattering albedo of an aerosol particle and make an educated guess about its refractive index. Other radiative parameters of single particles include the optical thickness and effective polarizability, related to their refractive index, shape, and size (Cremonesi 2020).

Light extinction and forward scattering

In a recent CFA campaign on an alpine ice core, we used the single particle extinction and scattering (SPES) method. With this in-line instrument, in addition to particle concentration, two optical parameters can be measured without calibration on a particle-by-particle basis (Potenza et al. 2015): the extinction cross-section and the optical thickness (C_{ext}, ρ). These parameters tell us how much power the particle removes from the incident light and the phase lag of the wave scattered by the particle (Potenza et al. 2016). As a general rule, a larger extinction cross-section corresponds to larger particles and vice versa; similarly, optically dense particles exhibit correspondingly high optical thickness. Some spikes in the particle
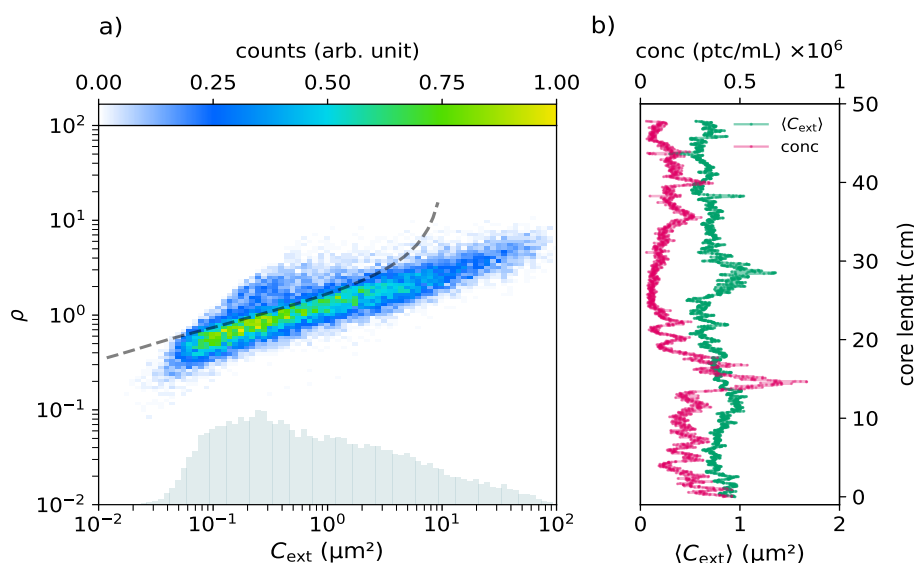

Figure 1: Data from an Alpine ice core. **(A)** Two-dimensional histogram of the extinction cross-section and the optical thickness. The histogram at the bottom corresponds to the cumulative C_{ext} distribution (arb. unit). The expected data for spheres with a refractive index of 1.55 is shown with a dashed line. Absorption is particularly high for particles giving signals above this line. **(B)** Vertical profiles of C_{ext} and particle concentration are reported as a function of the core length.
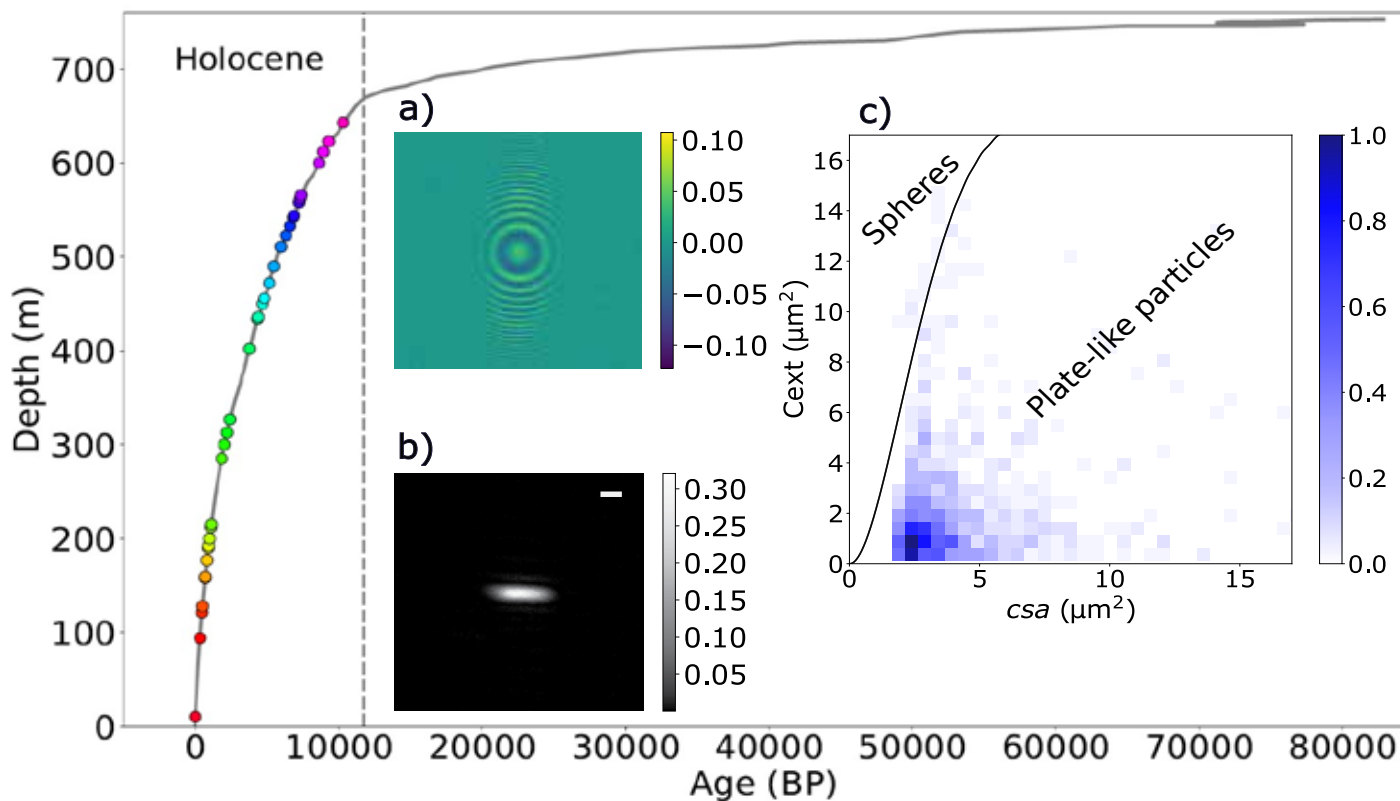
Figure 2: Age–depth relationship at Roosevelt Island ice core (Lee et al. 2020; Winstrup et al. 2019). The samples of Holocene age analyzed with the holographic technique are shown as dots. **(A)** Hologram fringes of a mineral dust particle and **(B)** corresponding reconstructed image. The white bar on the top-right corner is set to 2 μm. **(C)** (*csa*, C_{ext}) plane reported as a two-dimensional histogram and normalized on its maximum (dark blue), from a 313 m-deep sample.

concentration, related to advection events, show a peculiar trend of the combination of C_{ext}, and ρ. Figure 1 shows a snapshot of the optical parameters of a ~15 m deep Alpine ice core from the Adamello glacier (Eastern Alps, Italy). This location is affected by local natural and anthropogenic sources, in addition to the long-range transport of aerosols. Figure 1a shows the cumulative two-dimensional histogram of the extinction cross-section and the optical thickness for all the particles in the ice core. A variety of particle shapes, compositions, and sizes gives a widespread distribution along the two axes (Simonsen et al. 2018). The dashed line corresponds to the expected data for spherical particles with a refractive index of 1.55 (ranging from 0.3 to 2 μm in diameter), which is a threshold for identifying highly absorbing particles. The vertical profiles of C_{ext} and particle concentration are reported as a function of the core length in Figure 2b. Both parameteres depend on the characteristics of the particles and the transport pathways, therefore, C_{ext} and particle concentration do not always covariate.

Characterization by digital holography
Another technique that we integrated into our CFA system is digital holography microscopy, by which we investigate the optical and geometric properties of larger dust particles in the micrometer size range (Berg et al. 2022). As an example, we report an ice-core record from the eastern Ross Sea, as part of the Roosevelt Island Climate Evolution (RICE project, see Bertler et al. 2018; Lee et al. 2020; and Winstrup et al. 2019). In Figure 2, we show the age–depth relationship (gray continuous line), while

samples of Holocene age are identified on the timeline by different dots.

With the holographic technique we acquire the so-called hologram patterns (Fig. 2a), i.e. interferometric images where information about the size and optical properties of the particles are encoded. The holographic pattern is then processed numerically in real-time or post–measurement, without the need to check when particles are in the field of view. Moreover, multiple objects can be imaged at different focal planes simultaneously. The result of the reconstructed algorithm is an image of the silhouette of the particle, as shown in Figure 2b. We characterized insoluble particles suspended in meltwater as described in Ravasio et al. (2021; 2022). We obtained the value of C_{ext}, the cross-sectional area (*csa*), and the thickness over diameter ratio (*tdr*) of each particle, as well as the particle count.

The importance of performing both optical and size characterization is shown in Figure 2c. Here, we show the (*csa*, C_{ext}) data from one of the samples (313 m of depth), represented as a two-dimensional histogram and normalized on its maximum, and selecting only isometric-shape particles. We show with a black solid line the expected result for spherical particles from Lorenz–Mie theory (1.4–2.8 μm in diameter, refractive index of 1.55), as reference. We note that most of the data falls below this line and spans a considerable range of both *csa* and C_{ext}. Indeed, many particles are plate-like with *tdr* values between 0.1 and 0.25, which lowers the actual C_{ext} of the particles compared to spheres with the same geometrical cross-section.

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Exploring new molecular universes: How non-target screening analysis can open new perspectives in ice-core science

François Burgay

Ice cores are unique environmental archives for reconstructing the Earth's past climate. Each sample can contain thousands of different molecules, which, thanks to technological advances, can now be identified to gain a broader understanding of the Earth's system.

The organic challenge

Over the last decades, analytical chemistry applied to ice cores has developed rapidly. Among the most significant innovations, there are those related to the study of elements, which until the beginning of the 21st century was extremely challenging due to their very low concentration in ice, well below the detection limit of the analytical instrumentation. Until the mid-1990s, only a few elements could be analyzed simultaneously, and the analysis of a single sample could take several hours (Barbante et al. 1997). Today, an entire ice core can be continuously analyzed for virtually the entire periodic table of elements (Erhardt et al. 2019). The same applies for organic compounds, such as pollutants or wildfire tracers that are now routinely analyzed at extremely low concentrations (Vecchiato et al. 2020; Zennaro et al. 2014). The possibility to detect and quantify organics in ice samples has opened up new opportunities, such as investigating the anthropogenic perturbation of the environment, or allowing a deeper understanding of specific environmental processes. For example, whereas common inorganic proxies for wildfires, such as ammonium, only give us information about the occurrence of a biomass-burning event (Legrand et al. 2016), organic compounds, like methoxyphenols, can also tell us the type of vegetation that burned (e.g. grasses, conifers; Müller-Tautges et al. 2016).

However, the number of organic compounds that are usually measured only represents a small fraction of the overall organic burden, meaning that the identity of the large majority of the molecules remains unknown. Indeed, most of the analytical methodologies applied so far to ice cores are defined as targeted, meaning that only specific compounds are investigated. To put this into perspective, there are more than 60 million molecules recorded in the Chemical Abstracts Service (cas.org), while less than a hundred are routinely analyzed. These compounds are typically anthropogenic markers, terrestrial and marine biomarkers and biomass burning tracers (Giorio et al. 2018). If we step outside ice-core science for a moment, we can say that the approaches adopted so far are similar to those of a person walking through a meadow with a metal detector. What that person will find are pieces of metal, but they will not see, for example, fragments of plastic or the living beings that inhabit the meadow itself. Not seeing them does not mean that they do not exist, but they are simply invisible to the eye. Coming back to analytical chemistry: target methods, although essential, give us only a partial view of the chemical space. How, then, to proceed?

Non-target screening analysis

The development of high-resolution mass spectrometers (HRMS) unlocks the possibility of exploring what was previously invisible, by simultaneously detecting up to thousands of different molecules from a single sample by providing their exact mass (Fig. 1). The application of HRMS to environmental samples is a fast-growing research field. Methods have been successfully applied to freshwater, aerosol, soil and sediment samples (e.g. Ma et al. 2022). Generally, two approaches are followed: non-target screening (NTS) and suspect screening (SUS). The former refers to the identification in a mass spectrum of those masses that are particularly relevant according to specifically defined criteria (e.g. intensity, occurrence), followed by a characterization and confirmation using reference standards. The latter refers to a slightly different approach that involves the screening of a mass spectrum for specific masses related to a defined list of molecules, followed by a characterization through ion fragmentation and comparison with reference standards.

Despite being widely used in several different environmental matrices, NTS applied to ice cores is still in its infancy, meaning that, to date, the information we can get from ice cores is still under investigation. However, results obtained from the analysis of a single sample from the Belukha ice core (Siberian Altai, 4072 masl) highlight the great potential of the application of NTS (Burgay et al. 2023). Indeed, up to 313 different compounds have been detected, the majority of which (80%)
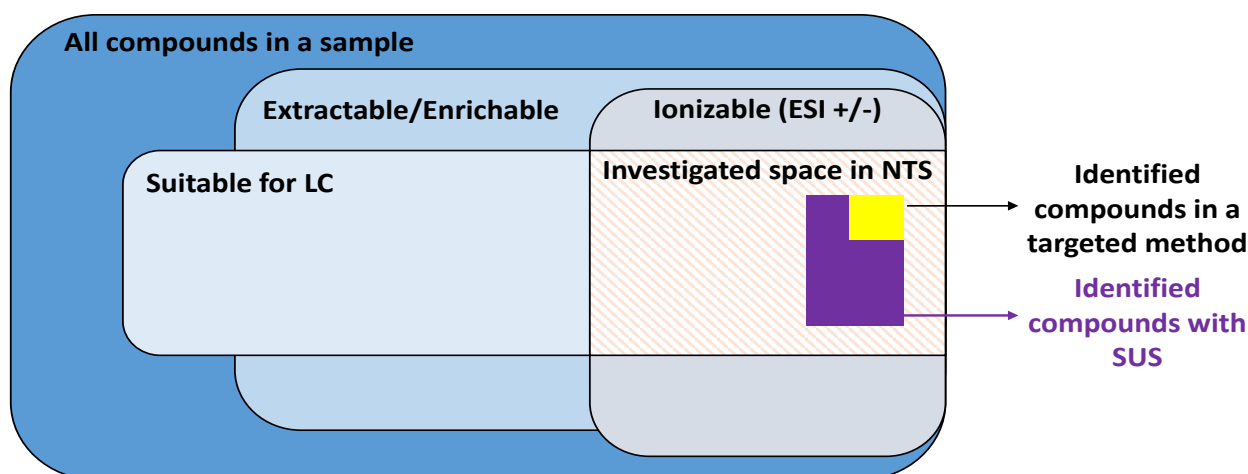

Figure 1: Example of the application of non-target screening (NTS, dashed orange rectangle) and suspect screening (SUS, purple rectangle) approaches when coupled to liquid chromatography (LC). These approaches enable the possibility to investigate a wider chemical space than standard target methodologies (yellow rectangle).
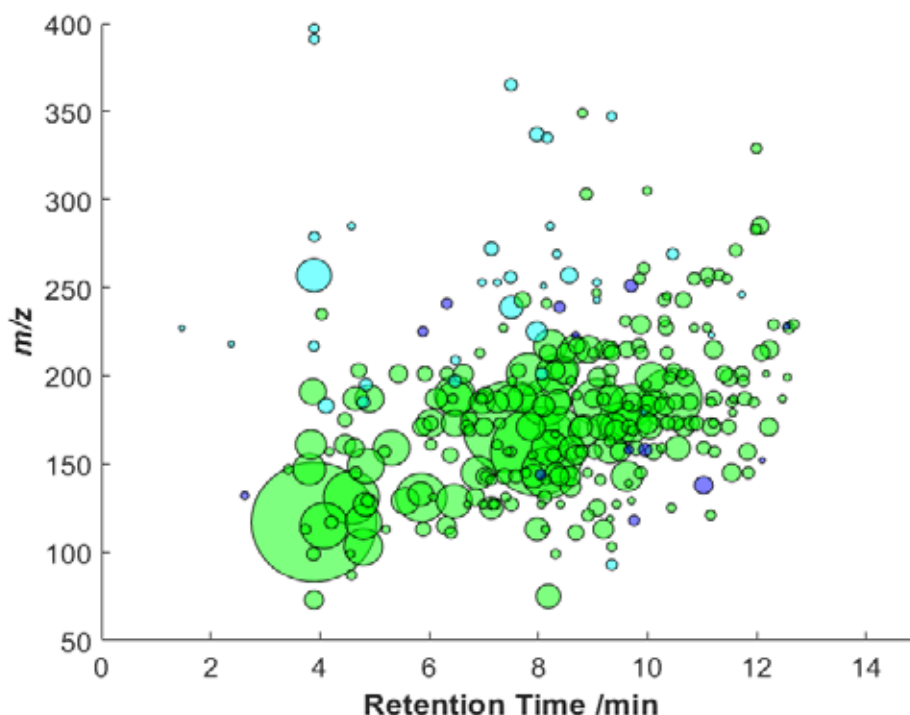
Figure 2: Mass-to-charge (m/z) ratios plotted against the retention time. The size of the circles is proportional to the area of the molecular ions. Green circles refer to compounds consisting of carbon, hydrogen and oxygen atoms. Purple circles refer to compounds that also have nitrogen in their structure. Light blue circles refer to compounds defined as "other", which contain other heteroatoms. Figure from Burgay et al. (2023) under CC-BY 4.0.

consist of carbon, hydrogen and oxygen. In addition, 7% of the molecules also contain nitrogen in their structure, while the remaining 13% contain other heteroatoms (Fig. 2). Focusing only on the most intense peaks, several carboxylic acids (e.g. succinic acid, glutaric acid, levulinic acid) and biomass burning tracers (e.g. *p*-hydroxybenzoic acid) were characterized.

Potentialities, challenges and future work
When applied to an entire ice-core record, the developed NTS workflow will allow scientists to understand how anthropogenic pollution has altered the aerosol molecular composition, and how the oxidative capacity of the atmosphere has changed between the pre-industrial and industrial periods. Additionally, NTS methods can be exploited for the identification of novel molecular proxies that can overcome limitations of existing proxies. For example, commonly used marine productivity proxies, such as methanesulphonic acid, may suffer from migration within the ice column, thus potentially compromising the reliability of paleoclimate reconstructions (Osman et al. 2017). However, phytoplankton also emits isoprene compounds, which can be oxidized in the atmosphere to secondary organic aerosol species (Hu et al. 2022) that are, in turn, deposited on the snow. Identifying these products using an NTS approach could provide unprecedented opportunities to test their suitability as reliable proxies for marine productivity.

Unfortunately, NTS methods are not universal. In other words, they allow the identification of hundreds or even thousands of new molecules, but many more may still be present in the ice-core samples. Coming back to the previous metaphor: NTS allows us to observe other materials as well, not just metal.

However, others still remain invisible to the eye. This is due to their different chemical (polar/non-polar) and physical (volatile/non-volatile) properties. For this reason, there are no methods or instruments that can cover this wide range of molecular heterogeneity. Continuous methodological development based on well-constrained scientific questions is, therefore, essential to fully exploit the potential of NTS for comprehensive ice-core reconstructions. To date, the few available NTS ice-core methods are optimized for the detection of polar substances, i.e. those that are easily ionizable by electrospray ionization and compatible with liquid chromatography (Burgay et al. 2023; Vogel et al. 2019). However, future developments should also focus on the identification of non-polar and/or volatile substances relying on other ionization techniques and instruments.

A further challenge is the characterization of the identified molecules. We have seen that the application of HRMS provide the exact mass of the compounds, making it possible to unambiguously define their molecular formula. However, there may be many compounds with the same molecular formula, but different structure, known as isomers. This highlights the need for additional efforts to uniquely characterize a compound, for example by comparing the fragmentation spectra and retention time of the unknowns with those of reference standards. However, standards do not exist for all molecules, especially for those formed after reactions in the atmosphere, which are of particular interest to ice-core scientists. To fill this knowledge gap, a novel approach known as aerosolomics has been recently developed (Thoma et al. 2022). In brief, chamber experiments have been carried out to determine the oxidation products of specific precursors, such as terpenes, i.e. biogenic-derived

molecules. When applied to environmental samples, this strategy would link the detected oxidation products to their respective precursors, assessing their oxidative pathways. For ice-core studies, this approach can shed light on past changes of the different oxidative pathways of terpenes, as well as on the temporal evolution of the source's strength.

As with any new scientific adventure, the difficulties and unknowns are many. However, the rewards of exploring a mysterious universe of molecules can be great. We are only at the beginning of this exciting journey, and there is much to discover.

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A whole ocean thermometer from atmospheric noble gas ratios

Sarah Shackleton

Marine-based reconstructions of ocean temperature have provided fundamental insight into past climate. The novel ice-core based proxy for mean ocean temperature from atmospheric noble gas ratios has demonstrated promise in furthering these insights.

Modern ocean warming

The oceans represent the largest source of thermal inertia in the climate system and play a key role in modulating the pacing of climate change. Measuring how much heat the oceans have taken up since the onset of the industrial era is important for understanding how the planet has responded to changes in our atmospheric composition driven by human activity. However, measuring total ocean warming is not an easy task, as heat uptake is spatially heterogeneous. Until recently, measurements of much of the ocean's temperature have been sparse, and few measurements exist of ocean temperature below 2000 meters, where almost half of the ocean's volume resides.

Probing ocean-temperature change before the instrumental era is an even greater challenge. Most of our information about past ocean temperature comes from marine-sediment records. However, as in the case of the instrumental era, ocean-temperature change at one location does not necessarily give you information about the global trend. In addition, most of our marine-sediment proxies for temperature provide information about sea-surface temperature, which represents a tiny fraction of the total ocean volume.

Changes in ocean temperature can also change its composition, including the quantity of gases dissolved in seawater. As the ocean warms, it can hold less gas, which leads to a net degassing of seawater as it surfaces and warms. This has important consequences for our atmosphere and climate; as seawater warms it can take up less CO_2, leading to an increase in atmospheric CO_2 and further warming.

Inert atmospheric gases trace ocean heat

This temperature dependence of gas solubility in seawater also has consequences for the inert (or non-reactive) noble gases, including krypton (Kr) and xenon (Xe). The larger the noble gas, the higher its solubility in seawater, and the stronger the temperature dependence of that solubility (Fig. 1).

Between the ocean and atmosphere, about 5% of xenon is dissolved in the ocean and 95% resides in the atmosphere. At the average ocean temperature (3.5°C), the solubility of xenon changes by about 4% per °C of warming. Therefore, if the whole ocean warmed by 1°C, the concentration of xenon in the atmosphere would increase by roughly 0.2%. This may sound like a tiny change, especially given that xenon has an atmospheric concentration of only 87 parts per billion. However, these small changes may be measured.

In ice cores, we can measure the ratios of xenon and krypton in air bubbles with respect to one another (Xe/Kr) or relative to N_2 (Xe/N_2 and Kr/N_2) to reconstruct global mean ocean temperature (Headly and Severinghaus 2007). While N_2 is not entirely inert and may be converted to bio-available forms via nitrogen fixation, this bio-available nitrogen represents a miniscule portion (<0.01%) of the total nitrogen in the ocean and atmosphere; even a dramatic change to the nitrogen cycle would lead to a negligible change in the total N_2 inventory. We may therefore treat N_2 as an inert tracer, as we do Xe and Kr.

Why is this a whole ocean thermometer?

As implied above, seawater will only degas or ingas when it is at the surface and may equilibrate with the atmosphere, so it is not necessarily intuitive why the atmospheric noble gas ratios reflect mean ocean temperature change rather than that of the surface. To gain insight, first we must understand that all of the ocean's temperature (including water at depth) is set at the sea
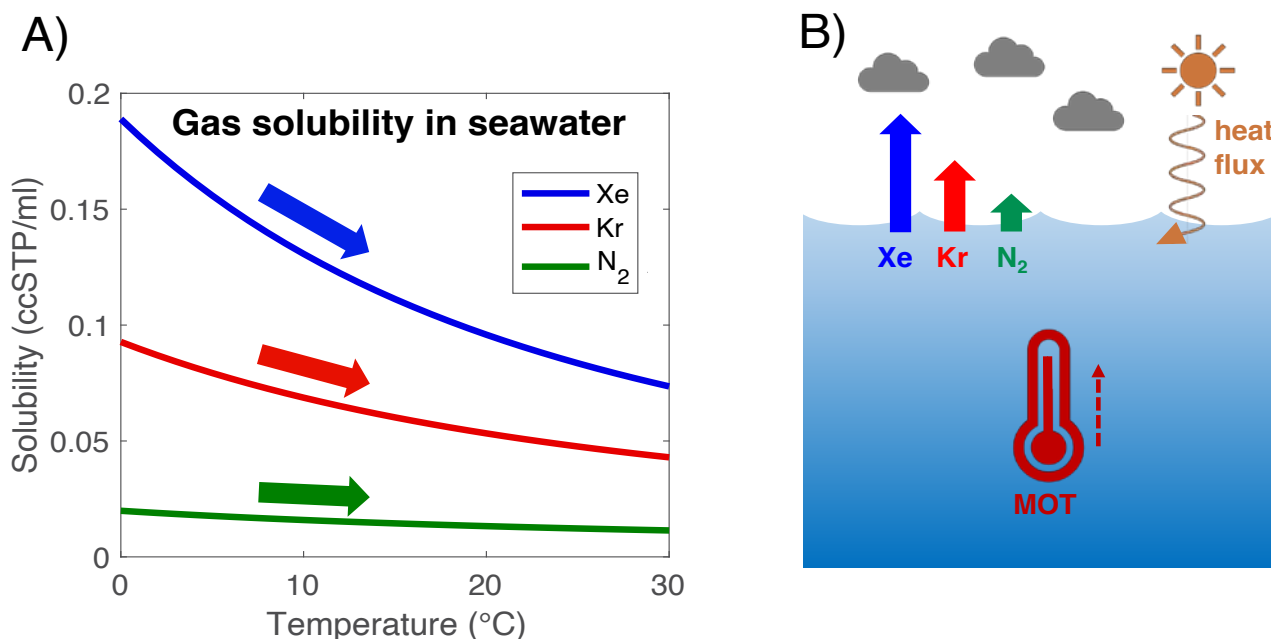
Figure 1: **(A)** Temperature dependence of inert gas solubilities in seawater (35 practical salinity units) and **(B)** schematic of the noble gas mean ocean temperature (MOT) proxy.
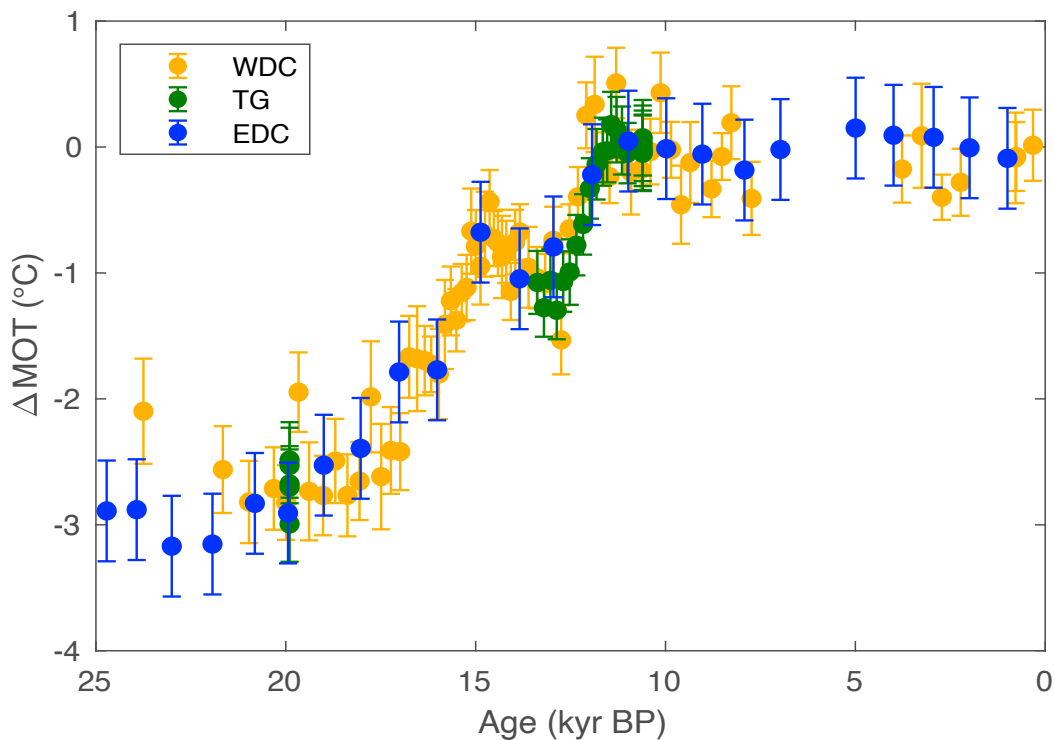
Figure 2: Published mean ocean–temperature reconstructions for the last 25,000 years from the West Antarctic Ice Sheet (WAIS) Divide (WDC, yellow; Bereiter et al. 2018), Taylor Glacier (TG, green; Shackleton et al. 2019; 2020), and EPICA Dome C (EDC, blue; Baggenstos et al. 2019) ice-core records. Values are shown as an anomaly relative to today. Errorbars indicate 1σ uncertainty.

surface. Geothermal heating may warm the ocean from below, but this term is miniscule in comparison to the ocean–atmosphere heat flux. When a parcel of water is cooled at the surface it will take up more noble gases before it sinks into the deep. Once at depth, it conserves these properties (heat and inert gases), which are only reset once the parcel resurfaces. This means that at any given time, the total sum of dissolved xenon, krypton, and nitrogen in all these parcels of water (which controls atmospheric Kr/N_2, Xe/N_2, and Xe/Kr) should reflect total heat content. Because the atmosphere is mixed on annual timescales, the atmospheric noble gas ratios track ocean temperature change with no lag.

