In retrospect

Forty years of ice-core records of CO_2

Jean-Robert Petit & Dominique Raynaud

In 1980, a method was found to determine the amount of carbon dioxide in ancient air trapped in polar ice — providing direct evidence that CO_2 is coupled to climate, and affects global temperatures in the past, present and future.

In the ancient ice sheets near Earth's poles, tiny bubbles trapped in the compacted layers of snowfall provide a natural archive of air from ages past, but one that is not straightforward to read. Forty years ago, the glaciologist Robert Delmas and colleagues developed a technique for reliably measuring the amount of carbon dioxide in the bubbles[1]. Their work paved the way for modern measurements showing that atmospheric CO_2 levels have been linked to Earth's temperature for hundreds of thousands of years.

Towards the end of the nineteenth century, Swedish scientist Svante Arrhenius became interested in the causes of Earth's ice ages. Through calculations, he estimated how changes in CO_2 levels might affect the atmosphere's ability to absorb heat from the ground, rather than allowing it to escape into space. He suggested that the cooler temperatures during glacial periods resulted from a decrease in this absorption[2].

This greenhouse theory was an alternative to the theory backed by James Croll, who proposed[3] that glaciation cycles arose from changes in Earth's orbit, amplified by natural feedbacks such as changes in snow cover. Another scientist, Milutin Milankovitch[4], refined this idea by looking at fine variations in Earth's movements and the resulting changes in insolation (incoming sunlight) at different latitudes. His orbital theory gained support from marine sediment records[5], which exhibit periodicities similar to Earth's orbital parameters. Thus, the orbital theory was promoted as a pacemaker of the ice age, with various feedback loops amplifying tiny changes in insolation.

In the 1960s, air inclusions in ice cores (Fig. 1) drilled from the depths of glaciers sparked interest as natural samples of the ancient atmosphere. To quote researchers at the time[6]: "if the CO_2 concentration were found to vary in time, one would have the means for testing the well-known greenhouse theory of climate change." Attempts were made during the 1960s and 1970s to obtain a reliable atmospheric CO_2 record from gas extracted by melting ice samples ('wet extraction'). But results showed unexplained high concentrations of CO_2, sometimes ten times that of today's atmosphere, and scattered over a bafflingly wide range of values.

The answer to the puzzle came from studies of the chemistry of polar ice. At Grenoble in France, Delmas was researching the acid rain that was decimating northern European forests. Suspecting that the industrial sulfur emissions thought to be responsible might be recorded in Greenland ice, he and his students Michel Legrand and Jean-Marc Ascencio developed a technique[7] for measuring ice acidity, adapted to be exceptionally sensitive to impurities and to avoid bias from ambient atmospheric CO_2. They discovered that, even without volcanic or human activity, the ice was tinged with sulfuric acid arising from sulfur compounds emitted by plankton. If an ice sample contained carbonaceous dust, melting the ice would allow the background acid to react with the carbonate. This, they thought, might be producing extra CO_2 in analyses of ice-core bubbles and confounding the CO_2 measurements.

To test their idea, Delmas and colleagues set up a dry-extraction system that avoided melting the ice — instead, the ice was crushed under vacuum in a vessel at −40 °C. They analysed selected samples from two Antarctic ice cores (Dome C and D10), which contained very few carbonates. For ice from the past 10,000 years, they found CO_2 levels comparable to then-current atmospheric values (around 300 parts per million; p.p.m.), with good reproducibility. For ice deposited during the last glacial period, around 20,000 years ago, levels were much lower, around 190 p.p.m. (Fig. 2a), thus confirming Arrhenius's prediction.

At around the time that Delmas *et al.* carried out their work, a Swiss group, using a refined version of wet extraction to analyse ice cores, also suggested[8] that CO_2 levels were depleted during the last glacial period. But the dry technique subsequently became widely adopted because of its greater reliability and accuracy. Delmas and co-workers' paper thus paved the way for today's more extensive comparisons of climate and CO_2 concentrations.

A milestone was reached in 1987 with dry analyses of an ice core more than 2 kilometres deep from the Vostok site in Antarctica. This provided a 160,000-year record[9–11] of temperature and CO_2, depicting a complete climate cycle in which CO_2 levels varied from 290 p.p.m. during the warm period to 190 p.p.m. in the cold period, and correlated with temperature. Over the following decades, the climate–CO_2 correlation was demonstrated over a period of 400,000 years from

