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**ANTARCTIC AIR BUBBLES
AND
THE LONG-TERM ICE CORE RECORD OF CO₂ AND OTHER GREENHOUSE GASES**

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Parts of this chapter have been adapted from earlier review papers (Raynaud et al. 1993, Raynaud 2012)

Keywords : Antarctica, air bubbles in ice, Arrhenius prediction, ice core record of greenhouse gases, carbon dioxide record, glacial-interglacial cycles, ice age, interglacial periods, paleo-climate forcing, the last deglaciation.

Abstract

Nature has been continuously sampling the atmosphere at the surface of Antarctica throughout the ages. Atmospheric gases trapped in Antarctic ice provide the most direct record of past changes in greenhouse gas levels during the past 800,000 years. The best-documented and reliable trace-gas records are for CO₂ and CH₄, and Antarctic ice is the key player in recording past atmospheric CO₂. They are archives of the past and a window to present and future of the interplay between greenhouse gases and climate. We discuss the pioneering work of glaciologists measuring CO₂ in the air extracted from Antarctic ice, which confirmed Arrhenius' prediction about the role of atmospheric carbon dioxide in ice age climate. We detail here how the ice core record has been progressively extended to 4 and then to 8 glacial-interglacial cycles, i.e. over the last 800,000 years. The Antarctic ice record highlights the tight coupling between atmospheric CO₂ and Antarctic climate on the timescales of glacial-interglacial cycles for the entire 800,000 year interval. This close linkage suggests that glacial-interglacial variations of CO₂ explain a large fraction of glacial-interglacial climate changes observed in the Antarctic ice record, which is consistent with modelling results. We present more

recent works showing a near synchronous phasing between Antarctic temperature and CO₂ during the last deglaciation and pinpointing the important role of oceanic circulation in both heat transport and CO₂ outgassing. We also explore shortly the prospect for investigating Antarctic ice older than one million years to document what is often called the enigma of the Mid-Pleistocene transition around one million years ago.

1. Introduction: ice cores are archives of the past and a window over the present and the future

When looking at the present and future evolution of our climate, the lesson of past changes is essential. Indeed, by putting present climate change in the perspective of the past, we can disentangle anthropogenic forcing from the “natural” evolution of the climate system. Further, anticipating the future evolution of global climate under the influence of anthropogenic forcing requires an understanding of the climate processes, or mechanisms, involved in the long-term evolution of the climate system at orbital time scales, as well as of the feedbacks between climate and the biogeochemical cycles of greenhouse gases.

Archives of past climates can be found in various environments like marine sediments, corals, lake sediments, soils, trees, fossils of fauna and vegetation, carbonate concretions and ice cores. They contain preserved physical characteristics, generally called climatic proxies, reflecting local or more global climatic conditions prevailing at a given time of the past. Climatic proxies enable scientists to reconstruct the evolution of past climate. This precious information related to how our climate system works is useful for testing and improving the hierarchy of climate models used to understand our present climate and to simulate future climate.

*** Insert Figure 1 ***

Caption: The wealth of information on polar atmosphere and climate provided by different proxies measured on Antarctic or Greenland ice cores (see text, section1). The figure shows a picture of a thin layer of ice under polarized light. The ice crystals appear with different colours, depending on their orientations, and the black spots are

air bubbles trapped in ice. The bubbles at trapping time roughly occupy 10% of the total ice volume.

Credit: from Raynaud, 2012.

Figure 1 illustrates the wealth of information related with polar atmosphere and climate provided by different proxies contained in Antarctic or Greenland ice cores. The snow that falls on the surface of the ice sheet washes out atmospheric dust and aerosols, which can be later measured in ice cores. The isotopic composition (D/H or $^{18}\text{O}/^{16}\text{O}$) of the snow H_2O molecules reflects the temperature of snow formation and thus provides precious information about the past evolution of the climate at the surface of the ice sheets (see chapter 1 of this book). Analysis of the air entrapped in polar ice has led over the last 40 years to a set of discoveries concerning the interplay between greenhouse gases and climate.