What can we learn?
Only a small number of studies have been published using this noble-gas-based technique in ice cores. However, they have shown the great potential of this proxy in probing the dynamic relationships between ocean-heat content and other components of our climate system.

• *Ocean circulation and ocean-heat content*

The first timeseries of mean ocean temperature came from the West Antarctic Ice Sheet (WAIS) Divide ice core and covered the most recent transition between glacial and interglacial climate (i.e. the last 25,000 years; Bereiter et al. 2018). This transition involved mean ocean warming in two pronounced steps, both of which occurred during millennial-scale disruptions in ocean overturning. This was later confirmed by two other reconstructions of mean ocean temperature over this interval (Baggenstos et al. 2019; Shackleton et al. 2019; Fig. 2) and suggests an important link between ocean circulation and heat content.

• *CO_2 and ocean temperature*

The relationship between CO_2 and ocean temperature is bi-directional; CO_2 warms our planet (thus warming the oceans), and due to reduced solubility, warmer oceans can hold less CO_2, thereby increasing atmospheric CO_2. The noble gas proxy for mean ocean temperature is well suited to probe this relationship, because the noble gases and CO_2 are measured on the same archive, which makes it possible to reconstruct changes in ocean temperature and CO_2 without uncertainty in the relative timing of these changes.

The links between ocean temperature and atmospheric CO_2 have been probed in several recent studies. Shackleton et al. (2021) examined the role of ocean cooling in lowering atmospheric CO_2 during an interval of abrupt CO_2 drawdown in the last glacial cycle. Haeberli et al. (2021) evaluated the relationship between atmospheric CO_2 and climate on orbital timescales by assessing mean ocean temperature and CO_2 records during the interglacials and glacial maxima of the last 700,000 years.

• *Ocean temperature, sea level, and ice volume*

Ocean warming contributes directly to sea-level rise through the thermal expansion of seawater. Mean ocean–temperature reconstructions may be used to quantify this direct role of ocean warming in contributing elevated sea levels during part warm intervals, such as the last interglacial (Shackleton et al. 2020).

Ice-core noble gases may provide additional constraints on past sea-level and ice volume through insights into records of the oxygen

isotopic composition ($\delta^{18}O$) of benthic foraminifera, which is set by ocean temperature and seawater $\delta^{18}O$. As mean seawater $\delta^{18}O$ is controlled by the growth and decay of ^{18}O-depleted ice sheets, global composites of benthic-foraminiferal $\delta^{18}O$ record changes in mean ocean temperature and global ice volume. Insight into the relative influences of ocean temperature and ice volume on $\delta^{18}O$ may therefore be gained by comparing contemporaneous records of global $\delta^{18}O$ and mean ocean temperature.

Conclusions
While mean ocean–temperature reconstructions in ice cores have shown promising results and offered new paleoclimatic insight, there is plenty to learn about noble-gas-based tools. Questions remain about the potential complexities of the proxy and ways in which the noble gases measured in ice cores may become decoupled from ocean-heat content. In the future, as much attention should be put into understanding the potential pitfalls of the proxy as in producing new records.

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Extracting paleoclimate information from stratigraphically disturbed "oldest ice"

Yuzhen Yan

Researchers have found ice as old as 2.7 million years in East Antarctica, but such ice has a disturbed stratigraphy and a complicated age–depth relationship. Nevertheless, innovative data analyses and sampling plans can still reveal valuable paleoclimate information.

Oldest ice, but in stratigraphically disturbed form

Ice cores contain a wealth of information about the Earth's climate history. The oldest continuous ice-core record comes from Dome C on the East Antarctic Plateau, with ice near the bottom dating back to approximately 800 kyr (EPICA community members 2004). A "holy grail" of the ice-core community is to obtain a record that extends to 1.5 Myr (Dahl-Jensen 2018), a time when the Earth's glacial cycles showed a shorter periodicty of 41 kyr and a smaller amplitude of changes than their more recent counterparts (Raymo and Huybers 2008).

While efforts to recover a 1.5-Myr-old ice core are currently underway in East Antarctica, researchers have obtained shallow ice cores near the ice-sheet margin that date as far back as 2.7 Myr (Yan et al. 2019). The ice came from the Allan Hills blue ice areas, where sublimation and a subglacial mountain range contribute to the movement of old ice toward the surface (Spaulding et al. 2012). Yet, interpreting the data from the "oldest ice" is challenging due to disrupted age–depth relationships (Higgins et al. 2015), uncertainties related to absolute dating methods (Bender et al. 2008), and alterations to the chemical composition of the trapped gases near the bottom (Yan et al. 2019).

If classic ice-core records are like a movie, disturbed ice resembles random, separate snapshots of the film. However, innovative data treatments and sampling plans can still extract valuable paleoclimate information from these "climate snapshots."

Asking different questions

The key to interpreting stratigraphically ordered deep ice-core records is the ability to convert depth into age continuously. This accounts for the biases due to the different accumulation rates between glacial and interglacial intervals. However, when ice stratigraphy is no longer continuous, such biases can greatly affect our observations. For example, from the Allan Hills ice dating back to 1.5 Myr, there are 33 discrete CO_2 measurements yielding an average CO_2 concentration of 232 ppm (Yan et al. 2019). This value does not necessarily represent the true average CO_2 concentration of the 41-kyr glacial cycles due to potentially incomplete or biased sampling from the disturbed stratigraphy.

Consequently, we need to reevaluate the data through a different lens. Instead of means and standard deviations, what other types of information can we learn from the individual climate snapshots?

One answer is the range of data, defined as the difference between the maximum and minimum values. While the problem of incomplete sampling remains, now we can quantitatively estimate what fraction of the true data range a certain number of points can capture. Critical to this question are the shape of the true CO_2 time-series and the relative abundance of interglacial- versus glacial-CO_2 samples preserved in the ice.

In the case of Allan Hills samples, Yan et al. (2019) constructed a synthetic CO_2 time-series based on the climate records from ocean sediments. Assuming that ice from interglacial periods is over-represented by a factor of 10 in the Allan Hills ice (Yan et al. 2021), we estimated that 33 discrete samples capture 81% of the true range (95% confidence interval: 56–99%; Fig. 1). Since the observed range of the 33 CO_2 samples from the 1.5 Myr ice is 65 ppm (from 214 to 279 ppm), the true glacial–interglacial range of CO_2 is estimated to be between 206 and 287 ppm, assuming that glacial and interglacial extremes are equally absent.

By comparison, atmospheric CO_2 varied between 300 and 180 ppm over the past 800 kyr. The result suggests a smaller CO_2 variability 1.5 million years ago, resembling the smaller temperature variability of glacial cycles at that time. The last 800 kyr's greater glacial–interglacial CO_2 range primarily resulted from a lower glacial CO_2 level (Yan et al. 2019).
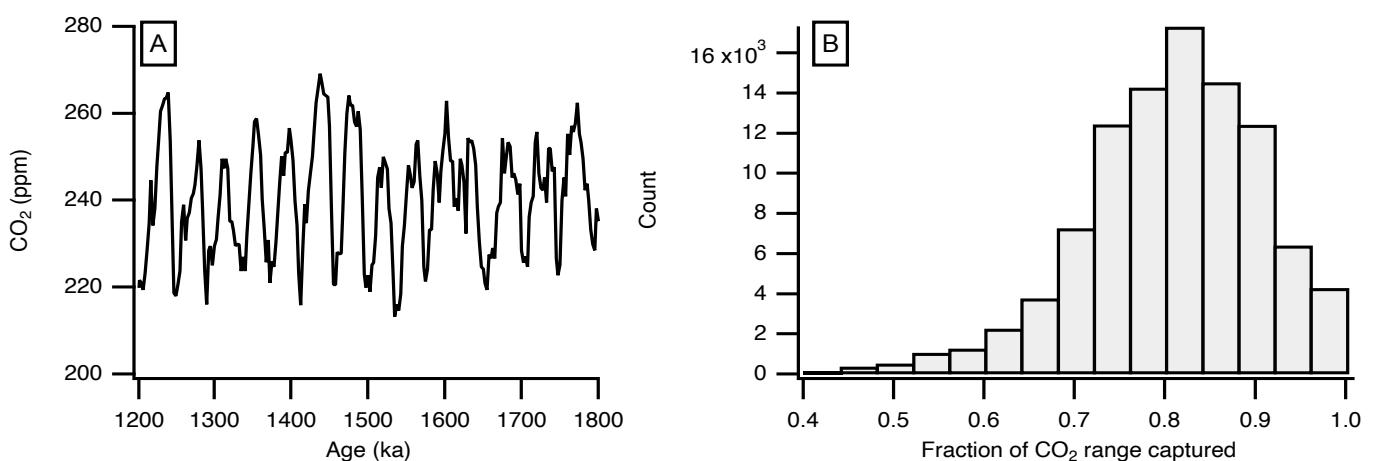
Figure 1: (A) Synthetic CO_2 time-series between 1.2 and 1.8 Myr, modified from Yan et al (2019). **(B)** Counts of the fraction of the recovered CO_2 variability (observed range/true range) of the synthetic CO_2 record by 33 discrete samples in Monte Carlo simulations (105 iterations). In each iteration, a 10-fold over-representation of interglacial periods in the ice was assumed.
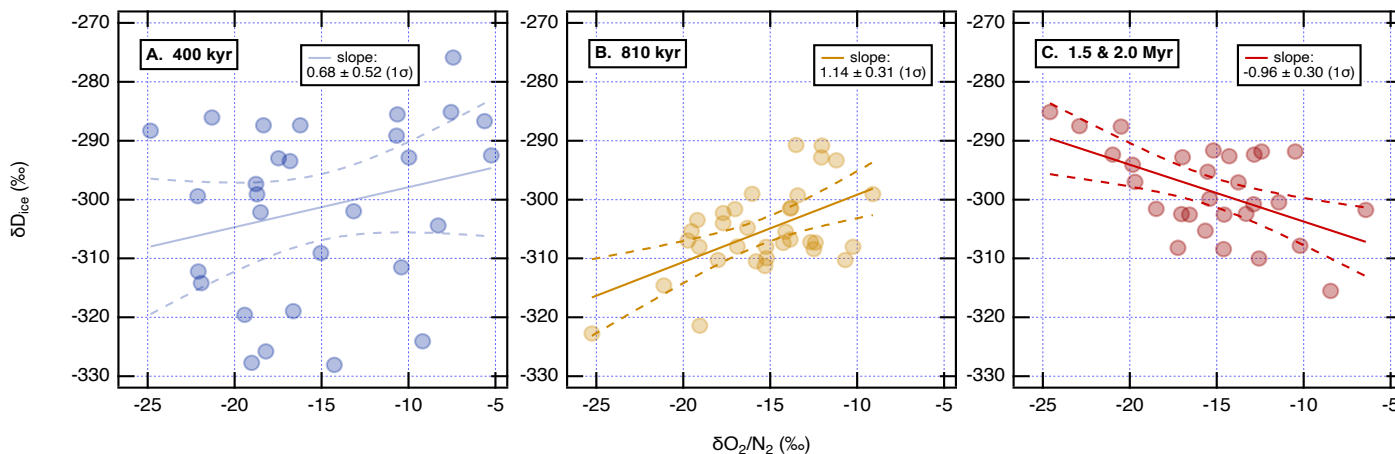
Figure 2: Relationship betewen the isotopic composition of the hydrogen in Allan Hills ice molecules (δD_{ice}) and $\delta O_2/N_2$ measured on ice dating back to **(A)** 400 ± 70 kyr (95% CI), **(B)** 810 ± 100 kyr, and **(C)** 1.5 ± 0.1 and 2.0 ± 0.1 Myr, modified from Yan et al (2023). The uncertainty associated with age arises from the fact that [40]Ar dating could not fully resolve the chronology of the blue ice, so the data are binned together to form a series of "climate snapshots".

Scatter plots instead of time-series

Another way to examine stratigraphically disturbed ice that is out of chronological order is to make property-versus-property plots. Measurements of different properties taken from the same depth should have a similar age regardless of the ice stratigraphy, making this approach particularly useful in evaluating the relationship between two properties of interest, such as CO_2 and Antarctic temperature proxies (Yan et al. 2019).

In addition to greenhouse gases, the composition of major gases trapped in polar ice reveals useful paleoclimate information. An empirical relationship between the oxygen-to-nitrogen ratio, expressed as $\delta O_2/N_2$, and local summer insolation has been established for over two decades (Bender 2002). Higher insolation corresponds to lower $\delta O_2/N_2$ values. By using $\delta O_2/N_2$ as an insolation proxy, we can evaluate the relationship between Antarctic temperature and local solar forcing. The isotopic composition of the hydrogen molecules in the ice, expressed as δD_{ice}, indicates local temperature.

Over the past 800 kyr, Northern Hemisphere insolation has paced Antarctic temperature on orbital timescales (Bazin et al. 2016; Kawamura et al. 2007). In this time period, a scatter plot between $\delta O_2/N_2$ and δD_{ice} measured on Antarctic ice shows a positive correlation (Figs. 2a-b), which means lower Antarctic temperature was associated with higher local insolation.

On the contrary, correlation between the $\delta O_2/N_2$ and δD_{ice} data obtained from the 1.5- and 2-Myr ice shows a statistically significant negative correlation (Fig. 2c), meaning that a warm Antarctica occurred during intervals with high local summer insolation. The most reasonable explanation is that Southern Hemisphere insolation paced Antarctic temperature in those 41-kyr glacial cycles (Yan et al. 2023). The result here supports the hypothesis that there were no precession-related ice-age cycles 1.5 Myr ago globally, because precession forcings are out-of-phase between the two individual hemispheres (Raymo et al. 2006).

More robust approach with large diameter samples

The examples above have a catch, however: limited ice availability means that the depths of measurements that determined gas composition differ slightly from those that constrained the age of the ice. As a result, certain assumptions had to be made about the age of the gas data, such as linking it to the nearest absolute age-control point. However, this assumption might not always hold true, since stratigraphic disturbance could occur between two age-control points.

Fortunately, engineers have developed a solution in the form of a large-diameter ice drill designed specifically for blue ice (Kuhl et al. 2014). This drill produces ice-core samples with an inner diameter of 241 mm, allowing for multiple measurements at the exact same depth. Although we still need to make the assumption that stratigraphic layers are perpendicular to the vertical axis of the cores, having an age-control point from the same depth is more accurate than attaching the data to the nearest age control points. In two austral summer field seasons (2019–20 and 2022–23), one such large-diameter drill was deployed in Allan Hills. A number of ice cores were successfully retrieved, and analyses are currently underway.

Conclusions

Ice older than 1 Myr has been found in blue ice areas in East Antarctica, but the disturbed stratigraphy prevents the establishment of a conventional timeseries. Rather, the blue ice data represent a series of "climate snapshots". Consequently, we must ask different questions about the data, or take advantage of the fact that properties measured at the same depth have similar age. Lessons learned from these climate snapshots preserved in the blue ice could prove useful in case stratigraphic disturbance is observed near the bottom of the future deep Antarctic ice cores dating back to 1.5 Myr.

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New perspectives on the isotopic paleothermometer

Mathieu Casado[1] and Anaïs J. Orsi[1,2]

Water isotopes in ice-core records are often used as a proxy of past temperature variations. Their use is based on an empirical relationship which requires care to limit the impact of the multiple contributions to the isotopic signal.

Water isotopes in ice-core records are a favored proxy of past temperature variations (Dansgaard 1964). The isotopic signal is formed by the distillation of the heavier isotopes during the advection of moist air masses from the oceanic areas, where evaporation takes place, to the precipitation sites in polar regions (Fig. 1a). As such, the temperature signal of precipitation integrates all the changes of temperatures along the pathway, following the geophysical fluid dynamic (Bailey et al. 2019). In addition, the isotopic signal is modulated by the precipitation intermittency at the ice-core drilling site (Casado et al. 2020; Münch et al. 2021), the local exchange between the snow and the atmosphere (Steen-Larsen et al. 2014; Wahl et al. 2021), the redistribution by the wind and its interactions with the local stratigraphy (Fisher et al. 1985), and snow metamorphism and diffusion inside the snow (Casado et al. 2021).

Isotopic composition of precipitation
Historically, the link between isotopic composition and temperature was assessed by spatially correlating the concurrent change of temperature and isotopic composition across Greenland and Antarctica (Dansgaard 1964). This spatial correlation was then used to convert isotopic records from ice core to past temperature records (Stenni et al. 2004) and supported by models ranging from simple Rayleigh models (Ciais and Jouzel 1994) to isotope-enabled global coupled models (iso-GCM) (Werner et al. 2018).

In a pure Rayleigh distillation model, the isotope-temperature relationship is dictated by the temperature control of the rainout fraction, under a moist-adiabatic framework (i.e. following the Clausius-Clapeyron law) (red dots in Fig. 1b). Using the spatial relationship between isotopic composition and temperature to predict the temporal relationship (space for time analogy) would work if the moisture pathways always remained the same, and the spatial gradients of isotope and temperature were evaluated directly over these moisture pathways. In reality, each precipitation event is associated with the advection of moisture air masses with different origins in terms of distance, temperature and humidity conditions (blue dots in Fig. 1b). This leads to the isotope-to-temperature relationships varying with space, time, and timescales, which is not reproduced by Rayleigh models. Yet, Rayleigh models are still heavily used for their simplicity compared to more complex models, such as iso-GCM which have shown the limits of the space-for-time analogy at timescales ranging from seasonal to multi-millennial (Werner et al. 2018). Newer distillation models using a moist-isentropic framework (i.e. not following Clausius-Clapeyron, but instead keeping the potential temperature constant) remain easy to use, and they can explain more features, such as the difference between spatial and temporal slopes (Bailey et al. 2019).

Archiving of the signal in the snow
As the signal is only recorded when snowfalls occur, the precipitation intermittency creates a significant modulation of the recorded signal (Casado et al. 2020). Overall, the aliasing of the seasonal cycle by precipitation intermittency creates a white noise contribution which can be more than 10 times stronger than the climatic signal at interannual and decadal scales. This can be easily visualized using the power spectral density, i.e. the amount of energy that is included in the signal at a given frequency, which shows that the peak associated to the seasonal cycle (Fig. 2a) is redistributed across frequencies (dashed blue arrows in Fig. 2b). In glacial times, winter precipitation is suppressed, which causes an under-estimation of temperature change. This effect is particularly clear during stadial–interstadial cycles in Greenland (Guillevic et al. 2013). In modern times, interannual variability in precipitation is driven by the presence of extreme events in winter (Servettaz et al. 2020). The diagnostic of precipitation intermittency is important for the analysis of each ice-core record. Isotope-enabled global climate models are the tool of choice to quantify the relationship between atmospheric circulation patterns and the precipitation water-isotope composition. The relatively small spatial footprint (100–200
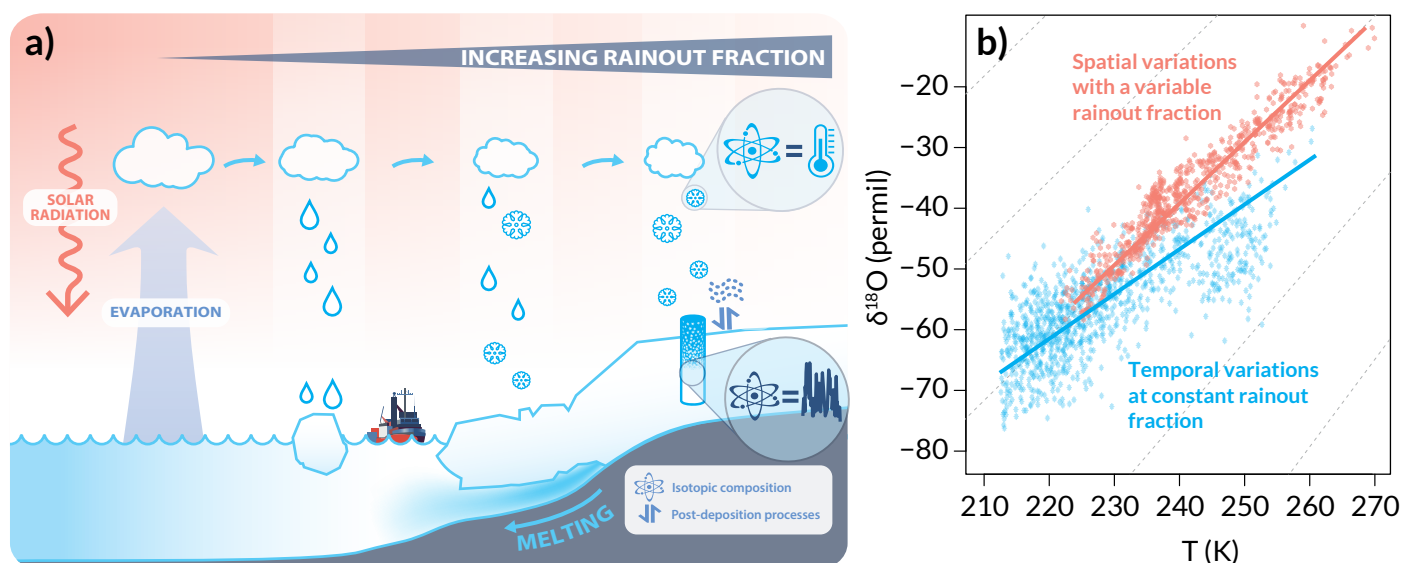
Figure 1: (A) Schematics of the acquisition of the isotopic signal in ice cores: Rayleigh distillation and diffusion; and **(B)** variations of isotopic composition as a function of temperature, across spatial gradients (red), and across temporal changes (blue).

a) Climatic signal over time

b) Signal archived in an ice core

c) Calibration with weather stations

d) Independent calibration
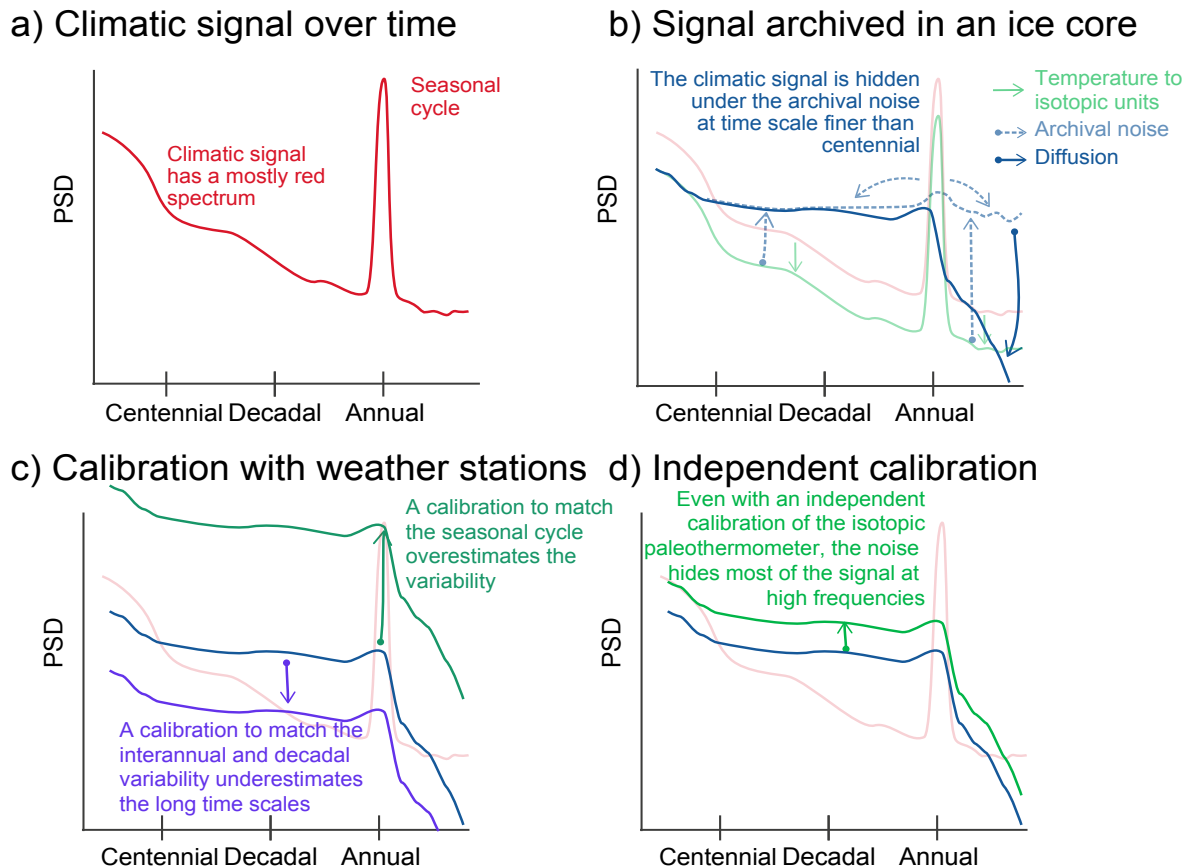
Figure 2: Description of the isotopic paleothermometer calibration through the power spectral density (PSD) at different timescales (centennial, decadal and annual) showing: **(A)** climatic signal spectrum; **(B)** alteration of the isotopic signal (solid blue line) compared to the climatic signal during archival processes; **(C)** calibration against short, recent temperature records at annual and decadal timescales; and **(D)** independent calibration that does not match the variability at a given scale, but does not remove the noise from the signal before the climatic reconstruction (inspired from Osborn and Briffa 2004 and Casado et al. 2020).

km) of precipitation events can also be used to design an optimal array of cores to average out the precipitation noise (Münch et al. 2021), and mitigate the impact of precipitation intermittency.