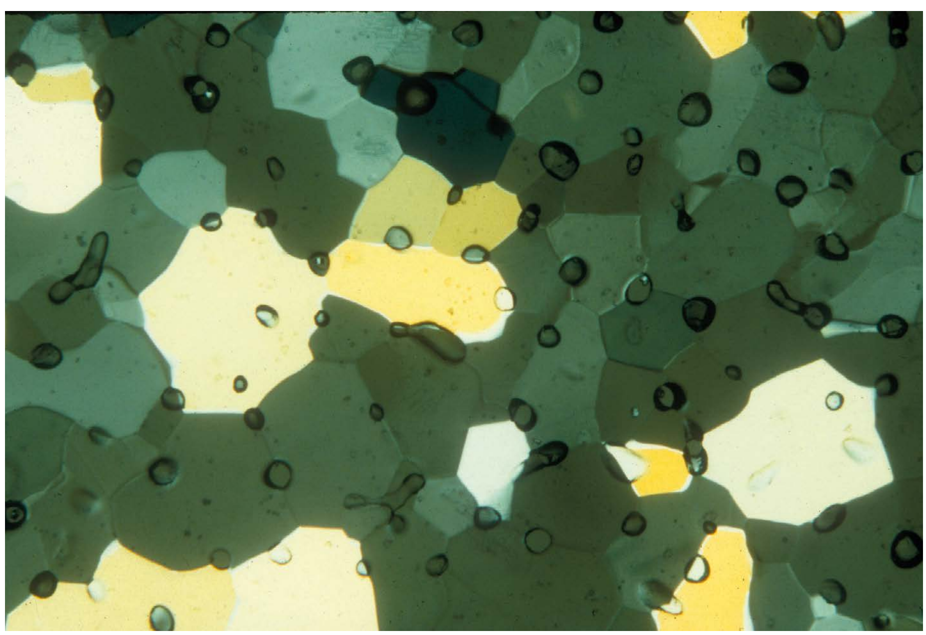

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Figure 1 | Ice record. This thin section of glacier ice, visualized using polarized light, contains ice crystals and trapped bubbles of ancient air.

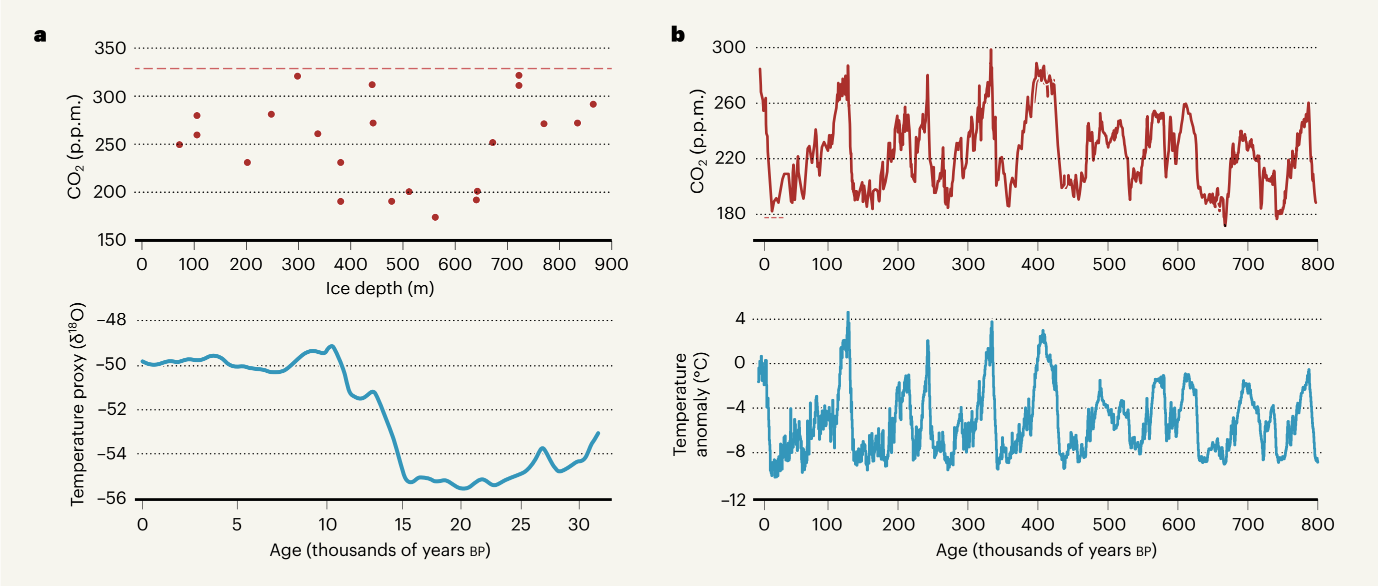

Figure 2 | Ice-core records past and present. a, Forty years ago, Delmas *et al.*[1] found a way to measure ancient atmospheric carbon dioxide levels from bubbles trapped in ice. Their results show that a dip in CO_2 concentrations coincided with the temperature drop associated with the glacial period around 20,000 years ago. Top: red dots show the authors' CO_2 measurements in parts per million (p.p.m.) and the corresponding depth of the ice; the dashed red line represents the CO_2 concentration in 1980, the time of the study. Bottom: blue line indicates oxygen isotope ratios[18] (a proxy for temperature) expressed as the quantity $\delta^{18}O$. **b**, Similar methods have now produced CO_2 records for much longer periods of time from deep ice cores. Here, CO_2 results from Antarctic ice march in step with temperature cycles (temperature anomaly represents the difference between the actual temperature and the mean temperature of the past millennium) over the past 800,000 years, revealing how strongly this greenhouse gas is coupled to Earth's temperature[13].

extended Vostok records[12], and then as far back as 800,000 years[13] (Fig. 2b) from ice drilled at another Antarctic site, EPICA Dome C.