The aim of the present chapter is to explain how scientists have been able to infer past changes of atmospheric greenhouse gases from polar ice cores and why Antarctic ice is the key player in establishing a reliable record of past atmospheric CO_2 . We will also discuss the degree of integrity of the ice core record of greenhouse gases and present the main trends of the ice core record of greenhouse gases at the orbital time scale over the last 800,000 years. Finally, we discuss the ice core record of greenhouse gases in the context of recent climate trends and the challenge of extending the Antarctic gas record beyond one million years ago.

2. Air trapping in ice

It is probably not so easy to date when the first prediction has been made, but since the mid-fifties (mid 1950's) appears the prediction that air bubbles trapped in polar ice may give information about the atmospheric air composition at the time the ice was formed (Scholander et al., 1956; Scholander et al., 1961). A nice and true Antarctic story happened in 1965. Claude Lorius, one of the major pioneer in ice core science, was drilling with a small group of glaciologists an ice core in Adelie Land, near Dumont D'Urville station. On the evening of a difficult day of drilling, the group had an aperitif

with glasses of whisky “on the rocks”. Tempted by sacrilege, the whisky was chilled with tiny ice cubes from the drilling and Claude Lorius looking in his glass, saw air bubbles released from their pressure and sparkling like champagne. He got the sudden intuition that Antarctic ice could well archive our past atmosphere. The story can be found in a book (*Lorius and Carpentier, Voyage dans l’Anthropocène, Actes Sud, 2010*). Indeed, the capacity of the Antarctic and Greenland ice formed in the dry snow zone (i.e. in absence of seasonal surface melting) to continuously sample over time a parcel of atmospheric air under the form of air bubbles is unique in the sedimentary world (figure 2).

*** Insert Figure 2 ***

Caption: Photo of a thin section of Antarctic ice (EPICA DC ice core) showing a myriad of air bubbles.

Credit: to be requested by the editor to luciasala2013@gmail.com, asking a high definition file of the photo and mentioning the use of the photo (Elsevier book)

The main processes involved in the air bubble formation and how the trapped air is kept in ice until it is analysed are presented here in sections 2.1 to 2.3, as well as how these processes may affect the integrity of the original atmospheric signal.

2.1 How air bubbles form.

Snowflakes accumulating at the surface of the ice sheet can already incorporate in the form of micro-bubbles a small amount of air enriched in CO₂ (Stauffer et al. 1981), but most of them should be lost during recrystallization process in the upper-layers near the surface (Schwander 1989). Also, in the warmest coastal areas, where summer surface melting can occur, refreezing of melted snow may enclose air, whose proportion of the gaseous components differs from the free atmosphere just above. This difference results from fractionation processes that occur during refreezing. Because of their different solubility coefficients in water, the most soluble components, like CO₂ and N₂O, become enriched.

Because of the enrichment of soluble gases occurring with melt, the best conditions for recovering a reliable atmospheric air record in ice are found in dry snow zones, where summer surface melting does not occur. After deposition at the surface, the snow is

progressively overlaid by new precipitations and transformed into firn, the intermediate stage between snow and glacial ice (figure 3).

*** Insert Figure 3 ***

Caption: Schematic cross-section of an ice core showing the transformation of snow into firn and bubbly ice and deeper of bubbly ice into clathrate ice. On the left side: ages of ice and corresponding depth levels as found in the EPICA DC ice core. Note that the age of the gas is younger than the age of the surrounding ice.

Credit: Figure 2.2 in Bereiter PhD thesis (Bereiter, 2012).

First, changes in the shape, size and orientation of the snowflakes take place until they reach the closest dense packing stage at relative densities of about 0.55-0.6. In this near-surface snow layer the pores still easily communicate with the free atmosphere and convection can take place under the influence of the wind.

Below this level is the firn column. In the firn column, plastic deformation of the ice material and recrystallization are the dominant processes of densification. Pores progressively become isolated from the atmosphere, enclosing a parcel of atmospheric air in airtight bubbles. We may note here that the transformation of snow into bubbly ice occurring at the surface of Antarctica is likely the largest experiment of sintering—a process well known in powder metallurgy and ceramic production, in which the powder is compacted and ultimately transformed into a solid mass without melting it to the point of liquefaction—on the planet. Sintering processes are strongly dependent on temperature and pressure. That is why the depth and age of the transition of firn into bubbly ice depend on the temperature and accumulation rate of the site. In Antarctica, this transition generally occurs between 50 meters (warm sites with high accumulation) and 120 meters (cold sites with low accumulation) beneath the surface, and takes between about 100 and 3000 years.