After the snow has been deposited, it can remain exposed near the surface for a long period of time, especially in low accumulation areas. This leads to a wide range of further alterations of the isotopic signal. Most interactions between the snow and the atmosphere, such as wind redistribution (Fisher et al. 1985), and sublimation and condensation (Casado et al. 2021; Wahl et al. 2021), also induce an aliasing of the signal, and create more white noise with a common structure of a few meters only (Münch et al. 2016). Inside the firn, snow metamorphism (Casado et al. 2021) and isotopic diffusion tend to lead to a low pass filtering of the signal, removing the high frequency variability (solid blue arrow in Fig. 2b). The impact of stratigraphic noise can be mitigated by stacking cores from a few meters apart, thanks to the very short decorrelation length of the noisy component. The diffusion effects can be numerically removed when the measurement noise is sufficiently low (Casado et al. 2020).

Limits of the isotopic paleothermometer
The variable isotope-temperature relationship, as well as these archival processes, limit the possibility for an absolute isotopic paleothermometer. Indeed, the temperature signal which can be simulated by a red noise signal (Fig. 2a), undergoes the conversion

into isotopic units (green curve in Fig. 2b), and then is heavily affected by diffusion and archival noises (blue solid curves in Fig. 2b). All these effects make it arduous to obtain a calibration by matching the isotopic signal with times series obtained from weather stations (Fig. 2c; Osborn and Briffa 2004). In addition, as weather stations at ice-core study sites (Antarctic, the Arctic, high mountain regions) usually have very short record length, and under the influence of climate change, the variability against which the isotopic signal is matched does not correspond to natural variability. Overall, even with a "perfect" independent calibration, if the noisy contributions are not removed, the variability is only well estimated at low frequency (Fig. 2d).

Conclusion
Although the interpretation of water isotopes remains challenging, there are exciting new developments in the interpretation of water isotopes in ice-core records beyond the linear isotopic paleothermometer. Comparing the different noisy components amongst several ice cores can provide information on past precipitation patterns, as well as on the wind conditions and the surface roughness. Combining several isotopic compositions (d-excess, ^{17}O-excess) also expands the scope of reconstructions from water isotopes, including the latent heat fluxes at the surface and within the firn (Casado et al. 2021). Infrared spectrometry offers new possibilities for high-resolution measurements in ice cores to study in situ post-depositional processes in the snow and

in the water vapor. Better measurements will support updated trajectory models, isotope-enabled global climate models, and proxy system models, making water isotope science an expanding field of research.

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Advances in triple oxygen isotope analysis and applications for ice-core paleoclimate science

Lindsey Davidge

Stable water-isotope measurements from ice cores reflect paleo-atmospheric thermodynamics along upstream moisture pathways. New analytical methods simplify the measurement of triple oxygen isotopes, which will improve measurement resolution and provide more complete information about the past atmosphere.

Water isotopes in ice cores ($\delta^{17}O$, $\delta^{18}O$, δD, deuterium excess, and ^{17}O excess) reflect past climate conditions

Stable water-isotope measurements (e.g. $\delta^{18}O$ and δD) from ice cores reflect temperature and other thermodynamic conditions of the past atmosphere. As atmospheric moisture moves poleward from evaporative source regions to eventual precipitation sites, mass-dependent fractionation processes progressively distill its isotopic composition. First-order, temperature-dependent equilibrium fractionation during precipitation is the dominant control on the observed ratio of heavy-to-light isotope abundance (i.e. $\delta^{17}O$, $\delta^{18}O$, or δD) at the ice-core site, and the water-isotope paleothermometer has consequently been a cornerstone of ice-core paleoclimate science for decades (e.g. Dansgaard 1964).

However, even these conventional applications of the water-isotope temperature proxy rely on quantitative models of upstream fractionation pathways. In other words, even though the condensation temperature exhibits large control on the water-isotope signal of the precipitation, the isotopic composition of the air parcel that condenses is predetermined by all upstream thermodynamic processes (e.g. Merlivat and Jouzel 1979). Modeling many unknown upstream fractionation processes (e.g. evaporation, atmospheric transport, and precipitation) is improved by the inclusion of additional

water isotope observations that reflect those processes.

Second-order water-isotope quantities like deuterium excess (d) or ^{17}O excess ($\Delta^{17}O$) – which are defined by the relationships between δD and $\delta^{18}O$ (d) or $\delta^{17}O$ and $\delta^{18}O$ ($\Delta^{17}O$) as indicated in Figure 1a–b –, are dominated by these upstream kinetic fractionation events, and they can therefore provide information about the integrated history of an air parcel that has reached an ice-core site. While d and $\Delta^{17}O$ both depend on temperature and humidity variations in the atmosphere, the sensitivities of d and $\Delta^{17}O$ during fractionation are different, e.g. the relative effect of evaporation temperature is more important for d, and the relative effect of evaporation humidity is more important for $\Delta^{17}O$ (e.g. Uemura 2010). Therefore, measuring d and $\Delta^{17}O$ together should provide the most complete information about the past hydrosphere. The differences between d and $\Delta^{17}O$ are highlighted in Figures 1c–f, which show seasonally resolved measurements of d and $\Delta^{17}O$ from three ice-core sections from Greenland.

Despite the theoretical potential for $\Delta^{17}O$ to be a complementary tracer to d, traditional ice-core work has not included $\delta^{17}O$ or $\Delta^{17}O$ due to measurement limitations. Most commonly, $\delta^{18}O$ and d have been used to reconstruct past condensation-site and evaporation-source temperatures, but this

method is imperfect because, in addition to the evaporation temperature, d is also influenced by other thermodynamic conditions during evaporation, atmospheric transport, and precipitation (Merlivat and Jouzel 1979). Including corresponding measurements of $\Delta^{17}O$ would provide an additional constraint for reconstructing the water-isotope fractionation pathways, and it is therefore desirable to produce records of $\Delta^{17}O$ and to develop climate models that account for $\Delta^{17}O$ (e.g. Markle and Steig 2022; Schoenemann and Steig 2016). The following sections describe recent improvements to $\Delta^{17}O$ measurement methodology and present existing ice-core records of $\Delta^{17}O$.

Recent advances in instrumentation improve temporal resolution of $\Delta^{17}O$ from ice cores

Although d has routinely been measured on ice cores for decades, measuring $\Delta^{17}O$ has only been possible for about 20 years (e.g. Barkan and Luz 2005), and observations of $\Delta^{17}O$ are limited in spatial and temporal resolution. However, new analytical methods have the potential to simplify the measurement of $\Delta^{17}O$ – which, when measured at all, is typically determined separately from other water-isotope quantities by discrete isotope-ratio mass spectrometry (e.g. Barkan and Luz 2005). Unlike d or $\delta^{18}O$, which vary in meteoric water by several or tens of "per mil" (‰, or parts per thousand), respectively, the natural variability of $\Delta^{17}O$ in precipitation is
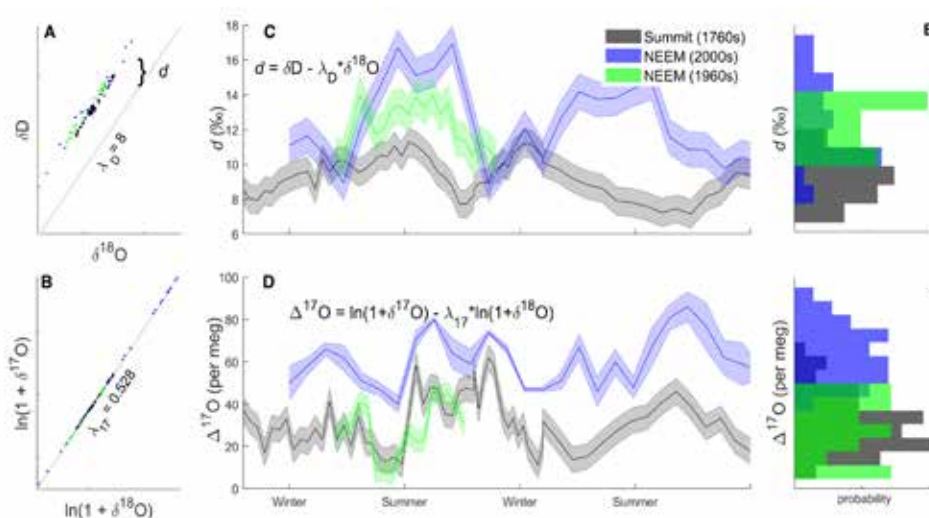
Figure 1: The relationships between δD or $\delta^{17}O$ and $\delta^{18}O$ – which define d and $\Delta^{17}O$ – are provided in **(A)** and **(B)**, respectively. Formal definitions of d and $\Delta^{17}O$ are given by the equations in **(C)** and **(D)**. (C) and (D) provide seasonally resolved records of d and $\Delta^{17}O$ from NEEM (Landais et al. 2012a) and Summit (Davidge et al. 2022), both ice-core sites in Greenland. The decade of the measured ice-core layers is provided in the legend – see the original publications for dating methodologies. All data were aligned to the seasonal cycle of corresponding $\delta^{18}O$ measurements to highlight seasonal patterns in d and $\Delta^{17}O$. Corresponding histograms of these same data are binned by the typical analytical uncertainty and highlight the differences in d **(E)** and $\Delta^{17}O$ **(F)** distribution observed at these sites.
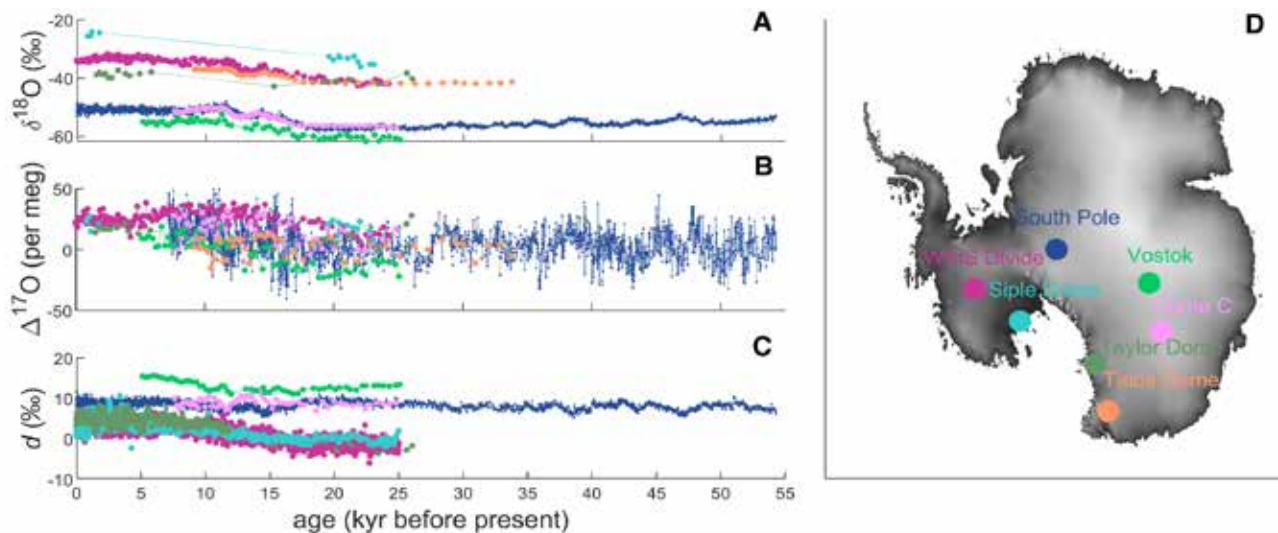
Figure 2: Corresponding measurements of δ¹⁸O **(A)**, Δ¹⁷O **(B)**, and *d* **(C)** for available Antarctic ice-core sites, whose locations are mapped in **(D)**. Continuously measured data from the South Pole is averaged to show 50 cm resolution for all isotope values (from Steig et al. 2021). All discrete data are shown at their measured resolutions. Details about data normalization protocols for Δ¹⁷O, and source information for all discretely measured data, are available from Schoenemann et al. (2013) and Schoenemann et al. (2014), respectively.

only tens of "per meg" (or parts per million), which exacerbates measurement difficulties. However, recent advances in cavity ring-down laser spectroscopy (CRDS) enable the simultaneous measurement of all stable water isotopes (i.e. $\delta^{17}O$, $\delta^{18}O$, δD, $\Delta^{17}O$, and *d*) with precision that meets or exceeds that of traditional methods (see Steig et al. 2014). CRDS is an appealing method not only because it can measure all water isotopes at once, but also because it can be combined with continuous sample melting strategies that are already in use for other ice-core analyses. Over the last 10 years, continuous-flow analysis (CFA) has been widely adopted by ice-core laboratories, and measurements of $\delta^{18}O$, δD, and *d* by CFA-CRDS are already routine for ice-core measurement campaigns (e.g. Emanuelsson et al. 2015). Recent work (Davidge et al. 2022; Steig et al. 2021) demonstrates that CFA-CRDS for all stable water isotopes can greatly reduce the analysis time for $\Delta^{17}O$ and it can therefore improve the time resolution of $\Delta^{17}O$ measurements. CFA-CRDS methods will be useful for improving the temporal and spatial resolution of $\Delta^{17}O$ to characterize the natural variability of meteoric $\Delta^{17}O$.

Recent work demonstrates that CFA-CRDS for $\Delta^{17}O$ can indeed improve the resolution of $\Delta^{17}O$ observations with high precision (<10 per meg), especially when CFA for $\Delta^{17}O$ is developed with specific attention to calibration strategies (Davidge et al. 2022; Steig et al. 2021). Steig et al. (2021) measured the lower 1200 m of the South Pole ice core by CFA-CRDS for all stable water isotopes, revealing significant millennial-scale variability in $\Delta^{17}O$ that is not observed in coarser records of $\Delta^{17}O$ from other ice-core sites, but that is co-incident with other climatic events recorded by *d* and $\delta^{18}O$ (Figs. 2a–c). However, they also identify the importance of frequent (i.e. daily) data calibration against multiple reference waters, adopting a new calibration method that utilizes more reference water measurements than typical CRDS strategies. Davidge et al. (2022) demonstrated that CFA-CRDS for $\Delta^{17}O$ performs as well as discrete methods by measuring replicate sections of an ice core

from Greenland; annually resolved data from that study are provided in Figure 1c–d. They also found that, though small, the greatest source of uncertainty for $\Delta^{17}O$ by CFA-CRDS is the calibration technique. Both studies suggest that the measurement resolution depends on the desired precision for $\Delta^{17}O$ and the rate of the continuous melter. Continuing to develop and implement CFA-CRDS methods so that more existing ice cores can be measured for $\Delta^{17}O$ will improve the spatial and temporal resolution of $\Delta^{17}O$, which is a critical step for studying atmospheric controls on second-order water-isotope quantities and refining interpretations of the paleoclimate record.

Δ¹⁷O data varies on seasonal, millennial, and glacial timescales
Utilizing CFA-CRDS to characterize the full range of variability in both *d* and $\Delta^{17}O$ – and the differences between them – should allow the decoupling of equilibrium and kinetic fractionation during evaporation, which will improve reconstructions made from water-isotope measurements. Because the signal-to-noise ratios for both *d* and $\Delta^{17}O$ are generally quite small, quantifying the relationship between them will be most straightforward on timescales and at locations where variability is greatest. Existing ice-core records of $\Delta^{17}O$ from both Greenland and Antarctica are provided in Figures 1 and 2. Figure 1c–d shows the seasonality of $\Delta^{17}O$ and *d* in Greenland glacial ice and indicates a seasonal magnitude of 40–50 per meg for $\Delta^{17}O$. Similar seasonal magnitudes have been observed over Antarctica (e.g. Landais et al. 2012b; Schoenemann and Steig 2016). Figure 2 presents deep ice-core records of $\Delta^{17}O$, *d*, and $\delta^{18}O$ from Antarctica, where the observed increase in $\Delta^{17}O$ between the last glacial period and the Holocene range from four to five per meg at some coastal sites (e.g. Taylor Dome or Siple Dome) to more than 20 per meg at inland locations like Vostok. The amplitude of millennial-scale variations observed in the CFA-CRDS record from the South Pole is more than 30 per meg (Steig et al. 2021). Efforts to pinpoint the specific controls on *d* and $\Delta^{17}O$ by comparing

measurements with climate reanalysis products (e.g. Landais et al. 2012a) or isotope-enabled climate simulations (e.g. Dütsch et al. 2019; Schoenemann et al. 2014) will be facilitated by corresponding, high-resolution measurements of all first- and second-order water-isotope quantities, and CFA-CRDS techniques provide a method for developing those data.

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Dive into the timescales of deep ice cores

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We review some of the possible methods for building optimized and coherent timescales of deep polar ice cores. We focus on drilling sites characterized by a low temporal resolution due to minimal accumulation of snow at the ice-sheet surface.

Deep polar ice cores are unique archives of past climate. Their investigation is valuable to study mechanisms governing the Earth's climate variations during the glacial–interglacial cycles of the late Quaternary. Precise ice-core chronologies are essential to determine the sequences and durations of climatic events, as well as questioning phase relationships between the external forcings and the climatic responses. One example of climate forcings are the orbital parameters governing the amount of solar energy received at the Earth's surface.

Three challenges are associated with the dating of deep ice cores:

i. A coat of unpacked snow (50–120 m), the firn, covers the ice sheet. The atmospheric air circulates freely within the firn. At the firn-ice transition, the air is enclosed in bubbles and no longer diffuses. Hence, the construction of two separate chronologies is required: one for the ice and one for the younger air.

ii. Most of the paleoclimatic information is recorded within the deepest part of the ice core, due to the thinning of ice layers from their deposition at the surface to the bottom of the ice sheet. Improving the timescales of

deep ice cores is therefore of great concern for the ice-core community, along with extending them further back in time.

iii. Ice cores drilled at sites characterized by high accumulation rates of snow at the surface (10-30 cm/year) are dated by counting annual layers via identification of a seasonal cycle in some records (Sigl et al. 2016). Conversely, some East Antarctic sites show comparatively low accumulation rates (1–5 cm/year), which prevent annual layers from being identified and counted. Chronologies of deep ice cores therefore involve other strategies, summarized below.

Glaciological modeling
Glaciological models simulate the flow and thinning of annual layers over time, from surface deposition down to the bedrock, thus providing the ice age–depth relationship (Parrenin et al. 2004). The model inputs are past scenarios of snow accumulation and temperature at the surface, estimated from water–isotope measurements, together with a calculated temperature–depth profile in the ice sheet. This strategy is highly dependent on poorly known boundary conditions and physical constants. Glaciological modeling is thus combined with dating constraints,

which are depths with a known ice or gas age.

Dating constraints
Absolute dating constraints in ice cores can be determined using radioactive isotope records. The ^{10}Be production rate in the atmosphere relates to the geomagnetic field and solar activities. The Laschamp Excursion, a rapid drop in the Earth's geomagnetic field intensity, is visible as a peak in the ice-core ^{10}Be records, and is independently dated with different series at 41 kyr BP (thousand years before 1950; Raisbeck et al. 2017). Ice-core ^{40}Ar records reflect past atmospheric concentration modulated by the radioactive decay of ^{40}K in the Earth's crust (Yan et al. 2019). Recently, ^{81}Kr measurements on ice samples of a few kilograms provided age estimates between 1300 and 300 kyr BP (Buizert et al. 2014).

Another approach, called "orbital dating", consists in synchronizing ice-core proxies to the Earth orbital parameters (or targets), whose variations are precisely modeled in time. The alignment of the proxy with its target gives ice- or gas-age constraints (Fig. 1). Three orbital proxies are used: $\delta^{18}O_{atm}$, $\delta O_2/N_2$, and total air content. The oxygen in air bubbles ($\delta^{18}O_{atm}$) is sensitive to ocean
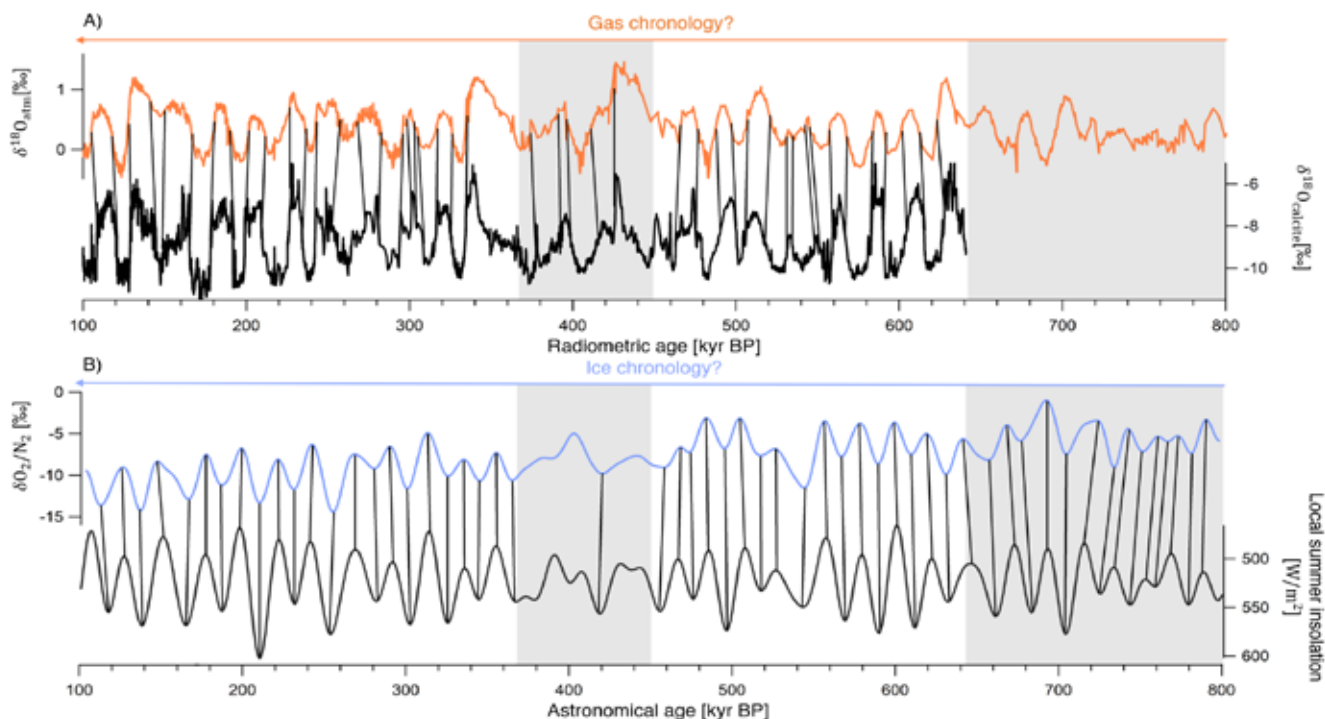
Figure 1: Synchronization of ice-core records with well dated series. Alignment of EPICA Dome C records of (A) $\delta^{18}O_{atm}$ and (B) $\delta O_2/N_2$ (Extier et al. 2018) to $\delta^{18}O_{calcite}$ from East Asian speleothems and local summer insolation, respectively. $\delta O_2/N_2$ is filtered in the insolation frequency band. Gray areas indicate time intervals of large dating uncertainty.
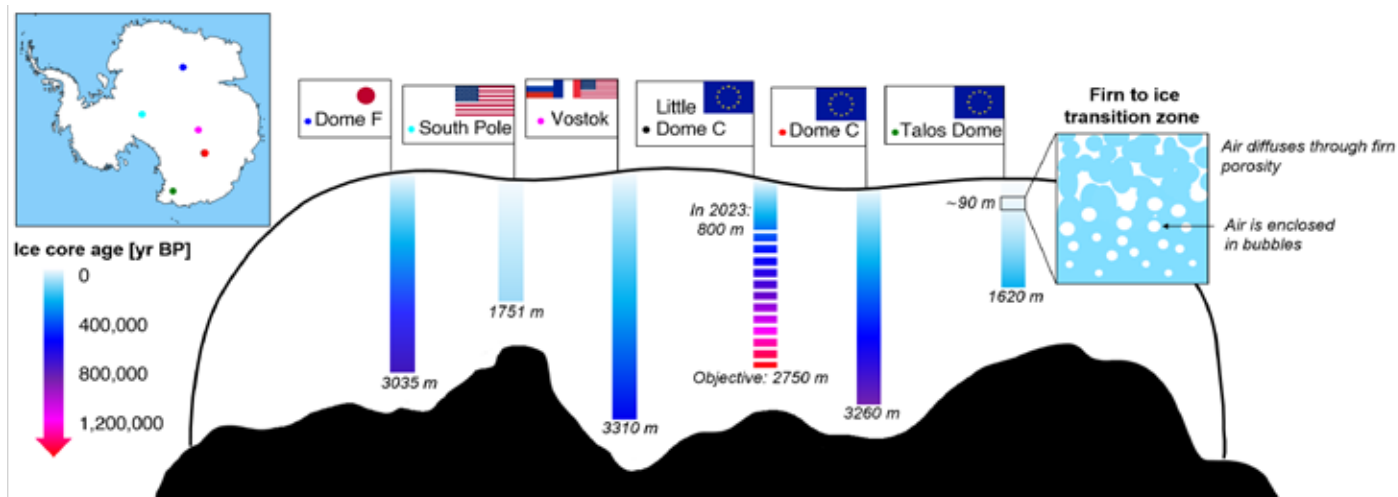
Figure 2: Deep East Antarctic ice cores and age scale. The numbers at the bottom of each ice core indicates the maximum depth drilled. Dome F (720 kyr BP), South Pole (54 kyr BP), Vostok (420 kyr BP), Dome C (800 kyr BP) and Talos Dome (340 kyr BP). The Little Dome C drilling aims to reach 2750 m, and 1.5 Myr BP.

water $\delta^{18}O$ (and, therefore, to the global ice volume), as well as to the biosphere productivity and the low latitude water cycle. Conversely, the oxygen in precipitation ($\delta^{18}O_{ice}$) depends on local temperature changes, and, thus, not used for orbital dating. $\delta^{18}O_{atm}$ was synchronized to the Earth's axial precession, delayed by 5000 years, because such a delay was observed during the last deglaciation. However, the lag of $\delta^{18}O_{atm}$ behind precession fluctuates. Rapid climatic instabilities linked to breakdowns of the Northern Canadian Ice Sheet (Heinrich-like events) occur during deglaciations, which could be responsible for occasionally delaying the response of $\delta^{18}O_{atm}$ to orbital forcing via changes in the water cycle (Extier et al. 2018). The variability of this delay induces a lack of confidence in the $\delta^{18}O_{atm}$–precession synchronization, associated with an uncertainty of 6000 years, which corresponds to the quarter period of a precession cycle. Further, the ice core $\delta^{18}O_{atm}$ and Chinese speleothems $\delta^{18}O_{calcite}$ signals display identical features. The two series show orbital-scale (induced by the precession forcing) and millennial-scale oscillations, both types of variations being associated with changes in the low latitude water cycle imprinted in $\delta^{18}O_{atm}$ and $\delta^{18}O_{calcite}$ (Fig. 1a).