So Delmas and colleagues' pioneering work covering a few tens of thousands of years sparked research that now gives us an accurate record of atmospheric CO_2 levels undulating with glacial–interglacial climate cycles for several hundred thousand years. This close correlation attests to the tight coupling between climate and carbon cycles during the past 800,000 years, and has stimulated climate scientists to consider them to be part of the same global system.

Four decades of 'dry' sampling of ice-core bubbles have contributed to our current understanding of the succession of glacial–interglacial cycles. Lying somewhere between the initial suggestions of Arrhenius and Croll, these cycles are seen as the combined effects of orbital variations and greenhouse gases, amplified by a series of natural feedbacks. Insolation changes driven by Earth's orbital and axial oscillations (Milankovitch cycles) set the timing of the glacial cycles. But greenhouse gases (mainly CO_2), together with the growth and retreat of the northern ice sheets, affect the radiation balance between absorbed sunlight and energy escaping back to space, thereby driving the size and shape of the changes.

The reliability of Antarctic ice as a natural sampler of past air has been confirmed by a reconstruction of atmospheric CO_2 levels over the past millennium[14], which covers pre-industrial CO_2 levels (280 p.p.m.) and which partly overlaps with the period when direct atmospheric measurements were made. Caution should be taken in analyses of ice from Greenland, where Delmas noted that windborne carbonaceous dust could cause *in situ* CO_2 production[15]. This is not the case for Antarctic ice, especially farther inland; but because outer parts of ice cores are always slightly contaminated by dust (from handling, storage or the atmosphere), dry extraction is needed even when analysing Antarctic samples. Last but not least, we know that current atmospheric CO_2 levels (407 p.p.m. in 2018; see go.nature.com/2j4heej) are probably unprecedented for the past 800,000 years[16].

"This pioneering work sparked research that now gives us an accurate record of atmospheric CO_2 levels."

One of the most intriguing puzzles in palaeoclimate science is why the periodicity of the climate cycle has changed: marine sediment records show that climate followed a 40,000-year cycle before 1.2 million years ago, but changed to 100,000-year cycles during the Mid-Pleistocene Transition, about 1 million years ago. Delmas and colleagues' legacy can be seen in an ongoing international Antarctic project that might shed light on this[17]. Known as 'Beyond EPICA Oldest Ice', it aims to extend the ice record to 1.5 million years ago by drilling down to 3 kilometres, to investigate greenhouse-gas levels and climate at that time.

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1. Delmas, R. J., Ascencio, J.-M. & Legrand, M. *Nature* **284**, 155–157 (1980).
2. Arrhenius, S. *Phil. Mag.* **41**, 237–275 (1896).
3. Croll, J. *Nature* **12**, 329 (1875).
4. Milankovitch, M. in *Handbuch der Klimatologie* (eds Köppen, W. & Geiger, R.) Part 1, 1–176 (1930).
5. Hays. J. D., Imbrie, J. & Shackleton, N. J. *Science* **194**, 1121–1132 (1976).
6. Scholander, P. F. *et al. Meddelelser om Grønland* **165**, 1–25 (1962).
7. Legrand, M. *et al. Anal. Chem.* **54**, 1336–1339 (1982).
8. Berner, W., Oeschger, H. & Stauffer, B. *Radiocarbon* **22**, 227–235 (1980).
9. Jouzel, J. *et al. Nature* **329**, 403–408 (1987).
10. Barnola, J. M., Raynaud, D., Korotkevich, Y. S. & Lorius, C. *Nature* **329**, 408–414 (1987).
11. Genthon, G. *et al. Nature* **329**, 414–418 (1987).
12. Petit, J.-R. *et al. Nature* **399**, 429–436 (1999).
13. Lüthi, D. *et al. Nature* **453**, 379–382 (2008).
14. Etheridge, D. M. *et al. J. Geophys. Res. Atmos.* **101**, 4115–4128 (1996).
15. Delmas, R. J. *Tellus B* **45**, 391–396 (1993).
16. Masson-Delmotte, V. *et al.* in *Climate Change 2013: The Physical Science Basis* (eds Stocker, T. F. *et al.*) 383–464 (Cambridge Univ. Press, 2013).
17. Fischer, H. *et al. Clim. Past* **9**, 2489–2505 (2013).
18. Lorius, C., Merlivat, L., Jouzel, J. & Pourchet, M. *Nature* **280**, 644–648 (1979).

Correction

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An earlier version of this article incorrectly credited the image in Figure 1. The correct credit is Vladimir Lipenkov.

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