2.2 Processes involved in the firn column

The air in the snow layer, which can reach down to about 20 meters below the surface under present-day conditions (Bender et al. 2006), can be mixed by convection and has a gas composition similar to the one of the surface air averaged over several years. Just

below, in the firn, the air column is still communicating with the snow layer above – and hence with the free atmosphere – but is in pure diffusive equilibrium, i.e. submitted to gravitational settling, which may affect the original records of the past atmospheric gaseous composition. The heavier gas molecules are preferentially enriched toward the base of the firn, according to the height of the diffusive column (Craig et al. 1988, Schwander 1989). Thus, when it is trapped in bubbles at the base of the firn column (figure 3), the air has a composition generally slightly differing from the atmosphere prevailing at the surface, which can be corrected for with confidence, using the isotopic composition of molecular nitrogen (a stable tracer in the atmosphere over the time scales considered here). At the firn-ice transition and below (see figure 3), because of the combined effects of air mixing by diffusion through the firn column and of the large number of bubbles that close-off at various times, the air in a piece of ice is not composed of molecules with a single age, but rather with a range of ages, constrained by the time it takes the bubbles to close. As a consequence, the record of air measured along an ice core is smoothed with time. Also, in principle, physico-chemical processes may take place between the gas and solid phases in the firn, which would affect the air composition. But no significant deviation has been observed between the composition of the air entrapped in recently formed ice and the contemporaneous atmospheric composition (see section 3.1). The only artefact revealed recently concerns Antarctic sites with a very low accumulation rate (a few centimeters of water equivalent per year). There, preferential enclosure of snow layers can create stratigraphic inversions that can slightly bias the bubble record as measured at high depth resolution (Fourteau et al. 2017), specifically when the trace gas being measured shows an important temporal trend in the atmosphere.

In conclusion, we can consider with confidence, and in the limit of the experimental uncertainties and of investigations at very high resolution, that concentrations in greenhouse trace gases measured in ice at the firn-ice transition provide a record, with some temporal smoothing, of their atmospheric contents at the surface.

2.3. Processes involved below the firn-ice transition

Below the firn-ice transition, i.e. after the complete bubble close-off, the ice is buried and flows following the ice flow lines at the site. The bubbles generally become more spherical, their size decreasing with depth, and the air pressure inside them proportionally increases. Several hundred meters below the surface, the increased load pressure leads to the formation of air clathrates, i.e. bubbles progressively disappear and the gas molecules become encaged inside the ice matrix to form air hydrates. We call this depth interval the Bubble-Clathrate Transition Zone (BCTZ, see figure 3). At the end of the process all the bubbles disappear and the ice is transparent, but still contains the same amount of air as in the bubbly ice.

Obviously, the quality of the ice core is essential when investigating the record of atmospheric gases enclosed in the ice, and non-fractured ice is a basic prerequisite for preserving the integrity of the ice core record of atmospheric gases. With increasing depth, the overburden ice pressurizes air bubbles and causes fracturing in the cores when they are depressurized during the drilling process upon arrival at the surface (Neff 2014), in particular in the BCTZ. When all the bubbles are transformed into air hydrates, the ice is ductile enough to resist fracturing, and this is the end of what we call the brittle ice zone. This brittle zone is a real concern for glaciologists measuring trace atmospheric gases in deep ice cores. The depth interval of the BCTZ depends on the temperature and snow accumulation rate of the site. It is generally found 400-500 to 1200-1300 m deep in the central part of East Antarctica, as observed along the Vostok, Dome C and Dome F ice cores. Special care has to be taken for coring non-fractured ice there and to avoid post-coring processes. This is not an easy challenge. The recovered ice should relax at the coring site, often during a complete year, before it is transported to the laboratories.