To improve the precision of the gas chronology, it is preferable to synchronize the $\delta^{18}O_{atm}$ variations with the $\delta^{18}O_{calcite}$ record from uranium-series-dated Asian speleothems (Cheng et al. 2016). In addition, Bender (2002) and Lipenkov et al. (2011) observed that the $\delta O_2/N_2$ and total air content records simultaneously oscillate with the local summer insolation (Fig. 1b). They formulated the subsequent hypothesis: insolation modulates near-surface snow properties (grain size and shape). This imprint is preserved as snow densifies in the firn and, later, affects the ratio $\delta O_2/N_2$ and the total air content in deep ice. The total air-content variations share more similarities with Earth's axial obliquity than $\delta O_2/N_2$, hence its insolation target is integrated over an extended summer interval. Wiggle-matching between $\delta O_2/N_2$ and total air content, and their insolation targets gives dating constraints with a relative uncertainty

varying between 1000 and 7000 years (Bazin et al. 2013). The orbital dating accuracy is liable to:

1. The choice of the well-suited orbital target;

2. its synchronization with the orbital proxy, which can be ambiguous when Earth's orbit is nearly circular; and

3. the poor quality of measurements in the deepest sections of the cores (gray areas in Fig. 1).

Other tracers supplying relative dating constraints, or stratigraphic links, improve the consistency between timescales of different ice cores over the last glacial–interglacial cycle. The synchronization of globally well-mixed atmospheric-methane records from Greenland and Antarctic ice cores brings in stratigraphic links with an accuracy of 60 to 500 years (Epifanio et al. 2020). Climate independent constraints, such as large volcanic eruptions, leave singular sulfate patterns in ice cores from both hemispheres. The detection of these deposits results in highly precise (within 5 to 150 years) stratigraphic tie points between cores (Svensson et al. 2020).

Connecting ice and gas timescales
The lock-in depth, indicating the depth threshold where the air is trapped in enclosed bubbles and no longer diffuses (Fig. 2), determines the age difference between the ice and gas phases at each depth. Through the diffusion column (the interval between the surface and the lock-in depth), the preferential downward diffusion of heavy isotopes increases the $\delta^{15}N$ fraction of N_2. Measurements of $\delta^{15}N$ in air trapped in ice cores yields a first estimate of the diffusion column thickness, and, therefore, of the lock-in depth. This depth can also be calculated with firn densification modeling (Bréant et al. 2017).

Bayesian dating tools
To build consistent ice-core chronologies combining independent synchronization, absolute and relative dating constraints, as well as glaciological modeling, Bayesian dating tools have been developed. Now, they have gained improved mathematical, numerical,

and programming capacities (Parrenin et al. 2021). Prior estimates of gas and ice timescales built by glaciological models are statistically adjusted by the Bayesian tools to comply with the dating constraints. These probabilistic tools use an inverse method, integrating all dating information and associated relative uncertainty, to produce a coherent timescale for distinct ice cores.

Perspectives
Deep ice-core chronologies strongly rely on gas measurements. To improve the chronological precision, it is crucial to collect highly resolved data from ice samples stored at cold temperatures (-50°C) to avoid gas diffusion and loss of signal for $\delta^{18}O_{atm}$ and $\delta O_2/N_2$. The dating accuracy is soon to be challenged by the upcoming Beyond EPICA ice core, expected to provide much more paleoclimatic information within a shallower depth range than present ice-core drillings (1.5 Myr BP zipped in ~2750 m, Fig. 2) (Fischer et al. 2013).

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Radiocarbon dating of alpine ice cores

Ling Fang[1,2,3], T. M. Jenk[1,2] and M. Schwikowski[1,2,4]

An accurate chronology of alpine ice cores is essential to interpret the climate-signal and atmospheric-pollution history archived in glaciers. The radiocarbon in water-insoluble organic carbon (WIOC) has emerged as a valuable tool for dating alpine ice cores.

The challenge of alpine ice-core dating

The most common ice-core dating approach is annual layer counting, which relies on seasonal variations in chemical and physical signals, such as ammonium, stable isotope ratios ($\delta^{18}O$, δ^2H) and solid electrical conductivity. However, pronounced thinning beyond a certain depth limits this approach in its application for ice cores.

To establish a complete age–depth scale down to the bedrock, simplified ice-flow models can be employed (e.g. Dansgaard and Johnsen 1969), but they are unable to resolve small-scale variations in ice flow (i.e. thinning/strain), particularly closer to the bedrock, where the often complex glacier geometries of high-mountain glaciers become increasingly important. Also, they rely on fundamental assumptions, such as constant accumulation, that likely do not reflect the actual conditions over time. Even complex 3D models cannot convincingly simulate the age of the deepest sections, if no additional age constraints are available (e.g. Licciulli et al. 2020).

Absolute time horizons can pin down the age of the ice. A valuable marker for alpine ice cores is the signal from atmospheric nuclear-weapon testing, showing up as a clear peak in 1963 CE in multiple proxies, such as tritium or cesium-137. Known volcanic eruptions, such as Katmai in 1912 CE and Tambora in 1815 CE, indicated by peaks in sulfate and conductivity, are also commonly used as time markers (Herren et al. 2013). Moreover, Saharan dust events during the 20th century (e.g. 1977, 1947 and 1901 CE) are well documented and can easily be identified in the European Alps (often visually, coinciding with peaks in calcium concentration in the ice cores). However, these events were only documented for the last two centuries, and these horizons cannot be established in deeper sections where no conventional dating techniques are applicable.

The development of radiocarbon analysis of WIOC

Radioactive nuclides entrapped in the ice offer an opportunity to obtain absolute dates. The environmental radionuclide ^{210}Pb, with a short half-life of 22.3 years, enables the dating of ice over roughly one to two centuries (Gäggeler et al. 2020). The noble gas ^{39}Ar and ^{32}Si with a half-life of 268 ± 8 years and of 144 ± 11 years, respectively, have been demonstrated as ideal dating isotopes for ice samples from the last thousand years

(Morgenstern et al. 2010; Ritterbusch et al. 2022).

The recent developments in atom-trap trace analysis (ATTA) have allowed scientists to substantially reduce the required amount of ice to 1–3 kg for ^{39}Ar dating (Ritterbusch et

al. 2022). The long-lived ^{81}Kr, with a half-life of 229,000 years, can date ice up to 1.5 million years old (Tian et al. 2019). However, due to the low abundance of ^{81}Kr, ~10 kg of Antarctic ice or 20–40 kg of ice from the Tibetan Plateau is recommended for sampling (Tian et al. 2019). Given the half-life of
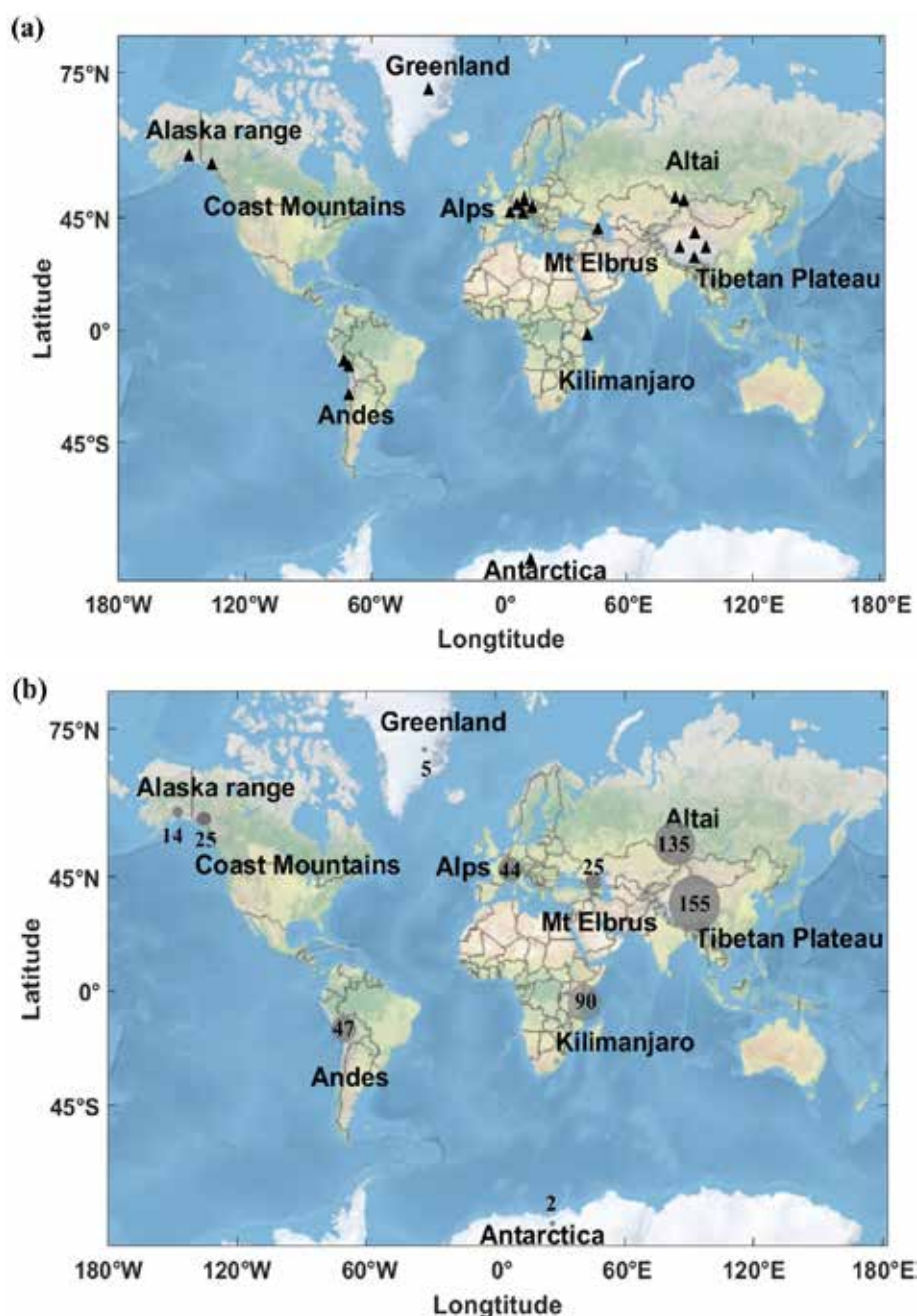
Figure 1: Map showing **(A)** the sites from which ice samples were ^{14}C dated with WIOC; and **(B)** the averaged WIOC concentrations (μg/kg) for different regions. The size of the gray circles on the map corresponds to the WIOC concentrations.

5370 years, radiocarbon (^{14}C) is considered the most suitable radionuclide for dating ice samples up to around 20,000 years old, covering most of the time range typically accessible by alpine ice cores (Uglietti et al. 2016).

Previously, ^{14}C dating of ice was only possible where sufficient organic matter such as plant, wood or insect fragments was found (Thompson et al. 1998). However, the occurrence of such findings is rare in glacier ice, and even when they are present, do not allow for continuous dating. To overcome this challenge, Jenk et al. (2009) introduced the use of water insoluble organic carbon (WIOC) for ^{14}C dating of alpine ice cores and Uglietti et al. (2016) later validated the method.

Carbonaceous particles are a major component of the atmospheric aerosol and deposit onto the glacier by precipitation. They are composed of two main bulk fractions: organic carbon (OC) and elemental carbon (EC). OC can be split into WIOC and dissolved organic carbon (DOC; see below) by solubility. WIOC and EC are separated based on their specific thermal properties (combustion temperatures). The micro-carbon ^{14}C dating method relies on the finding that WIOC originated solely from biosphere emissions prior to the use of fossil fuels (~1850 CE; Jenk et al. 2006). Once emitted, the ^{14}C decays according to its half-life time, starting the radiometric clock. A detailed method description for WIOC ^{14}C-dating can be found in Uglietti et al. (2016).

Various ice samples have been dated using micro-^{14}C WIOC since the introduction of this technique (Figs. 1–2). WIOC concentrations ranged from 2–15 µg/kg in samples from the Polar Regions to 155 µg/kg in ice from the Tibetan Plateau (Fang et al. 2021; Uglietti et al. 2016), while Alpine ice samples used for dating contained 44 ± 14 µg/kg on average (Fang et al. 2021; Uglietti et al. 2016; Fig. 1). To date, the oldest sample was determined with an age of ~22 kyr BP at the bottom of an ice core retrieved from Belukha (Russian Altai; Fig. 2). On Colle Gnifetti (CG03 core) in the European Alps, the oldest ice retrieved from the Alps was >15 kyr BP, and on Illimani in the Andes ~12.6 kyr BP (Fang et al. 2021; Jenk et al. 2009; Sigl et al. 2009; Uglietti et al. 2016; Fig. 2).

The majority of dated alpine ice cores, however, was younger than 10 kyr BP (e.g. Uglietti et al. 2016). The dating precision strongly depends on the ^{14}C content of the sample, defined by the carbon mass and the age of the sample, i.e. its ^{14}C/^{12}C ratio. The uncertainty decreases sharply with increased carbon mass due to the blank correction. Therefore, a total carbon amount of 10 µg, typically equivalent to around 300–500 g of ice, is recommended for reliable dating.

The most recent developments and outlook
In glacier ice, the higher concentration of DOC compared to WIOC (by a
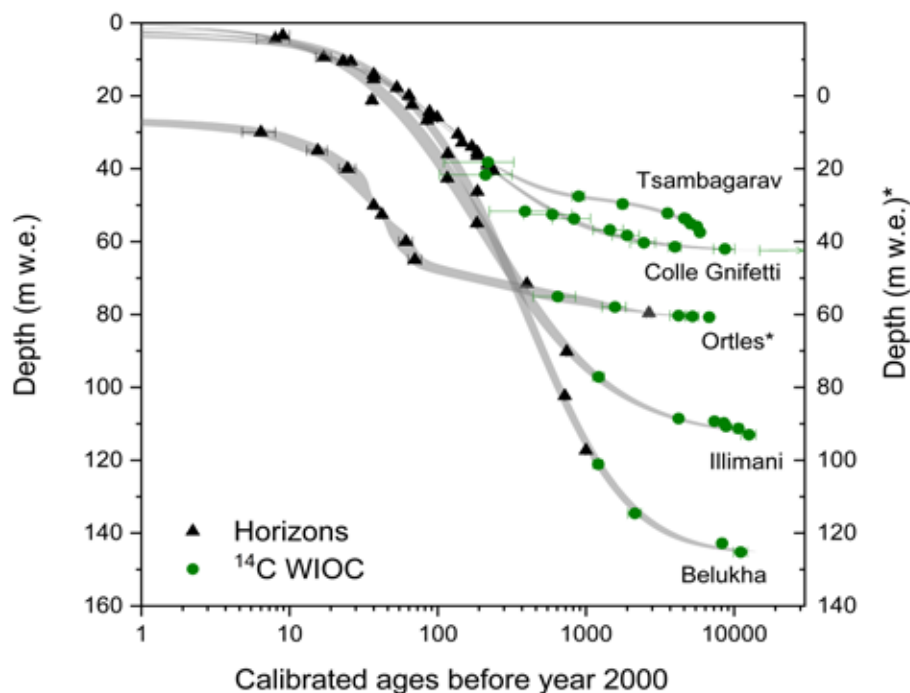
Figure 2: Ice-core chronology based on ^{14}C dating (modified from Figure 6 in Uglietti et al. 2016). Horizons and ^{14}C results are shown as black triangles and green circles, respectively. Gray shaded areas represent the 1σ range of the respective fit for retrieving a continuous age–depth relationship. To enhance visibility, the curve for the Mt Ortles glacier was shifted downward by 20 m water equivalent (m w.e.) and is referenced in the right-hand y axis, denoted with an asterisk (*).

factor ranging from 2 to 5; Fang et al. 2021) provides a motivation to investigate the possibility of using DOC for ^{14}C dating. The required mass of ice could potentially be further reduced, if WIOC and DOC were to be extracted from the same piece of ice. Two studies found that the DOC fraction can be biased in its ^{14}C/^{12}C ratio due to in situ ^{14}C production by cosmogenic radiation (Fang et al. 2021; May 2009). This limits the theoretically achievable gain in dating precision given by the higher carbon mass.

Nevertheless, Fang et al. (2021) showed the great potential of the DOC fraction to date ice from sites where in situ ^{14}C production is relatively low. This is the case for sites at altitudes of 4000–5000 masl and below (low radiation), and/or characterized by snow accumulation rates greater than 0.5–1 m water equivalent (less exposure) such as in the European Alps. Method details can be found in Fang et al. (2019), also describing the most recent setup allowing simultaneous extraction of DOC and WIOC samples for ^{14}C dating of ice, which was built at the Laboratory for Environmental Chemistry (PSI, Switzerland).

In conclusion, due to lower demands of ice mass and the time coverage of the lowest and oldest ice-core sections, ^{14}C analysis has become a crucial and widely applied tool for the dating of ice cores from mountain glaciers. Although the possibility of using the DOC fraction for ice-core dating has been demonstrated, further studies are needed to explore the full dating potential in terms of ice requirement and analytical precision, and accuracy for using both OC fractions, extracted from the same sample.

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Cosmogenic nuclide moraine chronologies from Patagonia: A globally synchronic response of mountain glaciers during Termination 1?

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Surface-exposure dating of moraines reveals that Patagonian glaciers fluctuated at the pulsebeat mimicked in polar ice cores from both hemispheres. These findings favor hypotheses that invoke coupled oceanic–atmospheric drivers to generate and propagate millennial-scale climate shifts during Termination 1.

Moraines as past climate archives

Mountain glaciers are very sensitive to climate oscillations, especially to atmospheric temperature and precipitation. When climate conditions favor glacier growth, ice mobilizes massive quantities of sediments, including large erratic boulders, which are piled up alongside the ice margins, forming sharp and elongated hilly landforms, called moraines. We assume they form mostly when glaciers are in close equilibrium with the local prevailing climate, culminating at the transition between cold and warm periods. Therefore, well-preserved sequences of moraines are valuable archives of the timing of terrestrial paleoclimate.

Cosmogenic nuclides (or isotopes) are mostly generated by the interaction between cosmic radiation and target minerals within rock surfaces exposed to the atmosphere. Given that these nuclides are naturally near-absent in most lithologies, their concentration will start building up when the rock begins to intercept cosmic radiation products. So, if the production rate of these nuclides is known, we can measure them and then calculate the "exposure age" (Schaefer et al. 2022). Continual refinement of surface-exposure dating based on in situ terrestrial cosmogenic nuclides, particularly ^{10}Be in moraine boulders, has allowed us to assign precise ages to former glacial oscillations and, therefore, to constrain the chronology of past climate variability.

The conceptual interpretation of ^{10}Be glacier chronologies (Fig. 1a) assumes that boulders in resting position at the highest part of the moraine ridges represent the cessation of its construction, so the surface exposure age of these boulders will pinpoint the onset of glacier recession (Fig. 1b). We prefer to sample tall and large boulders well embedded in the top of the moraine to prevent potential post-depositional displacements and/or exhumation that could provide anomalously young ages. We also aim to collect samples from glacially polished surfaces to try reducing inherited cosmogenic nuclides generated during prior exposure episodes, which could yield anomalously old ages (Fig. 1c). This sample approach permits us to diminish geological uncertainties affecting surface-cosmogenic-nuclide concentrations and,

thus, to obtain accurate ages for culminations of glacier pulses.

Patagonia: the southernmost mid-latitude continental landmass in the world

Patagonia, including Tierra del Fuego, spans between ~40° and ~56°S in South America, comprising both Chilean and Argentine territory (Fig. 2a). It is the only continental landmass that covers the entire latitudinal range of the Southern westerly winds (SWW), whose interaction with the Southern Ocean play a key role in global climate. Seasonal temperatures and precipitation in Patagonia are strongly correlated with low-level zonal winds indicating that regional climate is mostly driven by the migrating locus of this hemispheric wind belt. Additionally, the Austral Andes generates a strong orographic effect that promotes

a sharp transition between a western hyper-humid to an eastern semi-arid flank (Garreaud et al. 2013). Regional climate permits the existence of numerous mountain glaciers, including the Patagonian icefields, which constitute the most extensive ice masses of the Southern Hemisphere, outside Antarctica.

During the last glaciation, western Patagonia was covered by an ice sheet, which featured numerous outlet glacier lobes flowing towards both flanks of the Andes (Davies et al. 2020). These large glaciers formed a wide variety of ice-marginal landforms, including outstanding sets of moraines. This glacially shaped landscape has enabled Patagonia to play a major role in moraine-based paleoclimate reconstructions in the Southern Hemisphere.

Figure 1: Rationale behind surface-exposure dating of moraines considering **(A)** glacial; and **(B)** post-glacial stages. Red lines on the clocks in panel (B) depict the exposure time, while the size of the molecule scheme represents the concentration of cosmogenic nuclide. **(C)** Example of a moraine erratic boulder sampled for ^{10}Be dating. Photo credit: Gonzalo Amigo.
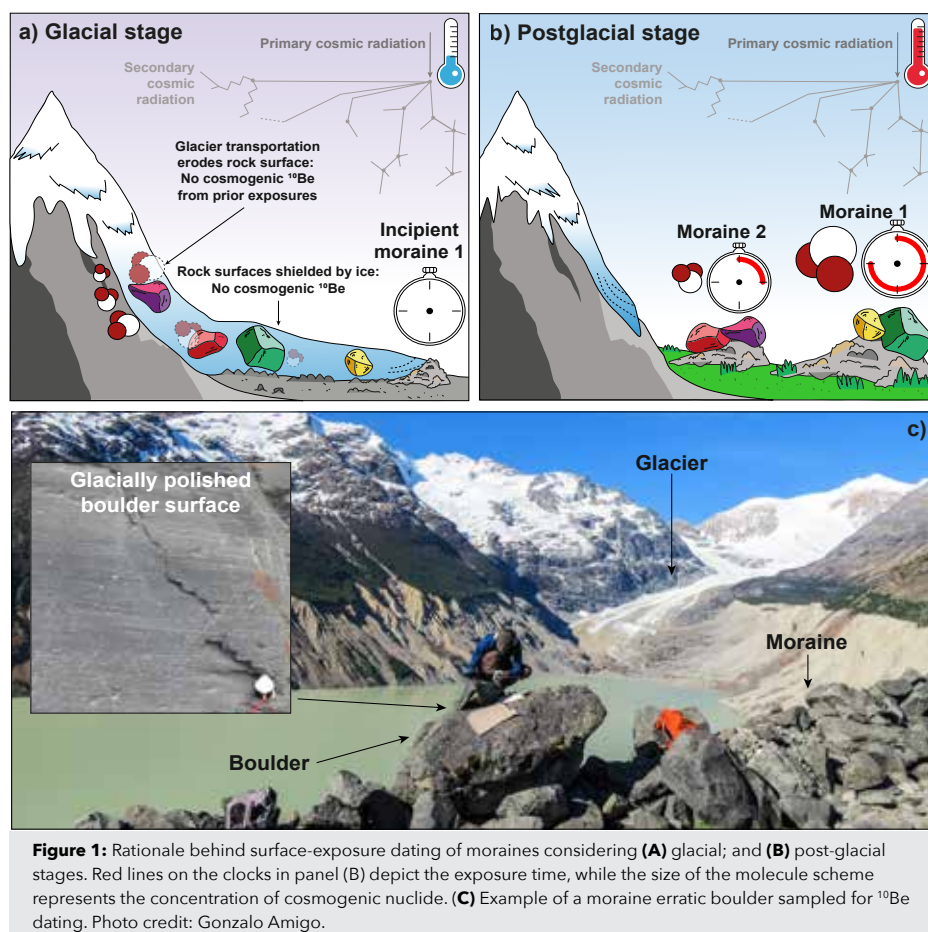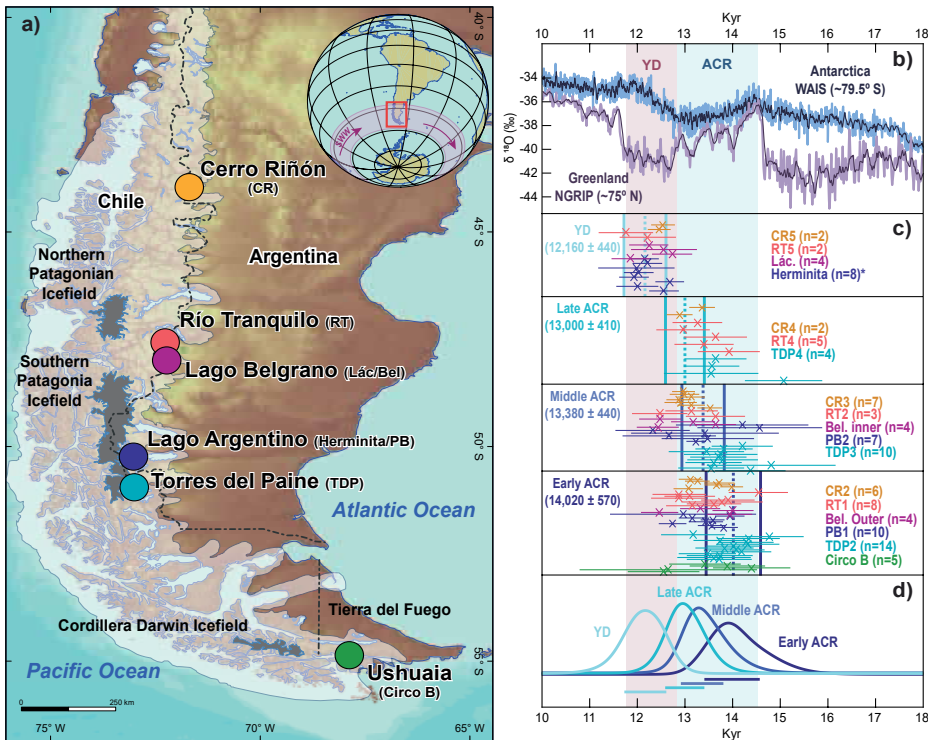
Figure 2: Selected glacial chronologies around Patagonia. **(A)** Circles show sites with name and label. White and gray shaded areas outline the former Patagonian Ice Sheet and the present-day icefields, respectively. **(B)** δ18O records from WAIS Divide (blue line) and NGRIP (purple line) ice cores. **(C)** Individual recalculated 10Be ages (Kaplan et al. 2011) per moraine by label and numeric morphostratigraphic order. *In Lago Argentino, although used to establish the Patagonian 10Be production rate, Herminita moraines 10Be concentrations are also consistent with glacier activity during the YD. **(D)** Bayesian relative probability plots of the selected Patagonian 10Be moraine chronologies.

Moraine-based T1 paleoclimate reconstructions in Patagonia

The end of the last glaciation, known as Termination 1 (T1), comprises a sequence of millennial-scale climate shifts that ultimately led global climate from cold-glacial to warm-interglacial conditions, between ~18 and ~11.7 kyr. δ18O from polar ice cores (Fig. 2b) exhibit a stepwise net warming trend interrupted by cold snaps between ~14.5–12.8 kyr in Antarctica, the so-called Antarctic Cold Reversal (ACR), and between ~12.7–11.7 kyr in Greenland, known as the Younger Dryas (YD). Millennial-scale climate shifts during T1 have been inferred as occurring synchronously, but in an out-of-phase style between hemispheres, which led to a proposed "thermal bipolar seesaw" as the potential mechanism responsible for this climate mode (Pedro et al. 2018). Therefore, deciphering the timing and geographical extent of both the ACR and the YD at planetary scale is imperative to properly test the influence of this hypothetical mechanism on global climate. To solve this fundamental paleoclimate conundrum, surface exposure chronologies of mountain glaciers offer crucial insights, including those from Patagonia.

Following pioneering cosmogenic dating of T1 moraines in Patagonia, recent highly resolved 10Be glacial chronologies are yielding unequivocal evidence of glacier pulses during the ACR and the YD from north to south. At Cerro Riñón valley in Lago Palena/General Vintter (44°S), Soteres et al. (2022) found moraine crests constructed between ~13.5–13.1 kyr and at ~12.4 kyr. In central Patagonia, Sagredo et al. (2018) documented moraine ridges formed between ~13.7–13.4 kyr and at

~12.0 kyr in the Río Tranquilo valleys around Cerro Cochrane/San Lorenzo (47.5°S). Furthermore, recent modeling analysis conducted by Muir et al. (2023) indicate that glaciers in Cerro Riñón and Río Tranquilo fluctuated in unison to a ~3°C cooling coeval with the ACR, followed by a ~0.5°C temperature increase coinciding with the YD. They concluded that glaciers in the northern half of Patagonia responded simultaneously to deglacial climate forcings. Nearby, in Lago Belgrano (47.8°S), Mendelová et al. (2020) reported moraines built between ~13.2–13.0 kyr and at ~12.4 kyr. In southern Patagonia, Ackert et al. (2008) and Kaplan et al. (2011) analyzed 10Be concentrations in moraine boulders while Strelin et al. (2011) used radiocarbon to date moraines at Lago Argentino (50°S), both constraining glacier advances culminating between ~13.2–13.0 kyr and at ~12.2 kyr. In the latter location, a Patagonian production rate for 10Be on rocks was also established, with implications for the accuracy of all Patagonian 10Be surface exposure ages. Further south, García et al. (2012) and Menounos et al. (2013) discussed moraines with ACR cosmogenic ages ranging between ~14.1–13.8 kyr in Torres del Paine (51°S) and ~13.4 kyr in Ushuaia (54°S), respectively (Fig. 2c).

Altogether, Bayesian 10Be ages probability correction of the Patagonian moraines reveal ubiquitous glacial advances/standstills in close morphostratigraphic order at least at ~14.0, ~13.4 kyr and ~13.0 kyr during the ACR, followed by pervasive ice retreat interrupted by a minor glacier pulse at ~12.2 kyr during YD times, spanning ~10° of austral latitude (Fig. 2d). Overall, these moraine

chronologies show an emerging scheme that mimics millennial-scale climate shifts detected in both Antarctic and Greenland ice cores during T1 (Fig. 2b). This is supported by similar mountain glacier records obtained in the Northern Hemisphere (e.g. Bromley et al. 2023), challenging the widely accepted interhemispheric "thermal bipolar seesaw" mechanism. Denton et al. (2022) offered an alternative hypothesis that reconciles the apparent global synchronicity in mountain glacier fluctuations by invoking extreme seasonality episodes in the North Atlantic. Accordingly, the isotope signature in Greenland ice cores might be reflecting regional hyper-cold winters rather than a hemispheric climate signal, particularly during the YD. Their hypothesis, dubbed Heinrich Summers, implies that the Antarctic-like fashion of millennial-scale climate oscillations would have prevailed in both hemispheres during T1. If correct, this would favor the SWW-Southern Ocean coupled system as the main driver to generate and globally propagate climate signatures at millennial timescales during the end of the last glaciation.

Since early naturalists began to investigate glaciations in South America over a century ago, Patagonia has united several generations of scientists from all around the planet to establish the region as a key site for past glacier and paleoclimate studies. However, further research is needed to better understand the present-to-future evolution of global cryosphere and climate.

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Searching for the secrets of tipping points in Greenland ice cores

John Slattery[1,2] and Louise C. Sime[1]

Greenland ice cores provide high-resolution records of Dansgaard–Oeschger events – abrupt climate transitions, which happened repeatedly during the last glacial. These records can allow us to understand past climate tipping behaviour and to predict possible future tipping points.

Climate tipping points

The ability for society to reliably forecast future anthropogenic climate change is challenged by the likely presence of climate tipping points. These are hypothesized thresholds of global warming at which certain subsystems within the Earth's climate, known as tipping elements, may undergo sudden and irreversible change in a process called a critical transition. Potential tipping elements that have been identified include the West Antarctic Ice Sheet, the Amazon Rainforest, and the Atlantic Meridional Overturning Circulation (AMOC) (Armstrong McKay et al. 2022, Wunderling et al. 2021). Were any of these elements to tip in future, it would lead to dramatic regional or global climate change, making this an extremely policy-relevant concern (Armstrong McKay et al. 2022). Furthermore, interactions between tipping elements raise the possibility of a disastrous cascade, with a domino-like effect allowing one abrupt change to lead to several more (Wunderling et al. 2021). Thus, quantifying the likelihood of passing a tipping point in the future has become a major focus of climate research.

Dansgaard–Oeschger Events

Dansgaard–Oeschger, or DO, warming events are a series of abrupt transitions in the climate between colder Greenland stadials and warmer Greenland interstadials that occurred repeatedly during the last glacial. These events were first observed in stable water-isotope records from Greenland ice cores, as shown in Figure 1. These stable isotope records show abrupt changes that suggest warming of up to 15°C in just a few decades (Kindler et al. 2014). This extreme rate of warming makes DO events the fastest instances of regional temperature change seen in the paleoclimate record, and so they are seen as the epitome of abrupt climate transitions. As well as the rapid warming inferred by stable water isotopes, Greenland ice cores show transitions in the annual layer thickness, as well as the concentrations of sea salt and mineral aerosols (Capron et al. 2021), respectively suggesting abrupt changes in precipitation, sea-ice extent, and atmospheric circulation in the North Atlantic region. Therefore, these ice cores contain a wealth of information about the climate changes that occur during DO events.

Beyond pure scientific curiosity, there are very practical and pressing reasons to be interested in DO events. There is compelling evidence that DO events are themselves the consequences of a tipping point being crossed (Boers 2018), in this case not because of human actions, but instead due to gradual internal changes within the climate system. A consensus has developed that at the heart of DO events lie transitions between strong and weak states of the AMOC (Li and Born 2019; Malmierca-Vallet et al. 2023; Vettoretti et al. 2022), a crucial system of ocean currents that transports large amounts of heat towards higher latitudes in the Northern Hemisphere and is possibly approaching a tipping point (Armstrong McKay et al. 2022). This hypothesized tipping point would be driven by different mechanisms to those involved in DO events, thus we cannot draw direct comparisons. Nevertheless, this possibility means that it is imperative that we develop a deeper understanding of past tipping behavior, as seen in DO events, such that we stand the best possible chance of understanding potential future critical transitions.

Greenland is, undoubtedly, where the best records of DO events are found, but their signatures can be seen further afield too. Approximately simultaneous with the local changes in surface temperature, precipitation, and sea-ice extent recorded in Greenland ice cores, speleothem records from East Asia and Atlantic marine-sediment cores show abrupt transitions in the large-scale atmospheric (Wang et al. 2008) and oceanic (Lynch-Stieglitz 2017) circulations. These changes are all intertwined due to a complex set of feedbacks between the three key components of ocean, atmosphere, and sea ice (Li and Born 2019; Malmierca-Vallet et al. 2023). The picture that emerges is a cascade of transitions, with an initial transition in one climate element leading to a transition in the next, and so on. What remains very unclear is the order of this cascade. Particularly important is the question
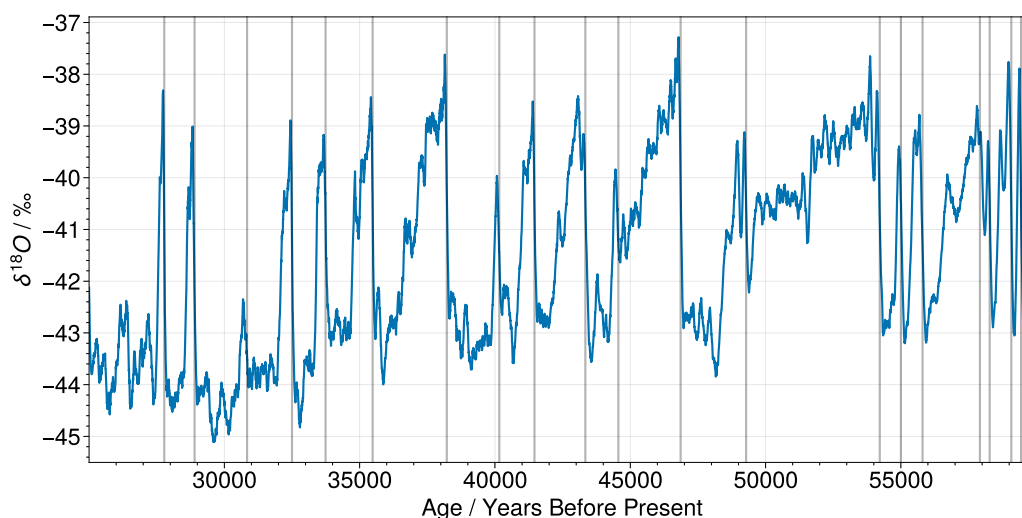
Figure 1: The famous Greenland δ18O record, in this case from the NGRIP ice core (Andersen et al. 2004). Less negative values of δ18O qualitatively correspond to higher temperatures. A 100-year smoothing has been applied. DO warming events are shown by gray vertical lines.
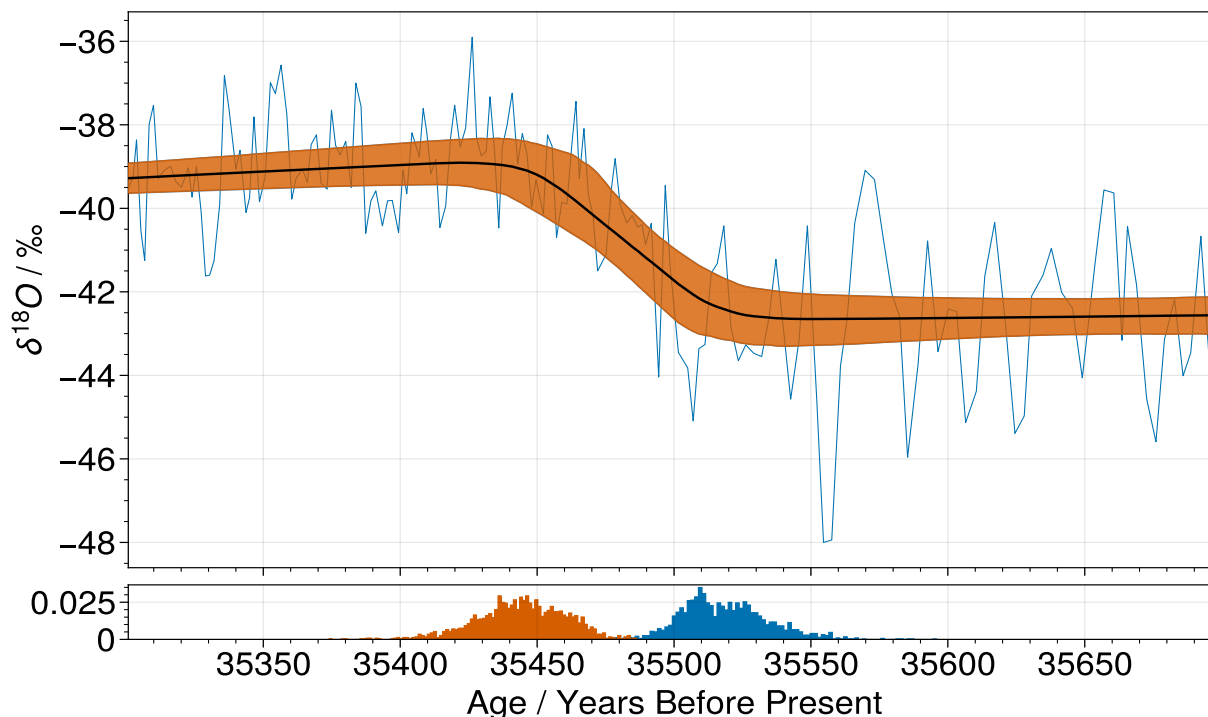
Figure 2: An example application of the Bayesian method to characterize a DO transition. The blue line shows the raw measurements of δ18O from the NGRIP ice core (Andersen et al. 2004). The black line shows the median fit, with the 90% uncertain range shaded in orange. The blue and orange histograms are, respectively, the probability distributions for the start and end of the transition.

of which element begins this cascade. Based on our current knowledge, we cannot rule out any of the three key climate components previously mentioned, or even narrow down the location. Every imaginable answer to this question has been suggested, with different researchers often arriving at different conclusions using simulations from the exact same model (Kleppin et al. 2015; Vettoretti et al. 2022)! At the same time, locating the start of this chain of causality is needed before we can be certain of the mechanism responsible for triggering DO events – which is ultimately the aim of this field of research.

Systematic timing differences
It is clear that a new approach is needed to better understand the cascade of transitions that occurs during a DO warming event. One option is to search for systematic timing differences between the different climate elements which show rapid change; a line of research for which Greenland ice cores are uniquely suited. A single ice core can provide independent measurements of multiple species associated with different components of the climate system at sub-decadal time resolution within a single archive, getting around the problem of dating uncertainties, which makes timing comparisons between different paleoclimate archives so difficult (Capron et al. 2021). The measurements that have been used to investigate the temporal phasing of DO events are the mineral-dust aerosol (Ca^{2+}) and sea-salt aerosol (Na^+) content from both the North Greenland Ice Core Project (NGRIP) and North Greenland Eemian (NEEM) ice cores, as well as the annual layer thickness (λ) and the water-isotope ratio (δ18O). These four measurements are respectively interpreted as reflecting the Northern Hemisphere atmospheric circulation, North Atlantic sea-ice extent, local precipitation rates, and surface-air temperature at the

ice-core site (Erhardt et al. 2019). This gives potentially independent data on four climate elements. It is important to note, however, that individual measurements are not always uniquely associated with a single climate element. For example, the δ18O of Greenland ice cores is both reflective of sea-ice change around Greenland, and temperature change at the ice-core site (Sime et al. 2019). For these reasons, whilst ice cores are fantastic archives of DO events, care is required when using these measurements to draw conclusions about the timing of changes across different elements.

Even with the excellent precision that ice-core measurements afford, pinpointing the timing of a tipping point in a noisy climate record is statistically challenging. The acceptance of this uncertainty, and resultant use of Bayesian inference to produce probabilistic distributions for the start and end times of DO warming events, has been a major step forward (Capron et al. 2021). An example of the application of this type of approach to a DO event in the NGRIP δ18O record is shown in Figure 2. Stacking all the DO events covered by the ice cores, we can then assess the mean differences in timing between the transitions in different core measurements. The first pioneering study to utilize this method indicated that the transitions in Ca^{2+} and λ systematically led those in Na^+ and δ18O (Erhardt et al. 2019), suggesting that atmospheric changes were in fact the first element of the DO warming event cascade, and apparently representing a breakthrough in our understanding.

Subsequent work showed that attempting to estimate the population mean time difference from a relatively small sample of DO events, of which each is itself uncertain, meant that the two-fold uncertainty inherent to this method had been underestimated.

Rigorously propagating this uncertainty revealed that the previously reported systematic timing differences were not statistically robust (Riechers and Boers 2021). Thus, the current picture is that the variation between individual DO events is too great, and the rapidity of the element cascade too rapid, for any certainty regarding the sequence of changes to be possible using the measurements currently available from ice cores (Capron et al. 2021). In future, new ice cores, higher resolution measurements, or improved analytical techniques may allow us to make further progress on this crucial problem. But for now, despite giving us tantalizing teases, the ice cores withhold their secrets.

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Marine Arctic Diatoms working group

Tiia Luostarinen[1], M. Oksman[2], A. Limoges[3], B. Caissie[4,5], C. Pearce[6] and K. Weckström[1,2]

Marine diatoms (*Bacillariophyceae*) are the most important primary producers in the world's oceans and are highly sensitive to changes in their environment (e.g. sea-surface temperature, salinity, and sea ice). Additionally, diatoms have a high species diversity, a well-known morphological classification, and their fossilized valves, which are made of silica, generally preserve well in sediments.

Due to these features, diatoms have been widely used as a paleoceanographic proxy for reconstructing past sea-surface conditions (Koç Karpuz and Schrader 1990). Diatoms have been used for both qualitative and quantitative reconstructions, which are often based on surface-sediment datasets. These datasets include information on diatom assemblages, as well as data on ocean-surface conditions (e.g. temperature and salinity) at each sampling site.

Multiple diatom surface-sediment datasets have been created for the Arctic region (e.g. Caissie 2012; Krawczyk et al. 2017; Miettinen et al. 2015; Ren et al. 2014; Sha et al. 2014). However, these datasets have been built using slightly different methodologies and diatom taxonomies. This can have an influence on the final reconstruction, depending on which dataset is used. Additionally, training sets are a valuable tool for understanding the autoecology of individual species (Oksman et al. 2019), which is essential for the robustness of both quantitative and qualitative reconstructions.

The Marine Arctic Diatoms (MARDI) working group (WG) aims to bring together diatomists working with paleoceanographic reconstructions, to align diatom taxonomy across different Arctic diatom datasets, and to unify the used methodologies in diatom-sample preparation.

Scientific goals and objectives
MARDI aims to improve the precision and re-liability of diatom-based paleoceanographic reconstructions in the Arctic and sub-Arctic areas. The WG launched in November 2022 and during its first months gathered 11 diatom surface-sediment datasets from (sub) Arctic regions, including over 1300 surface-sediment samples (Fig. 1).

The MARDI WG will align and harmonize diatom taxonomies in the datasets and integrate them into an open-access pan-Arctic database. MARDI aims to advance the use of quantitative diatom transfer functions, as well as develop new semi-quantitative approaches. Furthermore, the WG aims to bring together Arctic marine diatomists to agree on community-wide protocols for the preparation of diatom samples.

Harmonization of Arctic diatom taxonomy was initiated during the second MARDI workshop: "Harmonisation of (sub)Arctic diatom taxonomy" (p. 126) held from 6–8 June in Helsinki, Finland. The workshop brought 17 participants from 10 countries together to discuss issues in Arctic diatom taxonomy and methodology.

Upcoming activities
The next MARDI activities will include a series of mini-workshops focusing on the challenging diatom taxa identified during the taxonomic workshop. These one-day workshops will be organized in the upcoming months and will be held online, where each workshop will have a focus on one species.

The next in-person workshop will be held in June 2024 in Aarhus, Denmark. This workshop will focus on the statistical relationship between species and environmental variables, and on improving the robustness of quantitative reconstructions. Finally, a summer school has been planned for June 2025 in the USA (Iowa Lakeside Laboratory) and will be specifically targeted to early-career researchers.

Visit the MARDI website at pastglobal-changes.org/mardi and sign up to our mailing list to receive news and updates on our activities.

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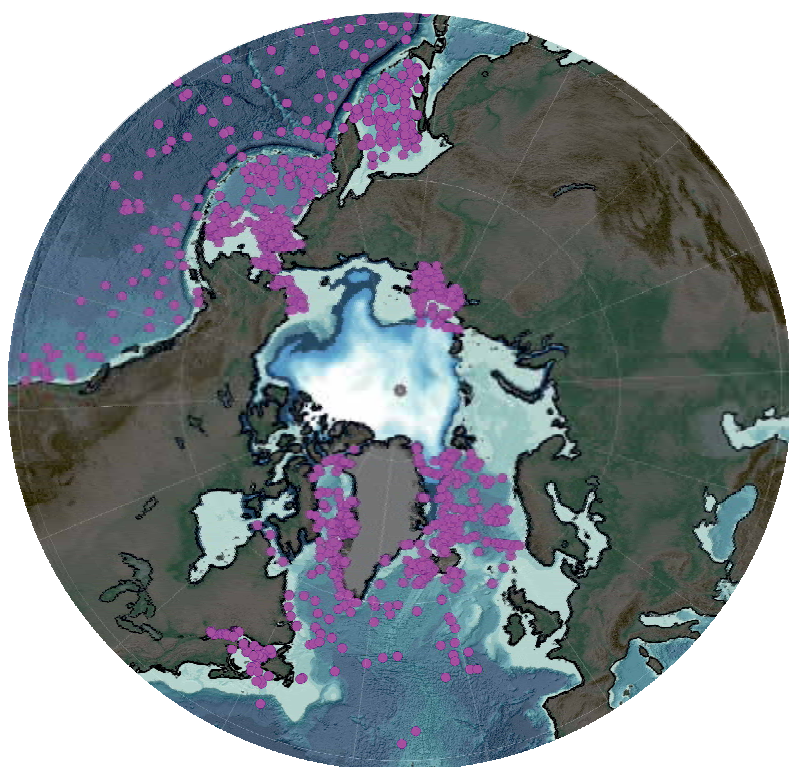
Figure 1: Map of the location of the surface-sediment samples with diatom floral data (purple dots) in the Arctic region (n>1300).

African Tree Ring Network for Resilience: Revealing climate change patterns and their impacts across wider spatial-temporal scales

Aster Gebrekirstos[1], H.G. Gracias[2], J. Ngoma[3], M. Mokria[4], L.H. Balima[5], S. Kapoury[6], A.O. Patrick[7] and E.A. Boakye[8]

Tree-ring-based proxies have been widely used in ecology and climate change studies for centuries (Fritts 1976), particularly in temperate regions. As trees grow, changes in environmental factors are recorded in the wood produced during specific time periods. Consequently, trees are key terrestrial archives, providing reliable insights into past climate and environmental variability on a year-by-year basis at local to regional scales, given that they can form annual rings and grow for hundreds of years (Fig. 1).

Tree rings enable the use of precise dating methods, and provide high-resolution paleoenvironmental information through different proxies. With the development in technology, tree rings are also important indicators of plant physiological responses to changing climatic conditions and for further understanding of long-term ecological and hydroclimatic processes. Given the versatility of dendrochronology, and the diversity of environmental questions that can be addressed, the field continues to grow with new frontiers and advances in technology. Methods that are applied to decode minutes, decades to multi-centuries of information include tree-ring analysis, wood anatomy, stable isotopes and dendrometers. The results provide insight into current and past climate and environmental variability at seasonal and annual resolution, and from local to regional scales. Tree-based information, therefore, elucidates climate change impacts on tree growth and provides evidence and data to help understand long-term climate and ecological processes (Gebrekirstos et al. 2014)

Scientific goals and objectives

Many livelihoods, economic activities and energy sources in Sub-Saharan Africa (SSA) are largely dependent on climate-sensitive natural resources. The climate crisis is increasing the frequency and intensity of floods, droughts, and heatwaves, with Africa expected to be among the global regions hit hardest (Tzachor et al. 2023). As climate impacts continue to negatively affect the population, economy and ecosystems in Africa, there is a need to increase scientific and research capacity and facilities on the continent. Establishing the African Tree Ring Network (ATRN) working group (WG) (pastglobalchanges.org/ATRN) is, therefore, an opportunity to advance the use of tree rings in the tropics, particularly in Africa in the fields of, for instance, paleoecology/hydroclimatology, forestry/agroforestry, biodiversity, ecophysiology, and restoration ecology, as a new frontier.

In recent years, dendrochronology in Africa has experienced a rapid expansion and is beginning to fill important gaps in existing tree-ring based data that is dominated almost exclusively by temperate regions (Gebrekirstos et al. 2014; Zuidema et al. 2022). For instance, based on tree-ring widths in *Juniperus procera* in Ethiopia, Mokria et al. (2017) reconstructed hydroclimate variability over the past 350 years. Gebrekirstos et al. (2009) also characterized co-occurring savanna species into opportunist and resilient species based on their response to rainfall variability.

A combination of tree-ring width and stable isotopes are also used to address questions related to water-resource management, agroforestry and climate-forest management feedbacks. For example, these techniques have been used to reconstruct changes in surface hydrology (Mokria et al. 2018), to determine which species is more productive, resilient and drought tolerant (Gebrekirstos et al. 2009), which species sequester more carbon (Sanogo et al. 2016), and to better quantify the carbon sequestration by tropical trees and forests (Zuidema et al. 2022). Yet this science is the least developed on the globe.

The main scientific objective of this WG is, therefore, to bring together African tree ring scientists and take stock of the development in terms of science, methods, data, human capacity, and facility on the continent. We will analyze the challenges and opportunities to advance tree-ring-based science in different environments and climate zones across the continent. We will provide improved methods, approaches, and best practices to enable cross-regional data analysis and synthesis to support informed decision-making on pressing environmental questions and climate issues, considering the diverse effects on African ecosystems.

We will organize meetings and workshops, field training, and citizen science initiatives to increase awareness in collaboration with international and regional partners, policy makers, and donors. We will also create a link between the tree ring, modeling, and multi-proxy communities to develop a vibrant network and advance scientific capacity in the continent, and beyond.

Upcoming activities

Visit the ATRN website at pastglobalchanges.org/ATRN and sign up to the mailing list for all information, news and activities. Send us an email to become a member of the ATRN working group.

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Figure 1: Baobab tree from Western Tigray (Ethiopia) that can grow for hundreds of years. Photo credit: Aster Gebrekirstos.

The combined use of paleoenvironmental reconstructions and glaciological modeling for assessing the effect of climatic variability on Andean cryospheric environments

Cinthya Bello[1,2,3], L. Perez[4], C. Torres[5], J. Arigony-Neto[5] and F. García-Rodriguez[4,5]

Dr. Cinthya Bello, from Perú, visited Centro Universitario Regional Este (CURE) - Universidad de la República de Uruguay as a PAGES-IAI (Inter-American Institute for Global Change Research) Mobility Research Fellow. From 12 March to 8 April 2023, she strengthened her knowledge in the application of paleoenvironmental science as a complementary tool to ongoing glaciological modeling for the reconstruction of past glacial environments.

An overview: periglacial system in the Peruvian Andes

The tropical Andes have been negatively impacted by hydroclimatic and socioeconomic changes in the context of global change (Drenkhan et al. 2018). In the Peruvian Andes, glaciers show significant ice loss equivalent to 1284.95 km² (53.56%) between 1955 and 1962, and during 2016 (INAIGEM 2018). In addition, recent studies confirmed the development of several high mountain lakes, as a result of glacier shrinkage (Colonia et al. 2017), which increase the glacial-lake outburst flood hazards (GLOFs). Despite the effort to develop an inventory and projection of future lake formation in the Peruvian mountain ranges, there is a lack of knowledge regarding the evolution of these periglacial systems. It is necessary to comprehensively assess their past, present, and future development under climate change scenarios to ensure sustainable water use. Therefore, paleolimnology represents a useful tool for studying periglacial systems because this interdisciplinary science uses chemical, physical, and biological information from the sedimentary record to reconstruct the environmental evolution of these systems on a millennial, secular, decadal, and interannual timescale (García-Rodriguez et al. 2009).

Thanks to the support of the PAGES-IAI Fellowship, I participated in a series of lectures dedicated to an overview of the different techniques used in paleolimnology in order to: 1) reconstruct the evolution of glacier lake systems; 2) analyze sediment cores with a multi-proxy approach for environmental reconstructions (e.g. lithology, geochemistry, dating); 3) use software for data handling, importing data and visualization (e.g. PAST, BACON); and 4) learn new approaches for the historical reconstruction of paleoenvironments (e.g. faunal remains).