Below the firn-ice transition, chemical and physical interactions between the gas phase and the ice matrix can occur and possibly affect the integrity of the atmospheric record, depending on the nature of the gas we are looking for and the method used for extracting the air from the ice (Kobashi et al. 2015). Since a special focus on the Antarctic ice record of CO₂ is made in this chapter, the example of this gas-trace will be treated in details below in section 3.2.

3. The ice core record of atmospheric greenhouse gases

The bubbles and clathrates in ice cores contain measurable records of trace gases in the atmosphere. We consider here the three well mixed and hence long-lived atmospheric trace greenhouse gases – CO₂, CH₄ and N₂O – that contribute most to current anthropogenic global warming, with a marked focus on the ice core record of past CO₂.

3.1 How precisely does the ice core record mirror past changes in greenhouse gases?

The degree of preservation of atmospheric greenhouse trace gases in ice cores is determined by various processes, which can alter the initial atmospheric composition, and is also limited by experimental uncertainties.

The choice of the sampling site is essential. It is primordial to avoid ice formation sites where summer melting can occur, especially when investigating the most soluble components like CO₂ and N₂O. In the case of CO₂, due to its very high purity level compared to Greenland ice, Antarctic ice must be preferentially chosen (see section 3.2.2). We note that the N₂O record can also be affected by geochemical and/or microbiological impurities incorporated in the ice (Miteva et al. 2016) .

The integrity of the ice core record of greenhouse gases depends on the quality of the ice, which can be fractured especially when drilling through the brittle zone. In the same zone, some fractionation may also occur during the transformation of bubbles to air hydrates, which can affect the gas composition at the centimetre scale (high resolution scale, see section 3.2.2 for the case of CO₂ fractionation between bubbles and air hydrates in the BCTZ).

So, providing that (i) we use appropriate analytical methods (for instance, precise CO₂ measurements require that the gas will be extracted from the ice by using a dry extraction method, as discussed in section 3.2.2), (ii) we select appropriate sampling sites and correct for gravitational fractionation through the firn column, and (iii) we carefully select ice samples, the ice core measurements can provide, within the experimental uncertainties, an accurate and faithful record of the smoothed changes in atmospheric greenhouse trace gases during the past. The smoothing effect, which depends on the site conditions (temperature, accumulation), removes high frequency

variations from the record. In some cases, small artefacts occur due to stratigraphic inversion during preferential layer trapping in the depth range where bubbles close. It should also be noted that overturned folds may exist in the basal layers of the ice sheet, inducing reversals in the stratigraphic order of the ice layers. In the case of the Vostok ice core, the climatic record provided strong indications in favour of a depth reversal in the stratigraphic order of the layer, which corresponds to the 3,320-3,345 m depth interval. The ice stratigraphy has been corrected for flow disturbance by establishing a common chronology with the record of the EPICA Dome C, which shows no ice flow anomaly for the ice of the same age (Raynaud et al. 2005).

Under the conditions stated above, the CO₂ measured in the ice is not a proxy but a true measurement performed on a parcel of air, which has been sampled during the past and preserved for long periods (as long as several hundred of thousands of years) in an ultra-clean container, the ice.

There are two ways to check the overall integrity of the ice core record of atmospheric CO₂ and more generally greenhouse trace gases.

The first is to measure air in firn air samples and recently formed ice, which overlaps in age with a record of air, whose composition has been directly measured in the atmosphere (instrumental records). This is possible for CO₂ since 1958, the year when the measurements of the first records of global significance started at the Mauna Loa Observatory and South Pole Station. This also requires an Antarctic ice record whose entrapped air extends into recent decades, as has been achieved at two sites, Siple Station and Law Dome (Neftel et al. 1985, Etheridge et al. 1996, Rubino et al. 2019). To match the instrumental record we need accurate CO₂ measurements in ice (say about ± 1 to 2 ppm) and accurate dating of the enclosed air. Furthermore, because the ice record of CO₂ is smoothed due to the diffusion through the firn and the air trapping processes (section 2.1), we should select sampling sites whose temperature and snow accumulation conditions allow a minimal smoothing effect, i.e. measured CO₂ concentrations averaged over a small number of years (possibly less than 10). A most extensive and accurate study has been obtained by Etheridge et al., (1996) who analysed the air extracted from three ice cores taken at Law Dome in East Antarctica. The Law Dome sites provide CO₂ concentrations averaged over about 12 years (D. Etheridge,