In addition, the article written by Stuart-Smith et al. (2021) was discussed. This study describes a rapid expansion of the Lake Palcacocha (Fig. 1a) since the pre-industrial era, located in the city of Huaraz (department of Ancash, Perú), due to the retreat of the Palcaraju Glacier driven by the anthropogenic increase of temperature by 1°C since 1880 CE. However, Lüning et al. (2019, 2022) has also demonstrated that Andean glaciers retreated significantly during the Medieval Climate Anomaly (1000–1200 CE), a warm climate period in South America, and questioned the conclusions by Stuart-Smith et al. (2021). This disagreement reveals a clear lack of a coherent network of paleoenvironmental data that represents a weakness in paleoenvironmental research (Fig. 1b).

Therefore, as part of this fellowship, a multidisciplinary group comprising researchers from Uruguay, Brasil and Perú prepared a research proposal with the aim of undertaking a paleolimnological study in the periglacial Lake Palcacocha in order to reconstruct the environmental variability over the last 2000 years. In addition, the proposal aims to improve the projections of climate models, and reconstruct the mass balance of Peruvian glaciers by using artificial intelligence algorithms and data from global climate models and reanalysis, such as CMIP6 and ERA5, respectively. Furthermore, our collaborative project will strengthen the academic relationship between Peruvian, Brazilian and Uruguayan research universities, promoting studies about paleoenvironmental reconstruction using paleolimnological methods to improve ecosystem management and conservation plans.

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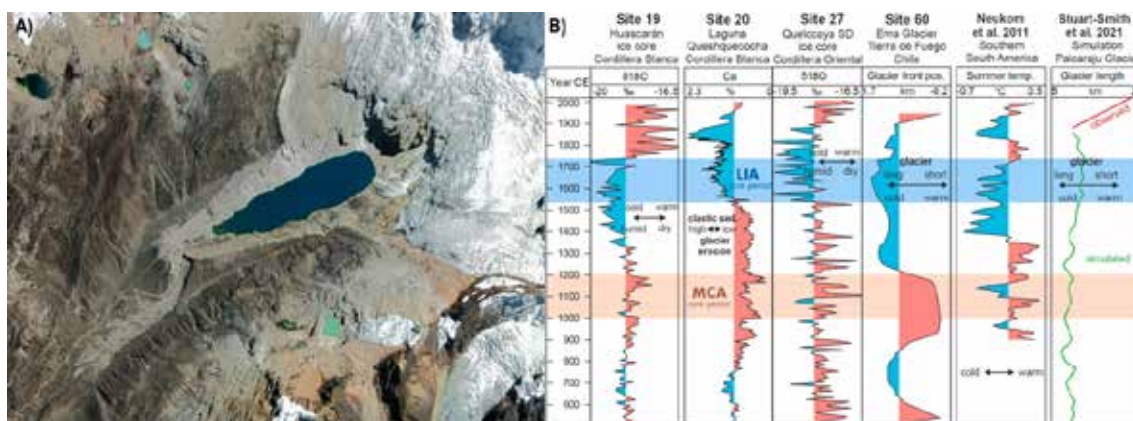
Figure 1: (A) Lake Palcacocha. **(B)** Temperature and glacier development in South America during the past 1500 years based on palaeoclimate proxies (site number listed on top; adapted from Lüning et al. (2022).

Archaeological evidence of continuous occupation of the Southwest Maputo Province, Mozambique

Décio Muianga[1,2,3]

Décio Muianga, an archaeologist from Mozambique, visited the University of Mpumalanga in Mbombela, South Africa, as a PAGES Inter Africa Mobility (IAM) Research Fellow. From 1 March to 3 April 2023, he analyzed lithic stone tools recovered from the excavation at Daimane site in southern Mozambique and compared these with stone tool collections from Mpumalanga province to better understand the technocomplexes, and dietary and subsistence changes that occurred during the Middle- and Late Stone Age.

Stone Age archaeological background in Mozambique

Mozambique is located in southeastern Africa and lies between two geographical areas, southern and eastern Africa, where the major developments of human evolution occurred during the Pleistocene and Holocene (Lombard et al. 2012; Mitchell 2012). Evidence of these cultural changes can be found at different sites throughout the country, particularly in southern Mozambique, which is rich in locations with lithics and ceramic remains (Kohtamäki and Badenhorst 2017; Menezes 1999; Muianga 2020; Saetersdal 2004). However, detailed and systematic studies of sequences with well-preserved deposits have not yet been performed. Thus, the Daimane site (Kohtamäki 2014) is a large and intact archaeological sequence that has not been systematically investigated and compared with many open-air sites from diverse chronological periods scattered across the landscape.

Aims of the project

The main objective of the lithic analysis at the University of Mpumalanga was to decipher the rich archaeological record of stone tools and artifacts, contributing to a deeper understanding of human prehistory in the region, and its relevance to the broader narrative of human evolution. The specific research questions whilst at the University of Mpumalanga were:

- What are the key lithic industries and typologies associated with the Middle Stone Age and Late Stone Age in the Lower Lebombo range in southern Mozambique?

- How can the archaeological sequence of the Stone Age deposits of the Daimane shelter, and the association with the surrounding open-air sites, contribute to the chronology of occupation in the area?

Answers to these questions will provide a better understanding of the different early inhabitants of the southeastern tip of Africa, and how the environment influenced the production and changes of the archaeological data recovered from excavations. They will also provide more evidence of lithic development analysis in southern Africa.

Research activities at University of Mpumalanga

The lithic analysis (including typological analysis and microscopic residue identification) of some of the stone artifacts recovered from the excavations in the Daimane II rock shelter was performed at the of University of Mpumalanga laboratory, and supervised by Dr Tim Forssman. These analyses, and comparisons of Stone Age tools (from Mozambique and South Africa), showed some similar typological features, as well as differences, in raw material selection by past hominids. The typological features, and the different technological complexes, were also documented with formal (stone tools used by hominids such as blades, scrapers, segments, etc) and informal (stone debris discarded during the production of formal instruments) tools identified, which correspond to different chronological periods of lithic production by hominids (Fig. 1). Besides the study of the artifacts described above, several sites in rock shelters in the Mpumalanga province were also visited, and large collections of lithics and rock paintings were analyzed for comparative purposes.

Conclusions, outcomes and future plans

The PAGES-IAM Research Fellowship enabled the analyses of parts of the lithic collections from the Daimane II. Lithic analysis has revealed a progressive increase in technological complexity over time, from the Middle Stone Age to the Late Stone Age. This is evident in the development of more refined tool forms, improved raw material procurement strategies, and enhanced manufacturing techniques. Another aspect the analysis revealed is the diversity of geological raw materials identified, not only in the excavated materials corresponding to the Middle-to-Late Stone Age transition, but also during the period of economy based on hunting and gathering, which continued until the 1800s in Mozambique and South Africa. Four publications about different aspects of the current research are currently in preparation, and they will be submitted to peer review journals.

The evidence of this complex process of occupation is well preserved in the archaeological deposits of the Daimane rock shelter. Thus, more chronological dating (e.g. radiocarbon, phytoliths, optically stimulated luminescence) and mineralogical analysis of the ceramics, and faunal remains analysis are underway. These results will bring forth a key contribution to understanding the long sequence of the Daimane site.

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Figure 1: Two lithic tools made out of jasper using the bipolar technique. Photo credit: Décio Muianga.

14th International Conference on Paleoceanography

Anna Nele Meckler[1], T. Trofimova[2], B. Risebrobakken[2] and S. De Schepper[2]

14th International Conference on Paleoceanography, Bergen, Norway, and online, 29 August–2 September 2022

The International Conference on Paleoceanography (ICP) has a 40-year-long tradition connecting the global research community that uses marine archives and modeling approaches to reconstruct and simulate the history of the ocean and its role in changing climate. Arranged by the community, this event is held every three years at different locations. In 2022, ICP was arranged for the 14th time (pastglo-balchanges.org/calendar/128671), hosted in Bergen, Norway, by the Bjerknes Centre for Climate Research, the University of Bergen, and NORCE Norwegian Research Centre (Fig. 1). ICP14 brought together 551 researchers from 33 countries (including 175 students) covering all subdisciplines of paleoceanography.

The conference program reflected the diversity of current paleoceanography re-search and was centred around five themes. In the first theme, "Climate and Ocean Biochemistry", a focus was set on the recon-struction of biogeochemical cycles, seawater chemistry and elemental cycling in the ocean, factors that are intimately coupled to global climate and marine ecosystems. The second theme, "Ocean Circulation and its Variability", addressed the state, rate and sensitivity of past ocean circulation and its

relationship to climate and carbon-nutrient cycling, while the third theme, "System Interactions and Thresholds", was dedicated to studies on interactions between the ocean and other Earth system components, and how these interactions generate climate variability across different timescales. This theme also covered ecosystem impacts of changes in the ocean and climate. New insights on the ocean and climate dy-namics during past warm climate states were presented under the fourth theme, "Improving our Understanding of a Warmer World". Finally, the fifth theme, "Innovation to Overcome Knowledge Gaps", aimed to bring the community up to date on the development of new proxies and approches to reconstruct and model climate change, and enhance our understanding of relevant processes. In addition, focus was set on how to integrate such different approaches to further enhance our understanding of the Earth system.

The conference followed the well-estab-lished ICP format: a limited number (28) of invited plenum lectures presented state-of-the-art results and ideas regarding each of the five themes of the conference. Three longer perspective lectures informed of new insights from adjacent research fields

that are relevant to paleoceanography. At ICP14, perspective lectures focused on the nitrogen cycle in the mixed layer and its impact on export fluxes, the global overturn-ing circulation, and the role of paleoceanog-raphy in the latest IPCC reports. In addition, a keynote talk highlighted advances in the organic geochemistry toolbox. The daily program also included five vibrant plenum discussions on the topics presented each day with all speakers.

The plenary program was complemented by extensive poster sessions allowing for ample discussion time. Poster sessions are the key element of every ICP, where the whole breadth of research is covered. The ICP14 program included 543 poster presentations, among which, 40 were virtual.

For early-career researchers (ECR), ICP contributes to professional development and provides an opportunity to connect with leading scientists, as well as their peers. To support participation of ECRs and scientists from low-income countries, 13 travel and virtual participation grants were provided thanks to funding from ICP13 and PAGES. The outstanding quality of ECR presenta-tions was noted by many of the participants, and three graduate students received a poster award sponsored by PAGES. To facilitate ECR networking, the PAGES Early-Career Network (ECN) organized an open ECR meeting focusing on scientific publishing.

In addition to the scientific program, net-working and discussions were facilitated at a range of social activities, another cherished ICP tradition. The social program of ICP14 included the icebreaker, a welcome recep-tion by the City of Bergen in the medieval Håkonshallen, a conference dinner, and the traditional Paleomusicology concert. The concert once again featured excellent and impressive performances by some of the conference attendees.

Outreach activities included an event for high school students by some of the ICP14 attendees and the Bjerknes Centre, strong social media presence, and visits of the Lego Ninja, a Bjerknes Centre local who frequently follows us during fieldwork and other activi-ties (Fig. 2).

ICP as a hybrid conference and other measures to widen participation
ICP14 was the first ICP to be held in a hybrid format with the aim to allow for participa-tion by those affected by travel restrictions related to the COVID-19 pandemic, as well as those who cannot, or prefer not to, travel for other reasons. In addition, the organizers
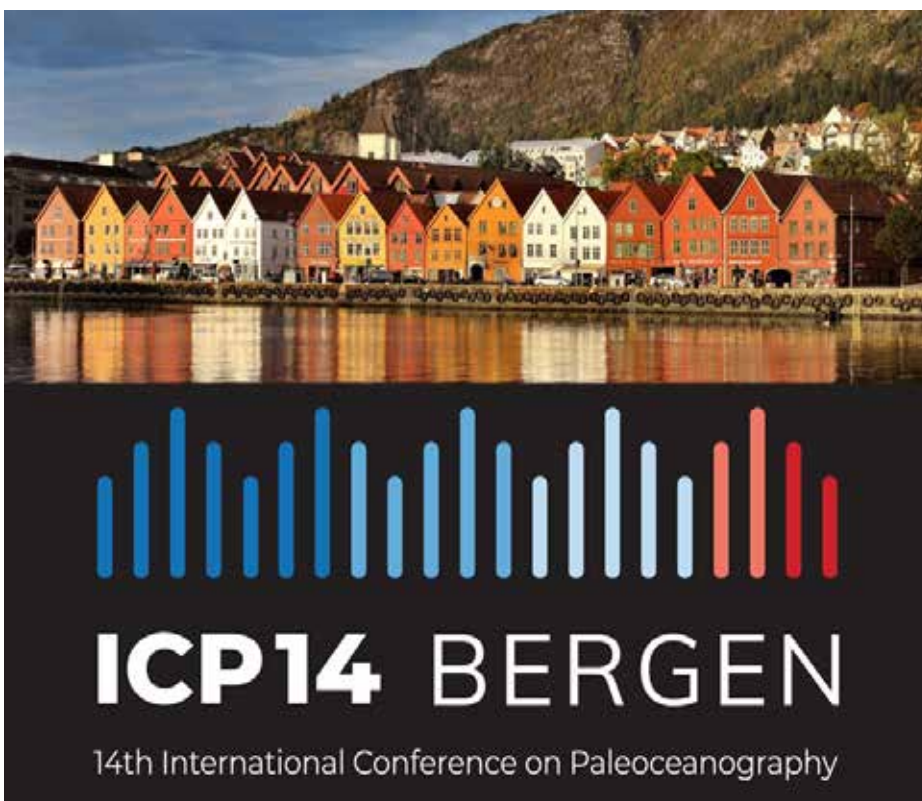
Figure 1: ICP14 logo inspired by the storage houses of medieval Bryggen in Bergen, the wharf of the Hanseatic League's trading empire from the 14th to the mid-16th century and the "warming stripes" graphic, first shown by the climate scientist Ed Hawkins at the University of Reading (showyourstripes.info). Image credit: Suet Chan.
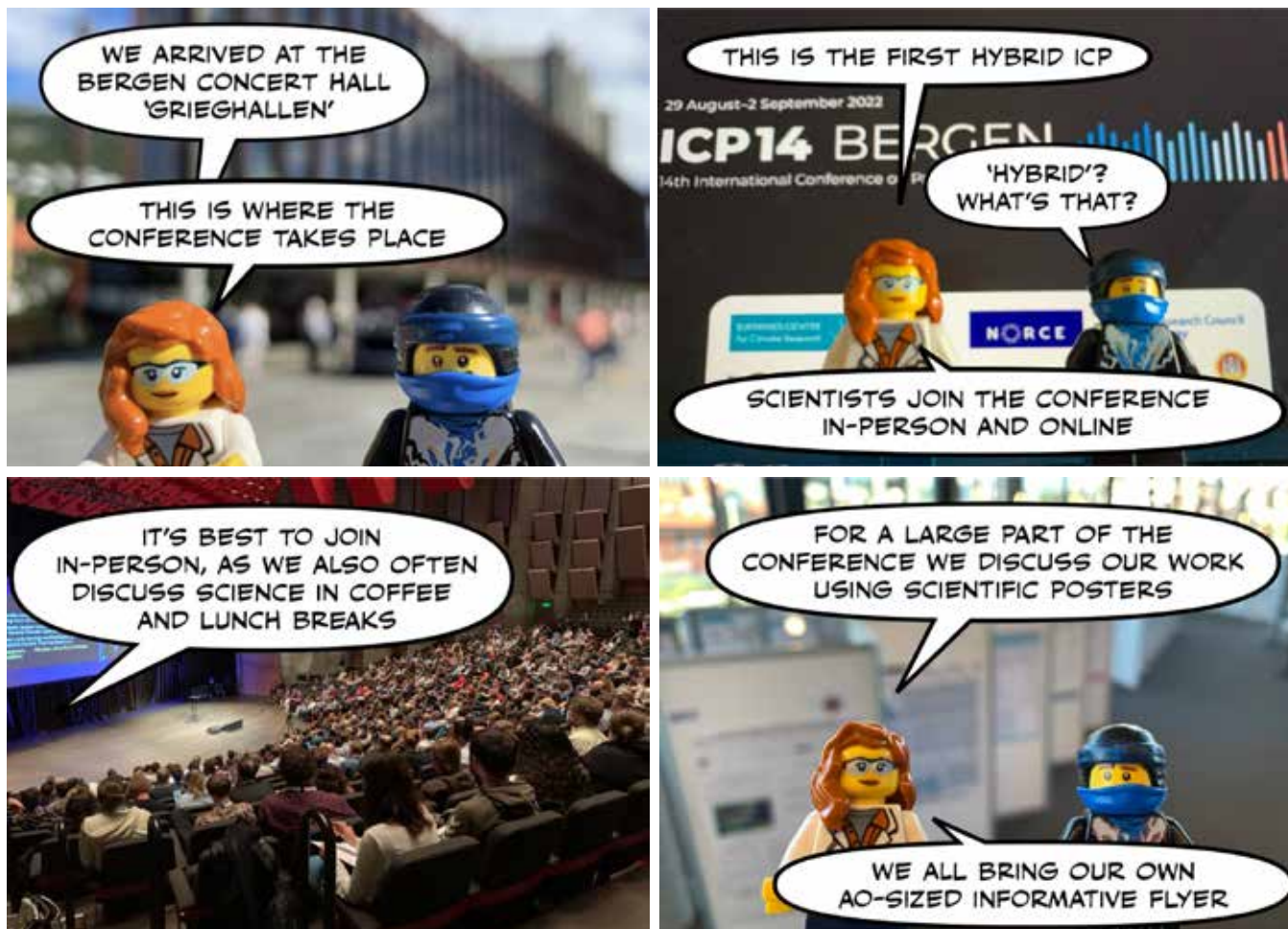
Figure 2: Excerpts from the Lego Ninja story (shorturl.at/CKST2) about its experience at ICP14. Image credit: Petra Langebroek.

hoped that the reduced costs for remote participation would allow more colleagues to participate. A digital solution allowed for remote participation of plenary speakers, poster presenters and other participants.

All registered participants had access to the digital poster gallery and were invited to contribute to discussions. The poster gallery was already available prior to the conference and for the two subsequent weeks. This opened opportunities for participants to preview posters, and to also continue visiting posters after the conference. Furthermore, the digital solution allowed for streaming plenary events or watching the recordings at more convenient times.

Given that ICP14 took place at the tail end of the pandemic, and unfortunately some participants fell sick during the conference, the hybrid format allowed speakers and other participants to continue their participation, and, in many cases, prevented the need for last-minute changes. However, while the hybrid format has many advantages, it is important to mention that it leads to a considerable cost increase, for the professional online platform and streaming solutions, and additional conference organization tasks. The community therefore needs to discuss whether the benefits of wider participation options, the added flexibility, and the potential carbon footprint reduction outweigh the extra costs and efforts that are needed.

A survey conducted among ICP14 participants after the conference revealed that the overwhelming majority (85% of 200 respondents) also support hybrid formats for future ICPs, and most respondents (almost 90%) did not mind some of the presentations being given remotely. Those that specified their reasons for online participation did so for various reasons (COVID-19 restrictions, personal reasons, lower costs, other commitments, health), but only few (less than 5%) due to the reduced carbon footprint.

Online posters were seen as added value to the conference by roughly half of the respondents, whereas 23% did not think so. The responses suggest that the online poster gallery was not used to its full potential in this first hybrid iteration of ICP. While about two-thirds of all respondents uploaded a virtual poster, only half of the in-person participants ended up looking at the online posters. Feedback suggested that if virtual-only posters are included (as was the case at ICP14), they should receive more dedicated attention during the meeting (e.g. pitch talk session, dedicated screens, more attention to discussion function for virtual posters).

Feedback on how to broaden participation at ICP included multiple aspects. Regarding speaker selection, most respondents support community nominations of speakers, with the scientific committee making the selection. Many respondents advocated for the importance of diversity in the scientific committee regarding both scientific and non-scientific aspects.

An idea brought up at the conference was the establishment of regional hubs for increasing participation and decreasing carbon footprint, while still allowing for networking. This suggestion was, however, met with varied responses from survey respondents. Around half of the respondents did not have a clear opinion, and the rest were divided into those seeing the positive sides regarding carbon footprint and widening participation in general, while others worry that the hubs would in fact prevent international networking and not help with diversity, equity and inclusion.

Overall, ICP14 was a great success. The community discussion regarding a potential hybrid future for ICP, and other adjustments, should be continued in order to keep this special conference a vibrant, cherished, and welcoming meeting place for the global paleoceanography community.

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2k-CVAS Topical Science Meeting: Centennial climate variability at regional scale in models and reconstructions

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Potsdam, Germany, 6–10 March 2023, jointly with 2k Network workshop: Hydroclimate synthesis of the Common Era and CVAS workshop: Role of scaling in the future of prediction & emerging themes

Understanding climate variability is at the heart of climate science and one of the main focus areas of several PAGES working groups (WGs). In particular, the Climate Variability Across Scales (CVAS) WG (pastglobalchanges.org/cvas) and the 2k Network (pastglobalchanges.org/2k-network) use different approaches to understand variability from sub-annual to millennial timescales.

To stimulate deeper interactions between the communities, the two groups gathered in Potsdam, Germany, in March 2023 (pastglobalchanges.org/calendar/134682). The week-long meeting started with individual two-day meetings of the 2k Network and CVAS WGs, discussing hydroclimate variability and climate variability mapping, respectively. Then the two groups joined for a Topical Science Meeting (TSM) on centennial variability. While it is a key timescale, similar to the one of anthropogenic warming, it is less studied and understood than decadal or millennial to multi-millennial timescales. This is partly due to the lack of a significant forcing on this timescale making the expected signal weaker than for glacial–interglacial cycles, for instance. In addition, analyzing centennial variability over the last 2 kyr is associated with many challenges, both on the data and climate modeling sides.

Many proxy timeseries at annual resolution are too short to faithfully reconstruct centennial variations, while longer series may have inadequate resolution or age control. In the meantime, while most climate models simulate some centennial-scale variability, the magnitude, especially regarding surface-temperature variations, is smaller than in proxy-based reconstructions and the spatial patterns vary greatly between models. A TSM on this subject was, thus, an opportunity to review the main issues and prepare actions to make progress on the most critical ones.

The goal of Phase 4 of the 2k Network is to reconstruct and understand hydroclimate variability during the Common Era. The first half of the workshop was used for plenary talks to set the scene for breakout sessions during the second half. An introduction on the history of hydroclimate research within the 2k Network, presented by Thomas Felis, was followed by two talks related to the first goal of the WG: to build a database to reconstruct spatiotemporal hydroclimate variability over the Common Era. Chris Hancock presented work on a Holocene hydroclimate database, and Bronwen Konecky described the process of building the Iso2k database. Seminars by Kira Rehfeld and Nathan Steiger focused on the integration of information from hydroclimate simulations and reconstructions.

The second half of the workshop was used for discussions within the three regional focus groups of Phase 4 to define the research questions and map out pathways towards answering them. The Tropical Pacific and South Asia group identified the reconstruction of ENSO-hydroclimate teleconnections and the variability of large-scale monsoon/circulation patterns as priority targets, whereas the Southern High-Latitude group focused on the reconstruction of extreme hydroclimate events and the understanding of atmospheric blocking events. The North Atlantic group identified large-scale atmospheric modes of variability during climate extremes of the Common Era as a first reconstruction target. All discussions included identifying sources of hydroclimate information, including those not yet in PAGES databases or similar (e.g. x-ray fluorescence [XRF] data), and addressing technical issues related to ensuring adherence to the FAIR data principles to increase interoperability of 2k data products.

The second workshop of Phase 2 of the CVAS project was held to bring together experts using different strategies for climate-related predictions/projections, discuss the possibility of scanning a larger parameter space in climate models and their effect on simulated climate variability, and discuss the progress on the variability mapping. In plenary talks and breakout groups, the experts presented their perspectives on the role of stochastic versus deterministic models and the best way to utilize climate models to improve confidence in climate projections. The discussion highlighted the importance of alternative modeling approaches and looked at first results from scanning the physical parameter space in climate models

Millenial Variability PSD$_{1000-3000\ years}$ (Pollen)
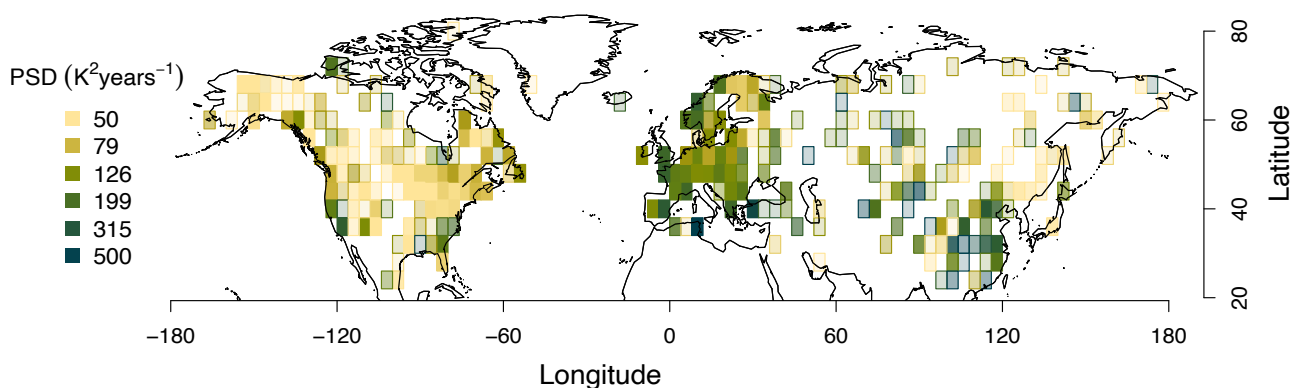
Figure 1: Figure modified from Hébert et al. (2022). Spatial pattern of millennial summer temperature variability from pollen-based reconstructions gridded on a 2° x 2° grid. The variability corresponds to the mean power spectral density over the 1000–3000 years timescale band.

Transient Holocene simulations
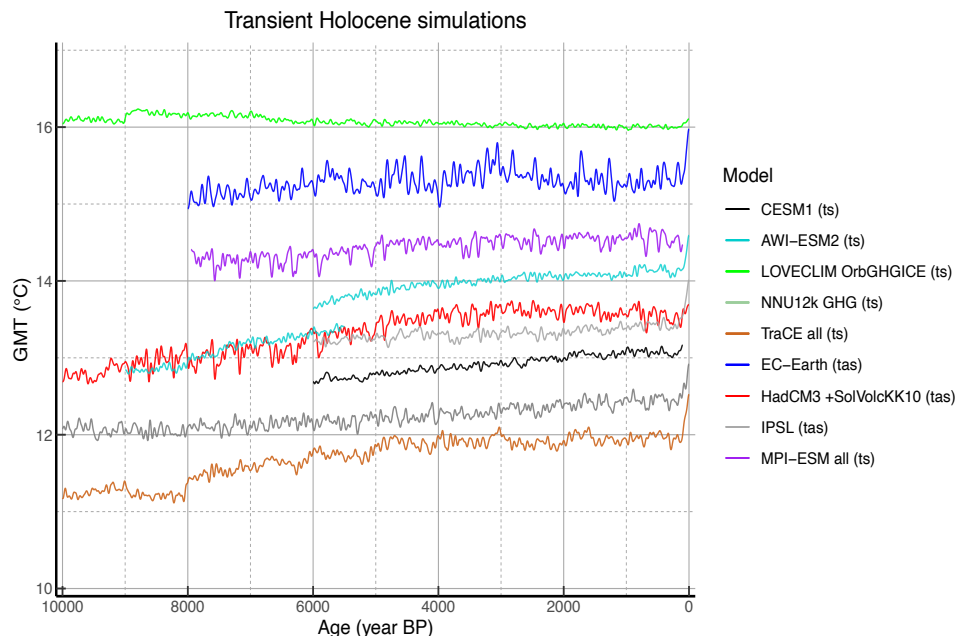
Figure 2: Figure modified from Askjær et al. (2022). Global Mean Temperature timeseries of the full forcing transient Holocene simulations filtered with a 60-year low-pass Butterworth filter. Age before present (BP) is relative to 1950 CE.

and its effect on climate variability. The group also prepared the first steps in defining a tuning target for climate models based on paleoclimate proxy data.

For the variability mapping, two groups were formed; one based on proxies calibrated to a physical variable, and one making use of the much larger dataset of proxy records that cannot be directly calibrated (e.g. XRF data). Both groups reviewed the databases to produce global maps of variability and presented their first feasibility experiments. The groups discussed the expected results and the associated hypotheses concerning the spatial structure, scaling, and proxy dependency. Robust patterns from the first mapping attempts concerning centennial temperature variability (such as the relation of variability on proxy type) were identified as input for the TSM workshop.

The 2k Network and CVAS groups then merged for the TSM. An overview of the current state of knowledge confirmed that the climate models reproduce global temperature centennial variability relatively well, related to the response to global forcing, but tend to underestimate the magnitude of regional temperature variations compared to paleoclimatic data, in particular in the tropics. This underestimation has already been suggested at multidecadal timescales in comparisons between model results and instrumental observations covering the past decades and increases when looking at longer timescales (i.e. the underestimation at multicentennial timescales is larger than at multidecadal timescales). While paleo observations indicate that centennial variability is widely present on Earth, the mechanisms leading to centennial variability in models are generally associated with changes in the deep-ocean circulation and deep-water formation, leading to larger amplitude variations largely restricted to the high latitudes. However, even though the changes in the Atlantic Meridional

Overturning Circulation are at the origin of the centennial variability in many models, the amplitude, origin, and spatial imprint of these changes remain strongly model-dependent. Some show the main changes in the Atlantic and Arctic ocean circulation while others also include more global interactions, including interactions with the Southern Ocean. In contrast, the simulated tropical variability at centennial timescales seems mainly controlled by the strength and response to volcanic forcing.

Based on breakout discussions, the group identified several avenues to pursue to gain a better understanding of the mechanisms responsible for centennial climate variability, and to determine the origin of model-data disagreements:

1) Developing a spatial fingerprint of the centennial variability from both models and data would allow us to test whether the climate variability simulated by climate models is consistent with proxy evidence and, furthermore, learn about the underlying mechanisms leading to variability.

2) Jointly analyzing the hydrological and temperature variability at the centennial scale offers many opportunities to better understand the processes at play by comparing their distinct characteristics.

3) Further studying the Southern Ocean and surrounding continents is particularly needed as centennial variability is observed in many records in the region, but a synthesis of the information provided by the various paleoclimate archives is still lacking.

4) Designing specific numerical model experiments in which strong perturbations are imposed, for instance by increasing the centennial-scale variability of the ocean component to levels deduced from paleoobservations, would enable investigation of the physical consistency of the proxy evidence.

5) Developing a better null hypothesis for significance testing of spectral peaks/oscillations based on a better characterization of the spectral continuum, driven by theoretical understanding and stochastic climate models. This will allow us to jointly study the continuum spectra and oscillations on specific timescales, and better differentiate physical mechanisms underlying centennial variability.

6) Additional work on proxy system models (PSMs) with a focus on the representation of centennial variability is needed to identify the PSMs that should be included routinely in our analyses, and the best way to include them.

Some of those points are already addressed by CVAS (4), the 2k Network (2, 3) or both groups (6), and will be further developed, while new groups were formed to work on the others (1, 5). Information and call for participation will be launched through the PAGES newsletter, but please send an email to the workshop organizers if you awould like to take part in some of the activities immediately.

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Challenges and opportunities for paleo-informed ecosystem conservation in Asia

Qiaoyu Cui[1], C. Kulkarni[2], E. Razanatsoa[3], Y. Li[4], J. Wu[5], M. Ji[6] and L. Zhou[4]

DiverseK workshop, Beijing, China, and online, 13–15 May 2023

Eastern Asian countries (including China, Mongolia, Korea and Japan) will face unprecedented socio-environmental challenges in the coming decades (IPCC 2021). Moreover, regional climate changes, together with land-use intensification and increasing livelihood demands, continue to represent a "perfect storm" in regions among the most populated in the world (Beddington 2009). A prime challenge for Asian countries is to identify a more sustainable, inclusive and spatially coherent approach to ecosystem management – a lack of which often results in conflicts between restoration targets and people's needs (e.g. Colombaroli et al. 2021).

The hybrid workshop (pastglobalchanges. org/calendar/129272) organized by the DiverseK working group (WG) (pastglobalchanges.org/diversek), with a focus on Asian ecosystems through a combined paleoscience-policy lens, offered opportunities to delve deeper into the issue and brainstorm a practical role of paleoscience in addressing it. The in-person component of the workshop was held in Beijing, China, which happens to be the first-ever Past Global Changes (PAGES) workshop held in China. The workshop spoke to the scientific goals of the DiverseK WG, i.e. to provide a new integrative, cross-disciplinary evidence base to enable better decision-making on pressing environmental issues and local struggles. The steps toward implementing the "Paleoscience for Policy" approach were discussed in great detail at the workshop. The synthesis of ideas during two discussion sessions included: i) the development of a network among paleoecologists and stakeholders in Asia with a common goal of effective ecosystem management; ii) a

dedicated discussion on the cross-comparison of management solutions under different national schemes within Asia (e.g. the steppe in China/Mongolia, fire management across India and China); and iii) the identification of best conservation approaches from the respective regions in light of the paleo-evidence base (pollen, macrofossils, disturbance regime indicators, and tree rings).

Two case studies presented at the workshop exemplified the existing challenges for conservation at species/community levels in forest and grassland ecosystems, highlighting the potential for integrative long-term studies in East Asia (Fig. 1):

1) *Pinus yunnanensis* forests in southwest China are considered an intermediary stage of succession toward evergreen broad-leaved forest (Tang et al. 2013). However, population dynamics (e.g. to what degree human impact is detrimental to the forest ecosystems) and the factors promoting forest succession (e.g. what drives *P. yunnanensis* succession?) need to be contextualized in light of long-term ecological changes. The paleodata can shed light on such socio-environmental aspects, acting as a critical asset for identifying best management practices in the wake of environmental changes (Jackson 2007).

2) Low biodiversity patterns across the woodland-steppe ecotone of southern Mongolia are considered to be the result of historical landscape fragmentation (Liu and Cui 2009). Yet, this information needs to be assessed from a longer-term ecological perspective (e.g. Whitlock et al. 2018). This information is critical for understanding the "baseline",

including the nature and degree of which ecological processes (grazing, fire, and other disturbance regime processes) are relevant for maintaining (or affecting) biodiversity in Asian steppe environments.

Workshop participants identified potential management issues that can be addressed by a collaboration between paleoecologists and protected areas members/ stakeholders in Yunnan and conservancy in Mongolia, for instance. In the future, the DiverseK community will continue to build collaborations in terms of publications, project applications, data sharing and field work, based on the networking that was established during the workshop.

The workshop provided a communication and exchange platform for the establishment of sustainable ecosystem management programs in Asia. This DiverseK WG effort has been a step towards enhancing dialogues among policymakers and paleo-ecology researchers on China's ecosystem management, thereby laying the foundations for future Sino-foreign collaborative research, including attracting early-career and developing-country researchers, to work on all-encompassing sustainable ecosystem management, through the lens of paleosciences.

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Figure 1: (Top left) Grassland ecosystem in north China. (Top right) The logo of the workshop. (Bottom left) *Pinus yunnanensis* forest in southwest China exhibiting fire-adapted traits: serotiny, thick bark, etc. (Bottom right) Macro-charcoal and burned phytolith (found in Xingyun lake sediment) were used to explore the long-term fire history of the forest ecosytem in Yunnan, China. Photo credits: J. Ming and Q. Cui. Logo image credit: X. Liu.

Setting a new research agenda for tropical peatlands, recent carbon accumulation and ecosystem services

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C-PEAT workshop, Pontiana, Indonesia, Poznań, Poland, Truckee, USA, and online, 8–12 May 2023

Carbon in peatlands through time
Peatlands play an important role in the global carbon cycle, namely as a large carbon store and a major source of methane emissions into the atmosphere. Across the globe, climate, peat fires, and land-use changes are impacting the peatland carbon balance and, in many cases, turning peatlands into net carbon sources. Peatlands are also unique ecosystems acting as global environmental archives – some tropical peats are dated back as far as 40,000 years old!

While conservation and restoration activities have gained in popularity and can slow down peat-carbon losses, a predictive understanding of peatlands' complex responses to current and projected changes is critically needed, particularly for tropical peatland functioning and recent peatland dynamics (especially in the last ~100 years).

Our current (and incomplete) understanding hampers the pressing need to transfer knowledge on peat-carbon cycling to managers, practitioners, policymakers, as well as to communities; it also limits our capacity to integrate peatlands into Earth System Models that forecast feedbacks to the global carbon cycle and climate system.

The main goal of the Carbon in Peat on EArth through Time (C-PEAT) working group (WG) (pastglobalchanges.org/c-peat) is to understand peatland dynamics over different timescales, from the past millennia into modern times, and make predictions about their future behavior in the face of global, as well as local, changes. To do so, we use peat-core records to reconstruct past ecohydrological and paleoclimate changes, and link said past conditions with changes in peatland dynamics. These paleo datasets are combined with modern-day measurements (e.g. gas-flux data) and models. Our group members are also working on nature-based climate solutions, including peatland restoration and conservation.

A truly global (and low carbon) meeting
This year's C-PEAT workshop (pastglobalchanges.org/calendar/136966) was held simultaneously in three international hubs (Indonesia, Poland and USA). While each hub had its own schedule of speakers and activities, all three hubs shared a similar research agenda (for the meeting guide and links to talks, see: shorturl.at/hjxJW). We also held daily two hour-long "global discussions" where all three hubs met online and shared the prior day's key messages and ideas.

A total of 48 in-person and 16 online participants gave talks, and an additional 30 online participants took part in the workshop. Day 1 focused on setting a research agenda for tropical peatlands; days 2 and 3 were dedicated to issues and potential solutions to quantifying recent peatland carbon dynamics, and day 4 was devoted to sharing recent progress on our current data community products and looking back at the work that had been done during the second phase of our WG.

We also outlined our research priorities for the next phase of C-PEAT (Fig. 1) while discussing ways to keep our core identity as paleo-peat scientists. Indeed, our community of practice has rapidly broadened over the past few years and now includes modelers and modern-measurement scientists, restoration and conservation scientists, as well as stakeholders specializing in carbon accounting. On day 5, some hubs organized field trips for the local participants. Lastly, the workshop has greatly broadened our core of scientists, particularly early-career and from low-and-middle income countries.

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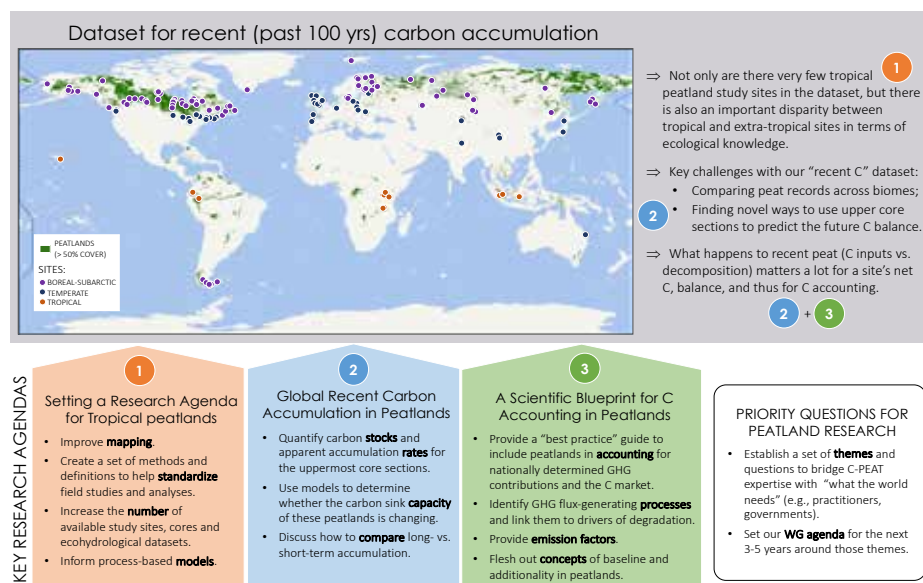
Figure 1: Key research agendas and priority questions for the future of peatland research and the C-PEAT working group.

Climate and Conflict Revisited: Perspectives from Past and Present

Sam White[1], D. Collet[2], K. Kleemann[3] and N. Maughan[4]

4th CRIAS workshop, Oslo, Norway, and online, 11–12 May 2023

Global warming has heightened scholarly and public concern over links between climate and conflict and has accelerated research into possible connections among extreme events, warfare, and political and intergroup conflict. Nevertheless, scholars have yet to reach firm consensus on past and present linkages between climate and conflict or a comprehensive integration of historical and current perspectives (Degroot 2018).

The workshop "Climate and Conflict Revisited: Perspectives from Past and Present" assembled researchers from the historical, social, and natural sciences to revisit the climate–conflict nexus (pastglobalchanges.org/calendar/136748). This event – a joint meeting of the PAGES Climate Reconstruction and Impacts from the Archives of Societies (CRIAS) (pastglobalchanges.org/crias) working group and the University of Oslo CLIMCULT project – took place at the Oslo Museum of Natural History. It included 15 presentations, with a public keynote address by Florian Krampe (Stockholm International Peace Research Institute) and a visit to the museum's Klimahuset to explore public perceptions of climate change and conflict.

The first day's sessions began with the archaeology of climate change and conflict during the Late Bronze Age and continued with case studies of medieval Iceland and Byzantine and Ottoman Macedonia. Christian Pfister (University of Bern) discussed pathways of causality between extreme weather and conflict in early modern Europe, and researchers presented new quantitative and qualitative analyses of climate and conflict in China and Central Europe from the 17th to 20th centuries. Stefan Döring (Peace Research Institute of Oslo) introduced studies of current climate change impacts on health and cooperation, followed by Natália Nascimento i Melo's (University of Évora) exploration of climate change and impacts in museum exhibitions. The second day began with a session on new historical databases and applications for spatial and temporal analysis of climate-conflict links. These included Societal Impact Event Records (SIER) for Ming and Qing China, the Historical Social Conflict Database (HiSCoD) database for 12th-to 19th-century Europe, and a collection of witchcraft prosecutions in Catalonia, Spain. Final presentations from Cedric de Coning (University of Oslo) and Silviya Serafimova (University of Sofia) emphasized epistemic pluralism in contemporary climate–conflict

studies and theoretical perspectives from peace studies.

Key themes emerged in workshop discussions, which demonstrated the importance of linking historical and contemporary perspectives. Several presentations explored climate variability and "slow violence" (Nixon 2013), such as withholding common resources or disrupting customary practices of coping during difficult seasons. Participants noted parallels between past and present pathways from climate to conflict, including the instrumentalization of extreme events

Figure 1: An illustration of the Historical Social Conflict Database (HiSCoD; unicaen.fr/hiscod/accueil.html), one of several new databases for the study of historical climate, extreme events, and conflict presented at the workshop. Image credit: N. Maughan.

to initiate or legitimize violence. Current research based on abundant climate and societal data indicates delayed and displaced impacts, arriving through complex pathways. This raised questions about how best to identify links between climate and conflict in historical data, where to find appropriate spatial and temporal scales for quantitative analysis, and how to overcome problems arising from incomplete or biased reporting in historical sources. Researchers in both current and historical fields also identified common challenges in communicating results, such as how to convey the balance between natural and human agency. Participants expressed hope that historical case studies illustrating past choices and possibilities could improve public messaging and refine both simplified histories of climate-driven conflict and reductionist projections of inevitable conflict under global warming.

The workshop concluded with a roundtable discussion of current needs and future possibilities in the field. Participants planned a thematic review explaining historical insights into climate and conflict for researchers in the social sciences and peace studies, as well as museums and public institutions. The meeting included more than two dozen participants representing over a dozen countries, as well as an international online audience. The CRIAS organizers hope for further representation from countries beyond Europe and East Asia in future meetings.

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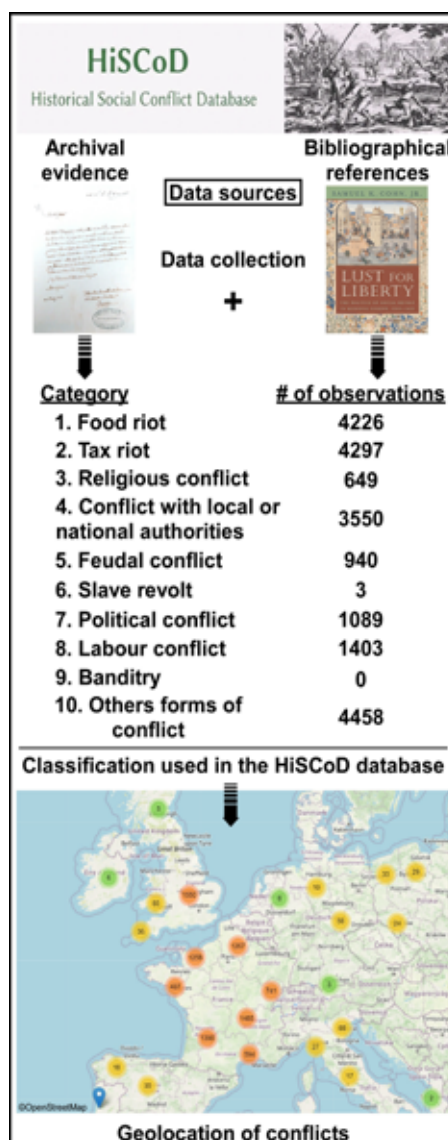
Paleo sea level and ice sheets for the Earth's future

Natasha L.M. Barlow[1], A. Rovere[2,3] and A. J. Meltzner[4,5]

4th PALSEA workshop, Singapore and online, 17–20 July 2022

The fourth meeting of the current phase of the PALeo constraints on SEA level rise (PALSEA) working group (WG) (2019–2022) (pastglobalchanges.org/palsea) was held in Singapore in July 2022, following the World Climate Research Programme sea level Grand Challenge meeting (pastglobalchanges.org/calendar/129138). The meeting was co-organized by PALSEA, and Aron Meltzner and Adam Switzer, from the Earth Observatory of Singapore (EOS), with support from EOS Director Ben Horton. The meeting focused on pulling together the lessons learnt from both the 2019–2022 phase of PALSEA, as well as the workshops that had gone before since PALSEA's inception in 2008 on the topic of "paleo sea level and ice sheets for the Earth's future". This was the first time that a PALSEA workshop has been held in hybrid format. It was wonderful to reconnect face-to-face with the community, and provide more comprehensive access to the meeting.

The meeting started with a series of optional field trips, with many in-person attendees taking the opportunity to explore the landscapes of Singapore and the sea-level archives studied by the EOS research teams. An early morning boat took participants across the water to St. John's and Lazarus islands to see fields of living and fossil microatolls that provide unique insights into relative sea level (Fig. 1). The mangroves at Pulau Ubin provided a first coring experience for some delegates, where they explored the use of wetland sea-level indicators. A third trip took a stroll through the Sungei Buloh Wetland Reserve, followed by an amazing lunch!

A series of oral presentations, lightning talks and virtual poster sessions filled the following three days. Many early-career researchers were present at the meeting; for many, it was their first in-person conference due to COVID-19. Following PALSEA tradition, it was wonderful to see these researchers have the opportunity to present their science and explore other ideas, with a safe space to ask questions. Of particular note were significant developments in 3D Earth modeling (building on the 2021 PALSEA workshop), innovative approaches to reconstructing late Quaternary ice-sheet histories, and the application of artificial intelligence to proxy sea-level data. Several presentations also highlighted the improvements in open-access standardised sea-level and ice-sheet databases made by PALSEA and associated projects.

One of the main points of discussion was centred on the role of paleo sea-level and ice-sheet science in understanding the future, as perfectly highlighted by invited speaker Tamsin Edwards. In particular, concern was raised that a statement in IPCC AR6 Chapter 9, taken in isolation, might be misleading: "Given uncertainties in paleo sea level and polar paleoclimate, and limited temporal resolution of paleo sea level records, there is low confidence in the utility of paleo sea level records for quantitatively informing near-term GMSL change" (IPCC 2021).

The audience reported instances where such phrasing was taken out of context, diminishing the importance of paleo-climate research within the broader climate science discipline. We agree that the limitation of paleo data means that its application to modeling decadal climate change may be restricted, however it does not prevent their use in climate modeling on longer timescales. As a paleo sea-level and ice-sheet community, we concluded that it is essential to report the full AR6 quote where the line above follows with: "Nonetheless, the paleorecord does contextualise sea level and can test projection models" (IPCC 2021). These are the key roles paleoscience can play in the Earth's future – and we must continue communicating this effectively.

PALSEA has now completed this phase as a formal PAGES WG. The outgoing leaders are working with an exciting new team who will lead the international sea-level and ice-sheet community to tackle the research challenges and priorities identified as part of the 2022 meeting. We thank all the participants who engaged in this workshop and the supporting organizations: PAGES, EOS and the International Union for Quaternary Research (INQUA).

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Figure 1: Coral microatolls, such as this example from St John's Island in Singapore which was visited as part of the meeting, are used by the Earth Observatory of Singapore to reconstruct changes in past sea level in the region. Photo credit: Aron Meltzner.

Geohistorical perspectives on functional connectivity patterns

Konstantina Agiadi[1] and Bryony A. Caswell[2]

Q-MARE workshop, Sesimbra, Portugal, and online, 25 May 2023

Across the marine environment, the movements of living organisms facilitate the flow of matter, genes, and energy at various temporal and spatial scales, and they are collectively referred to as Marine Functional Connectivity (MFC; Darnaude et al. 2022). Human activities and climatic change have strong impacts on MFC today, but the scientific community struggles to disentangle and evaluate them due to the lack of long-term, pre-impact monitoring data, and their unprecedented nature. Geohistorical data (i.e. data from Earth and human history) can be instrumental for identifying baselines and deciphering long-term trends and the variability of MFC, resulting from changes in the distributions, life histories, and migration of species, which may be due to natural or anthropogenic causes (Fig. 1).

Historical records include documents, paintings, museum collections and archaeological artifacts (i.e. evidence of human activities), and organismal remains (e.g. shell middens). These can be used to track the pathways, rates and consequences of species distributions and movements at decadal to millennial timescales. Additionally, they provide information on how human activities have contributed to functional connections and disconnections. For instance, the transport of non-indigenous species along shipping routes ("hitch-hikers" on wooden hulls), and for aquaria and aquaculture, has been documented from at least the 1200s (Hoffmann, 2023; Holm et al. 2019; Lotze et al. 2014), whereas the more recent construction of physical connections, such as the Suez Canal, has led to unprecedented rates of biological invasion (Por 1971).

Geological records, on the other hand, include fossils, sediments and the biogeochemical data that can be derived from them. These provide information about changes in species distributions and ecology and the consequences on MFC of natural environmental changes at millennial to million-year timescales. Sclerochronologic and genetic methods applied to fossil remains (e.g. mollusc shells, mammal bones and teeth, and fish otoliths) further offer high-resolution reconstructions of the life histories of marine organisms and can be used to identify evolutionary events and past environmental changes.

This workshop organized by the Q-MARE working group (pastglobalchanges.org/q-mare), brought together 20 scientists from 10 countries, covering a wide range of disciplines ranging from ecology and paleontology to archaeology and history (pastglobalchanges.org/calendar/134692). The aim was to draft a research roadmap that explores how to obtain and use geohistorical data in the study of MFC. Reiterating the definition of MFC for the workshop participants, the meeting started with the presentations of historical examples and case studies of MFC, and continued with discussion in groups, and altogether, around three main questions: 1) What geohistorical data could be used to understand MFC?; 2) What resources are available for such work?; and 3) How should these data be analyzed and interpreted?

The diversity of data types and resources echoed the multidisciplinarity of the group (Fig. 1). Fossils and their assemblages, historical archives, archaeological remains, ancient DNA, and biogeochemical data can give information on MFC at multiple different temporal and spatial scales. Both vertical and horizontal seascape connectivity can be inferred, as well as the role of long-term drivers of MFC. The group identified specific archives and resources that are available, openly accessible or not, and noted information on how to access them. For each data type, we described the information captured, and any challenges associated with its use and analysis. We highlighted the role of proper recovery and identification of fossil, historical and archaeological material in the correct interpretation of the results. For each of these different data types, we identified examples that illustrate their contribution to understanding MFC. Finally, we concluded with the goal to publish the roadmap in the upcoming months, so stay tuned!

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Figure 1: Overview of Marine Functional Connectivity (MFC) processes, their long-term drivers, and how geohistorical data can help unravel their changes over time.

Moving forward by looking back: Past and future volcanic impacts on climate and society

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5th PAGES VICS workshop, Bern, Switzerland, and online, 22–24 May 2023

The Volcanic Impacts on Climate and Society (VICS) (pastglobalchanges.org/vics) working group (WG) has, since 2015, aimed to promote work that improves reconstructions of volcanic forcing, enhances understandings of volcanically induced climate variability, and deepens understandings of societal impacts and human responses to eruptions. As Phase 2 of VICS ends, this workshop (pastglobalchanges.org/calendar/26993) offered a valuable opportunity for the community to meet in-person for the first time since 2019, to share results and discuss future directions.

An interdisciplinary group of researchers covering proxy reconstructions, climate modeling, history, archaeology, volcanology, anthropology, biology, atmospheric science and risk mitigation joined the workshop, with around 70 people attending in Bern and ~20 more joining online. The presentations included 13 invited talks covering the wide range of workshop themes, with over two-thirds of the invited talks given by early-career researchers (ECRs).

The chronological scope of the volcanic eruptions and impacts discussed spanned from the Last Glacial Period to the end of the 21st century. Geographically, all continents were covered, with eruptions spanning four orders of magnitude (Volcanic Explosivity Index 4 to 8). Building on previous efforts for the Common Era, sulfur injections from Holocene volcanic eruptions have been reconstructed using polar ice-core records (Sigl et al. 2022; Fig. 1). This reconstruction allows us to estimate the frequency of Little-Ice-Age-type events in the Holocene, constrain global temperature projections in the 21st century (Chim et al. 2023), and

quantify the risks of future volcanic eruptions (Cassidy and Mani 2022).

Model experiments increasingly emphasize that time of year, latitude, and eruption column height, and not just sulfur emissions, are crucial for understanding aerosol dispersal, and climatic effects (Marshall et al. 2019). Forensic geochemical analyses are shedding light on the strength and date of the mysterious Kuwae eruption in Vanuatu – a recurring case study for the VICS community. The search for the timing, size and impacts of this eruption is complemented by ongoing efforts based on oral traditions and intense volcanological fieldwork.

Several contributions emphasized that accurate and precise dating of eruptions is critical for understanding their climate effects (Reinig et al. 2021). Novel tools and integrative approaches in ice-core sciences, dendrochronology, radiocarbon dating, climate modeling and documentary records (e.g. using medieval lunar eclipses, as in Guillet et al. 2023; or ancient Babylonian dust-veil observations) that better constrain the timing of eruptions, potentially to the season, were discussed. Examples included the large caldera-forming eruptions of Samalas (1257 CE), Thera (ca. 1600 BCE), Aniakchak (1628 BCE), and Atitlan, as well as other impactful events.