personal communication) and covering the 1959–1978 period; the reproducibility of CO₂ values measured on the same annual ice layer is better than 1.2 ppm (one standard deviation). Atmospheric CO₂ concentrations are nearly identical at Law Dome and South Pole, and the two records should overlap closely (allowing for the smoothing of rapid variations such as seasonality), unless there are errors in the dating of the air entrapped in the Law Dome ice. The results show that the CO₂ Law Dome record overlaps tightly, within the measurement uncertainty, for up to 20 years with the atmospheric South Pole record (figure 4).

*** Insert Figure 4 ***

Caption : CO₂ mixing ratios (in part per million, ppm) measured on ice cores from the Law Dome (Easr Antarctica) and from the atmosphere at South Pole Station (from, Etheridge et al , 1996). The CO₂ Law Dome records tightly overlap for up to 20 years with the atmospheric South Pole record.

Credit : Etheridge et al., 1996.

Since then, these results have been reproduced and extended to CH₄ and N₂O (MacFarling Meure et al. 2006), (Rubino et al. 2019). This evidence convincingly confirms the integrity of the ice core record of atmospheric CO₂ and other greenhouse trace gases, at least for recent periods.

A second way to check the integrity of the ice core record of greenhouse trace-gases, especially over long periods of the past, is to assess the degree of agreement between records from various ice cores obtained from different types of contemporaneous ice (for instance with and without air hydrates, at sites with different temperature and snow accumulation rate conditions, with different crystal sizes and fabrics) and also to measure again the same ice core record after a while to check its stability with time (Barnola et al. 1991, MacFarling Meure et al. 2006).

3.2. Antarctica: a location of choice for hosting past atmospheric CO₂ records

3.2.1 From Svante Arrhenius prediction to the ice record of atmospheric CO₂

At the end of the 19th century, the Swedish scientist Svante Arrhenius predicted, in a famous historical paper, that the cooler temperatures in glacial periods (with respect to the contemporaneous time) resulted from a decrease of about 40% of the capacity of CO₂ to absorb the heat from the ground (Arrhenius 1896).

The second part of the 20th century was the time of the pioneering works on gases trapped in ice. At this time we already aimed to confirm or reject Arrhenius' prediction by investigating how different the CO₂ content of the air extracted from ice formed during the last glaciation was compared to ice formed during the Holocene or to recent values. Several attempts were made during the 1960's and 70's, to get a reliable atmospheric CO₂ record from the gas extracted from polar ice, but all of these attempts failed. The results showed such unexplained enriched (with respect to the atmosphere) and scattered CO₂ levels that, both at the Bern and Grenoble glaciology groups, we even thought that the hope to get a record of the past atmospheric CO₂ could well become illusory. The two groups suspected that some extra CO₂ was trapped in the ice matrix itself. The question was: how could we identify separately the CO₂ trapped in the ice matrix from the atmospheric CO₂ initially enclosed in the air bubbles?

Searching how to overcome this challenge, the Bern laboratory extracted the gases by melting the ice under vacuum into two fractions, a first one before complete melting of ice and the second one after an integral gas extraction (Berner et al. 1980). They assumed that the first extraction fraction was representative of the composition of the air enclosed in the bubbles at close-off. In Grenoble, after different tests, the decision was made to develop a dry extraction method by crushing the ice under vacuum (figure 5) in order to avoid melting of ice and to eliminate as much as possible the contamination problems linked with the ice lattice (Delmas et al. 1980).

*** Insert Figure 5 ***

Caption: Dry method of gas extraction from ice used for CO₂ measurements in the Grenoble laboratory. The picture shows a closed stainless container with metallic balls inside for pulverising ice samples under vacuum and extracting the gas for CO₂ measurements.

Credit: photo D. Raynaud.

In both laboratories CO₂ content was measured by gas chromatography. The results of the two groups, based on measurements from sections of different ice cores (mainly from Antarctica but also one from Greenland), have been published almost simultaneously in 1980 (Berner et al., 1980; Delmas et al., 1980). For the first time, they suggest experimentally that atmospheric CO₂ concentrations have been as low as about 200ppm during the Last Glacial Maximum.