As the impact of large volcanic eruptions on Northern Hemisphere summer temperature is relatively well understood, many contributions focused on other aspects, including the effects of eruptions on winter climate, monsoon circulation, Sahel precipitation, storm tracks and Southern Hemisphere temperatures. It was highlighted that not all

societal impacts of eruptions are necessarily negative (e.g. increased fish catches following the ecosystem response to sea-surface cooling).

Looking towards the future, we discussed how we can use knowledge of past volcanic activity to better prepare for the climatic effects and economic risks of future eruptions (Mani et al. 2021). Negative volcanic effects may particularly occur in regions where most of the world's present-day food production takes place, posing a significant risk to food security.

The workshop ended with a discussion regarding the future of the VICS WG. The overriding conclusion was that the open, supportive and diverse community that the VICS WG has developed since 2015 needs to be maintained. As the goals of the WG for Phases 1 and 2 have been largely achieved, new aims will be identified: possible developments discussed include a stronger focus on impacts in Asia and the Southern Hemisphere, exploring how past volcanic impacts could inform future work on solar radiation management, a greater focus on time periods earlier than the Holocene, and future predictions.

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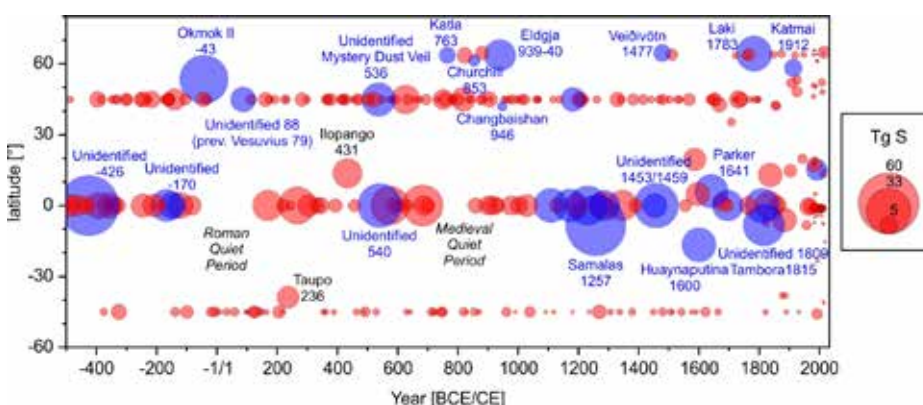
Figure 1: Volcanic stratospheric sulfur injections (VSSI) of eruptions over the past 2500 years from ice cores, grouped by known and estimated locations. Circle areas are proportional to VSSI. Eruptions highlighted in blue were discussed at the workshop. Modified from Sigl et al. (2022).

Harmonizing marine Arctic diatom taxonomy for improving paleoenvironmental reconstructions

Mimmi Oksman[1], T. Luostarinen[2], A. Limoges[3], B. Caissie[4,5], C. Pearce[6] and K. Weckström[1,2]

2nd MARDI workshop, Helsinki, Finland, 6–8 June 2023

Marine diatoms are highly sensitive to changes in their environment, such as changes in temperature, salinity, and sea ice, which has made them a widely used proxy for paleoenvironmental reconstructions (Koç Karpuz and Schrader 1990; Miettinen et al. 2015; Oksman et al. 2019). For a long time, fossilized diatoms have been used to produce qualitative reconstructions of past climate. In the late 1980s, the demand for quantitative paleodata by the modeling community promoted the development of modern diatom calibration datasets (Caissie et al. 2012; Koç Karpuz and Schrader 1990; Krawczyk et al. 2017; Miettinen et al. 2015) that enabled quantitative estimates of past sea-surface conditions. The development of calibration datasets has been fast since the early 1990s. Today, several diatom datasets exist from the (sub)Arctic regions, together including more than a thousand surface-sediment samples. Each dataset includes information about modern diatom assemblages in the surface-sediment and modern surface-ocean environmental data from the same location. These calibration datasets also allow the study of species autecology, knowledge of which is essential for the robustness of diatoms as a paleo proxy.

However, slightly different methodologies and taxonomies have been used to build these datasets, as they were gathered by different independent research groups. This can lead to inconsistencies in diatom-based climate records. The MARDI (Marine Arctic Diatoms) working group (WG) (pastglobalchanges.org/mardi) was launched in

November 2022 to integrate and harmonize the various datasets into one open-access database. Read more about MARDI objectives and activities in this issue (p. 112).

On 6–8 June 2023, 17 diatom enthusiasts (40% early-career researchers) from 10 countries (Canada, Chile, Denmark, Finland, Greenland, India, Italy, Sweden, Turkey, and USA) gathered in Helsinki, Finland, for the 2nd MARDI workshop with the title "Harmonization of (sub)Arctic diatom taxonomy" (pastglobalchanges.org/calendar/136750). The main aim of this workshop was to agree upon the identification criteria of common Arctic diatom taxa – a first critical step to enable integration of the different datasets. Prior to the workshop, about 30 of the most common and taxonomically challenging high-latitude diatom species were listed (Fig. 1). During the workshop, each species was individually discussed, with focus on key features for identification. While consensus was achieved among participants on the majority of the species, important issues that still need to be solved were raised for some. For example, what has previously been identified as the vegetative cell of *Bacterosira bathyomphala* in sediment stratigraphies could in fact be the primary valve of the heterovalvate resting spore. Such issues can have a significant relevance to paleoenvironmental reconstructions if vegetative cells and resting stages represent different ecological conditions.

A second important topic of the workshop was to discuss different sample-preparation methods and evaluate if certain methods/practices can influence the diatom assemblage by favoring particular physical features (e.g. highly silicified or small/large valves). The common diatom microscopy slide preparation methods were presented, followed by a discussion of their possible (dis)advantages. MARDI has designed an interlaboratory comparison and counting exercise to test disagreement between different methodologies and the statistical reproducibility of sample preparation. Diatom slides for microscopic identification were prepared by workshop participants following the most common methodologies used by diatomists, and these will be analyzed according to the protocol agreed upon during the workshop. Findings from this exercise will be presented in a future publication.

On the third workshop day, participants performed an identification and slide counting practice to test if there were significant

identification differences when counting a diatom microscope slide without taxonomic keys, and with limited time for identification. This exercise provided amusement, but also important insight into how challenging diatom taxonomy is, and hence, the element of subjectiveness involved in identification.

The main outcome of the workshop was the agreement on the taxonomy of the main ecologically relevant taxa, and identification of the knowledge gaps that might affect diatom reconstructions. High-quality images of the taxa discussed at the workshop will be uploaded to an open-access database (diatoms.org), with inclusion of detailed descriptions of species morphology and key identification features. This tool will then be available for everyone working with marine Arctic diatoms. For some species, discussions will continue in the form of mini-workshops that MARDI will organize in the upcoming months. These mini-workshops will consist of half to one-day online meetings open to everyone.

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Figure 1: Common Arctic diatom taxa were described and discussed in the taxonomic session of the MARDI workshop. Photo credits: Beth Caissie, Christof Pearce and Mimmi Oksman.

Shedding light on current developments in Paleo-Ecological Genomics

Kathleen R. Stoof-Leichsenring[1], U. Herzschuh[1,2,3], L. Heinecke[1] and Z. Taranu[4]

1st *sed*DNA Meeting, Potsdam, Germany, 6–9 June 2023

The first sedimentary DNA (*sed*DNA) meeting under the overarching theme "Shedding light on current developments in Paleo-Ecological Genomics" took place from the 6–9 June 2023 at the Alfred-Wegener-Institute (AWI), Helmholtz Centre for Polar and Marine Research in Potsdam, Germany (pastglobal-changes.org/calendar/129294). More than 125 colleagues participated in the first-of-its-kind meeting to bring this scientific community together, to exchange ideas and discuss new avenues.

*Sed*DNA symposium with talks and posters

The first two days consisted of 18 invited keynote talks and more than 80 exhibited posters, of which 62 were presented in the poster lightning sessions. The topics covered Quaternary paleo-metagenomic investigations on lake, permafrost, and marine sediments, as well as archaeological sites, to recover changes of different taxonomic communities (plants, mammals, human, microeukaryotes, etc.) and full ecosystems. Moreover, new method developments on *sed*DNA and *sed*aDNA (sedimentary ancient DNA), and new advances in bioinformatic tools and statistics, were presented.

Talks were followed by a meeting of the *sed*aDNA Scientific Society and a great poster session, including the ice-breaker. Networking events, such as an excursion to the UNESCO World Heritage Site at Park Sanssouci and a conference dinner at the scientific campus at Telegrafenberg in Potsdam, gave everyone the opportunity to connect with other members of the *sed*DNA community.

Method discussions and hands-on workshops

During the third and fourth days, participants dove into methodological discussions during paleo-genetic laboratory tours around AWI, and laboratories led by other ancient DNA research groups were presented to view layouts and set ups. After exchanging experiences and ideas on *sed*DNA methods in nine breakout groups led by early-career researchers (ECRs), four workshops on metabarcoding and metagenomic pipelines, and detecting critical transitions using *sed*aDNA records, the latter as part of the Paleo-Ecological Genomics (PaleoEcoGen) (pastglobalchanges. org/paleoecogen) working group (WG), started in two parallel sessions. Positive feedback was shared throughout the workshop, and peer support by all members of the community was evident throughout.

PAGES PaleoEcoGen workshop

Approximately 25 people took part in a two-day workshop with the PaleoEcoGen WG focusing on the detection of critical transitions in *sed*aDNA data (Fig.1). The first day of the workshop consisted of a statistical tutorial in R, where an example dataset and R script were presented by Zofia Taranu. In particular, three statistical approaches were introduced: 1) Latent Dirichlet Allocation (LDA; also known as Topic Models) to explore how to reduce the dimensionality of *sed*aDNA data by identifying groups of co-varying taxa (i.e. grouping taxa into "community types" or topics); 2) Change-point analysis to identify periods of pronounced turnover in community-types, where given that the approach is a type of fuzzy clustering, two or more community types can co-occur in different proportions

within a time period; and 3) Dynamic Linear Models (DLMs) to test whether transitions in community-type occurrences were approached critically. During the second day of the workshop, participants ran the R script on their own, either using the example dataset or their own *sed*aDNA datasets. This gave the group a chance to identify issues and troubleshoot. It was a great opportunity for everyone to work together to improve modeling approaches and cater it to a variety of *sed*aDNA data, most notably those that differ in time frame and dynamics through time.

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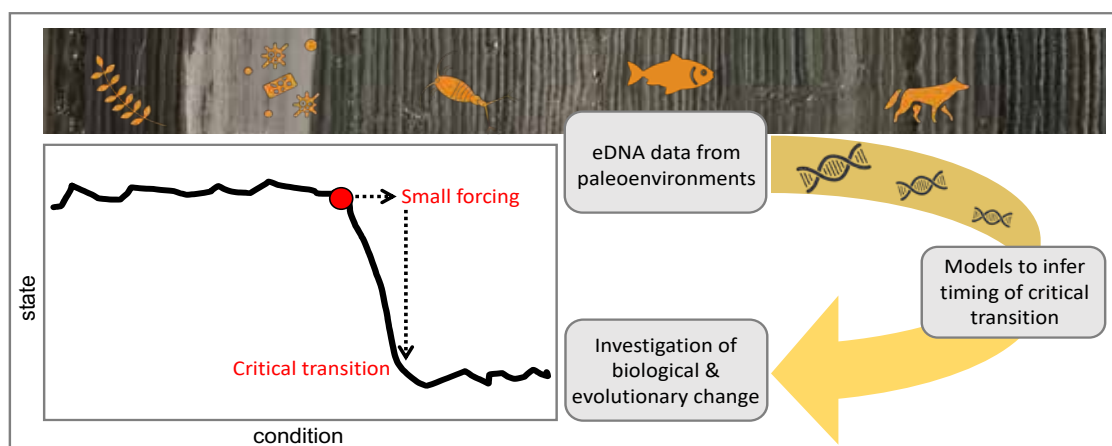
Figure 1: (Left) Schematic representation of a critical transition between two states triggered by a small forcing. (Right) Simplified workflow of the proposed approach to identify past critical transitions, and evaluate subsequent biological changes based on ancient environmental DNA timeseries derived from lake-sediment cores. Modified from Monchamp et al. (2021).

MioOcean Temperature Synthesis Meeting 2

Sevasti Modestou[1] and Sindia Sosdian[2]

PlioMioVAR workshop, Utrecht, Netherlands, and online, 8 June 2023

Arguably, the most important existential crisis facing modern society is that of climate change, caused by anthropogenic greenhouse gas emission. One way to understand how Earth's climate responds to changes in greenhouse gas concentrations, and thus how to predict, plan, and guide society through such a crisis, is to study past climate change. During the Miocene Epoch (~23 to 5.3 million years ago), Earth's climate experienced significant temperature and ice-volume fluctuations, which were coupled to marked changes in atmospheric carbon dioxide (CO_2) concentrations. In fact, the Miocene represents the most recent period in geologic history when Earth's climate experienced CO_2 concentrations equal to those predicted for the coming decades by the Intergovernmental Panel on Climate Change (e.g. Fig. 10.20 in Meehl et al. 2007). This, in conjunction with a similar continental configuration, makes the Miocene a crucial and relevant analog to better understand modern climate change.

A large number of studies have published estimates of Miocene ocean temperatures. These studies determined past temperatures using a variety of compounds, known as geochemical proxies (e.g. organic molecule thermometers like $U^k_{37}{'}$ or TEX_{86}, or inorganic elemental or isotopic thermometers such as Mg/Ca, clumped isotopes (Δ_{47}), and stable isotopes). Usually, such studies only focused on one or a few specific location(s) in the ocean(s) (e.g. Modestou et al. 2020; Sosdian et al. 2020). There is currently an urgent need from several communities, mainly the climate modeling, paleoclimate, and policy-making communities, to summarize and synthesize data in order to make it more accessible to advance our understanding of modern climate change. The MioOcean Temperature Synthesis working group (a subgroup of PAGES' PlioMioVar working group [pastglobalchanges.org/pliomiovar]) aims to update and synthesize existing ocean-temperature proxy data, compile them all into a databank for open access, and ultimately generate a global temperature atlas for specific Miocene time slices relevant to modern climate change.

The second workshop to date, MioOcean 2 (pastglobalchanges.org/calendar/137169), aimed to bring our large group of researchers together to provide updates on synthesis progress, discuss ongoing issues, find solutions, and specify how the group's outputs will take shape. One major hurdle for each proxy is to update the method used to translate raw data into temperature. Part of the meeting was dedicated to determining the most state-of-the-art methods of temperature calculation for each proxy, in order to begin recalculating temperature from raw data. Another major hurdle is to consider how to make data from different locations comparable in the time domain, which is solved by the stratigraphers and geochronologists comprising the group who specialize in generating age models for the Miocene sediments and rocks the proxy data are derived from. This group also presented their vision for moving the synthesis forward, and what that might entail. Finally, MioOcean is working in close partnership with a climate modeling initiative, MioMIP (Miocene Model Intercomparison Project). Climate modelers use paleoclimate data to validate and compare model outputs. However, if data are conflicting or have poorly defined uncertainties, that critical comparison and validation work becomes very difficult. To this end, MioOcean hosted several MioMIP participants to receive their feedback and guidance on how best to compile ocean temperature data to ensure that the new compilations are as useful as possible for the modeling community.

The workshop followed another conference (MioMEET; Utrecht, 5–7 June 2023) for reasons of sustainability; since the two communities overlap, most participants were already gathered in the beautiful Dutch city. An international group of 32 scientists met in Utrecht on 8 June (MioOcean 2), and 15 participants who were unable to travel also joined online. The workshop was a success in many ways, but most importantly, it was the first time the group was able to gather in person. Online meetings are convenient (assuming one wins the timezone lottery), and much more environmentally friendly, but getting to know one another in real life adds to the energy and motivation of a scientific working group.

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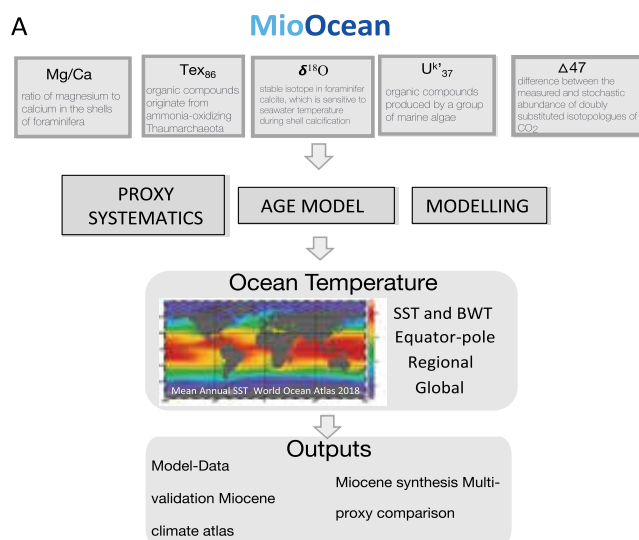
Figure 1: (A) Workflow of the MioOcean Temperature Synthesis. **(B)** Sindia Sosdian, of the MioOcean Steering Committee, facilitating discussion during the meeting.

Building a controlled vocabulary for the international lipid biomarker database

Harleena Franklin[1], E.K. Thomas[1], J.W. Williams[2], J.M. Aguilar[3], I.S. Castañeda[4], K.H. Freeman[5], N. McKay[6] and C. Morrill[7]

Achieving global-scale insights into past climate variations requires the careful assembly and standardization of networks of proxy databases (Kaufman et al. 2020; Konecky et al. 2020; Walter et al. 2023). Moreover, it is expected that scientific data are openly and readily shared online. These expectations were formalized through the FAIR Guiding Principles (Wilkinson et al. 2016), which created a standard framework that open scientific data should be findable, accessible, interoperable, and reusable.

Controlled vocabularies are essential infrastructure to meet the FAIR principles, thereby enabling global-scale data syntheses and subsequent scientific research. Controlled vocabularies are sets of terms constrained by specific rules that allow for concise and unambiguous usage (Wojcik 2006). Several community-led controlled vocabularies are emerging in paleoclimatology and paleoecology, including the PaST Thesaurus (ncei.noaa.gov/products/paleo-climatology/paleoenvironmental-standard-terms-thesaurus) employed by the NOAA World Data Service for Paleoclimatology (Morrill et al. 2021) and the steward-curated taxonomies used by the Neotoma Paleoecology Database (Williams et al. 2018). As the volume and variety of empirical data in paleoclimate research expands, controlled vocabularies developed by experts and consistently shared paleodatabases become ever more essential.

Lipid biomarkers are common in climate and environmental studies, especially in the near-recent times, and represent readily analyzed lipids that have homologous series distributions, ratios, and isotope abundances with high utility for the paleoclimate community. Despite this, these have no comprehensive controlled vocabulary for paleoclimate and environmental use, although the International Union of Pure and Applied Chemistry (IUPAC) dictionary (goldbook. iupac.org) exists for many compounds. Here, we present a draft controlled vocabulary that encompasses several major classes of lipid biomarkers commonly applied for paleoclimate research. To facilitate interoperability among data resources, the NOAA World Data Service, LiPDverse, and Neotoma have all agreed to adopt this vocabulary. This vocabulary is being developed as an open process, and we welcome community input.

Because the task of cataloging and establishing vocabulary rules for thousands of lipid biomarkers is non-trivial, we have begun with some of the most commonly used lipid biomarkers in paleoclimate research: branched and isoprenoidal glycerol dialkyl glycerol tetraethers, n-alkanoic acids, n-alkanes, alkenones, and long-chain diols. We have developed a list of lipid biomarker names as they are commonly used in the paleoclimate literature, and include the IUPAC term for each compound, to avoid ambiguity. This list is published as v 0.1.0 on Google Sheets (tinyurl.com/ILBD010) and is available for comment. We are seeking community input to check for completeness and accuracy within these classes by 31 January 2024. We would also welcome participation by individuals or teams interested in leading development of a list for other classes of lipid biomarkers.

When the community input period is complete, we will update and publish v 1.0.0 of the International Lipid Biomarker Controlled Vocabulary on Zenodo, with updates and future versions possible afterwards. We will also incorporate v 1.0 and subsequent versions into the controlled vocabularies maintained by NOAA, LiPDverse, and Neotoma. If there are other databases interested in using this controlled vocabulary, please contact us. With a controlled vocabulary in place, the next steps will be to harmonize the vocabulary in lipid biomarker datasets currently on public paleoclimate databases, and gather and add datasets not yet on these public databases. Anyone interested in contributing vocabulary or datasets can contact Harleena Franklin at harleena@buffalo.edu. Documentation of the process being developed here may be useful to experts seeking to develop controlled vocabularies for other proxies.

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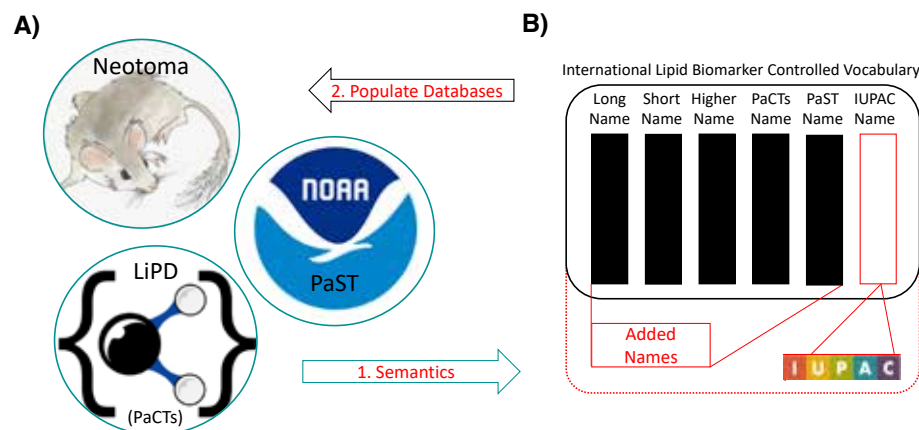
Figure 1: **(A)** Schematic representation of the process used to develop a controlled vocabulary for use in the International Lipid Biomarker Database. This vocabulary is based on previously established language frameworks (semantics) developed by global paleodata resources such as Neotoma, NOAA, and LiPD. Each new biomarker name is assigned a long name (e.g. branched diakyl glycerol tetraether Ia), short name (e.g. brGDGTIa), a higher-order name (brGDGT), and equivalent names from the PaCTs, PaST, and IUPAC controlled vocabularies. Usually, the PaST and PaCTs names are more generic than those proposed here. **(B)** Once the controlled vocabulary is established, we will add those new terms back into other databases for increased interoperability across paleodata resources. We view this as an iterative and ongoing process, with new additions to the controlled vocabulary list to be provided by participating experts and new publications describing lipid biomarker compounds. We invite community input to these names and processes.

Claude Lorius (1932–2023)

As a young man in his twenties, Claude Lorius experienced the extremely difficult living conditions in Antarctica at the end of the 1950s. In July 1957, together with two French colleagues, he spent an entire year "voluntarily buried" at the Charcot Station. The year 1957 marks the beginning of an exceptional career, during which Lorius went on 22 expeditions, totaling six years in the field.

He was a pioneer in polar glaciology. Based on the isotopic approach originally developed by Willi Dansgaard, Claude Lorius and Liliane Merlivat adapted and applied the approach in Antarctica, and found a linear relationship between the isotopic composition of precipitation (heavy isotopes of hydrogen and oxygen) and the temperature of formation. These results formed the basis for the developement of an "isotope thermometer" and the reconstruction of past temperature variations from deep ice cores.

In 1965, while contemplating the air bubbles released from melting ice cubes in his glass of whisky, he realized that ice could be the window into archives of the atmosphere.

His primary objective then became drilling at Dome C, in the heart of the Antarctic continent, to extract an ice core for analysis. Thanks to logistical support from the US National Science Foundation (NSF), and the perseverance of engineers and drillers, scientists were able to accurately obtain the first analyses of properties such as dust content, crystal size, ice chemistry and air-bubble composition that were trapped in the ice found at the Dome C site.

During the International Geophysical Year (1957–1958), the Soviet Union established a permanent station in East Antarctica, at the Vostok site. Due to his personal contacts, Claude Lorius managed to initiate a collaboration between the French and Soviet teams. Drilling depth reached 2083 meters on 11 April 1982. The oldest ice in this location was estimated to be 150,000 years old, meaning that coring would cover the whole of the previous warm period, the Last Interglacial, which peaked around 130,000 years ago, and entered the previous ice age. The link between major climatic cycles and variations in the Earth's orbitally forced insolation, as demonstrated in 1976 from deep-sea core records, was confirmed by the Vostok isotopic recording (Lorius and Merlivat 1977). More importantly, however, throughout the last 150,000 years covered by the core, the CO_2 concentration was found to be closely correlated with the temperature deduced from the isotopic analysis of this ice (Lorius et al. 1990).

At the end of the 1980s, Claude Lorius, together with other early visionary paleoclimate researchers at the time, such as Hans

Oeschger, was instrumental in the establishment of the PAGES initiative. As members of the International Geosphere-Biosphere Programme (IGBP) Working Group, they met for the first time in July 1988 in Bern, Switzerland, to discuss "Techniques for Extracting Environmental Data from the Past". This meeting lay the foundations for what one year later became the birth of PAGES: the IGBP Core Project on Past Global Changes. After the official launch of Past Global Changes (PAGES) as a registered organization in 1991, Claude Lorius served as one of the first PAGES Scientific Steering Committee members from 1991–1996.

The start of the 1990s proved a challenging time for the Soviet drillers who were confronted with the end of communism in the USSR. Despite this, operations at the Vostok site continued and American scientists joined the project. Claude Lorius, with the assistance of a colleague from Grenoble, Jean-Robert Petit, put all his energy into ensuring this collaboration continued. In January 1996, the depth of 3350 meters was reached, with this ice record covering 420,000 years (Petit et al. 1999). The record demonstrated that Antarctic climate and greenhouse gases go hand-in-hand throughout this period, characterized by four glacial–interglacial cycles. This confirmed that variations in insolation are at the origin of the major climatic cycles, and those of the greenhouse gases play an amplifying role. This extension of records also put the role of human activity into perspective; throughout the last 420,000 years, the quantities of carbon dioxide and methane present in the atmosphere have never been as high as they are today.

Very quickly, the drilling project took on a European dimension. It was the beginning of "EPICA" (European Project for Ice coring in Antarctica). Claude Lorius was determined for drilling to reach the bedrock in Antarctica at Dome C, and this was achieved in January 2005 when the bedrock was finally reached

at 3260 meters. This success owes a great deal to Claude Lorius' confidence and determination.

One of his primary aims was to show that data from the past can provide relevant information regarding the future evolution of our climate, and to raise the alarm about global warming linked to the increase in the greenhouse gases resulting from human activities. He devoted most of his time to this from the 2000s through activities on the Anthropocene and his messaging in the film "Antarctica: Ice and Sky" (French original: "La glace et le Ciel") by the Oscar-winning director Luc Jacquet.

Claude Lorius had a concrete vision of how polar ice can contribute to knowledge of our climate and environment. He was a true leader, a tough scientist, and someone whose undeniable charisma inspired a whole generation of researchers. He was a member of the Academy of Sciences and received the CNRS Gold Medal in 2002. He also received numerous prestigious international accolades, including the Tyler, Balzan, Bower and Blue Planet prizes. In 2021 he was decorated "Grand Officier" in the French order of the Legion of Honor – the highest decoration in France.

Claude Lorius passed away on 22 March 2023.

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Claude Lorius in Antarctica, 2008 (commons.wikimedia.org/wiki/File:Claude.Lorius.jpg).

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