Of course, these pioneering works on glacial and Holocene ice had to be confirmed by more and more accurate measurements, but they supported, 84 years later, Arrhenius' prediction and are an essential milestone in the discovery of the long-term ice core record of CO₂ and other Greenhouse Gases.

3.2.2 Antarctica: the place to go for the best ice core record of past atmospheric CO₂

Following the pioneering work of Delmas et al. (1980), the glaciological community largely adopted the dry extraction method to extract air trapped in ice for CO₂ measurements. Indeed CO₂ can be slowly produced in situ in the ice after bubble close-off by carbonate-acid reaction or oxidation of organic material, when the ice contains enough impurities (carbonate dust particles or organic material). CO₂ measurements performed on the gas extracted from Greenland ice can show peaks, which are not observed in Antarctica on ice with the same gas age, and which cannot be explained in terms of atmospheric composition change. These "CO₂ deviations" observed in the Greenland record are attributed to the high level of impurities in Greenland ice compared to Antarctica. This disqualifies the Greenland ice for getting a reliable and accurate atmospheric CO₂ record. However, due to the very high purity level of the atmosphere over Antarctica, such CO₂ artefacts of the gas extracted from Antarctic ice are on the whole negligible, and reliable ice records of atmospheric CO₂ are provided by Antarctic ice cores. It is worth to note that only one long Antarctic ice core CO₂ record (Dome Fuji ice core) has been measured using a wet extraction method (Kawamura et al., 2003) and also partly using a dry extraction method (Kawamura et al., 2007). Although similar major glacial interglacial CO₂ trends are revealed with both methods, we observed significant differences, especially in terms of CO₂ concentration levels.

Concerning the question of the zone of transformation of bubbles into gas hydrates (see section 2.2 above), it is worth noting that high resolution CO₂ measurements performed on Antarctic ice sampled from this zone and just below reveal at the centimetre scale a large and unexpected scatter of the data (up to 25 ppm) around the mean atmospheric composition (Lüthi et al. 2010). Lüthi et al. proposed an explanation involving episodically increasing clathrate formation followed by diffusion processes from bubbles to clathrates, but the mean atmospheric CO₂ composition is not affected if CO₂ values are averaged over a longer depth scale (10 cm and more in the case of the EPICA DML ice core). However, significant differences (up to 10 ppm) are observed between ice cores where bubbles coexist with clathrates, compared with ice cores of similar ages where only bubbles are encountered (Shaefer et al., 2011). This indicates that care must still be taken for CO₂ measurements relying on samples from the bubble-clathrate transition zone.

Regarding methane, both Greenland and Antarctic ice cores have proven to give access to a faithful record of its changes in the atmosphere. It is only when addressing centimetre-scale measurements of CH₄ in Greenland ice that some artefacts could appear, possibly resulting from in-situ production through a microbial mechanism (Rhodes et al., 2016). However, such local artefacts do not affect the main features of the temporal record. Indeed, the combination of Greenland and Antarctic CH₄ records has been extensively used to measure the tiny difference of concentration between the two poles, an indirect tracer of the latitudinal distribution of methane sources and sinks, and thus of the causes of its past changes (Chappellaz et al., 1997 ; Baumgartner et al., 2012)

4. The ice core record of greenhouse gases over the last 800,000 years

Since the pioneering works published in 1980 and leading to the discovery of a glacial-interglacial atmospheric CO₂ signal, as mentioned above, a lot of work and progress has been made on deep ice core drilling and on reconstructing ice records of past atmospheric greenhouse trace gases: CO₂, but also CH₄ and N₂O.

The ice core record of greenhouse gases provides information on different temporal scales: from centennial and millennial scales to the Milankovich astronomical cycles. The major variations of water isotopes (δD and $\delta^{18}O$) in Antarctic ice cores allow us to reconstruct Antarctic temperature variations over the last 800,000 years, which cover 8

glacial-interglacial cycles. Atmospheric CO₂ closely generally parallels temperature variability as reconstructed during that period (Luthi et al., 2010; Fischer et al., 2010; Petit et al., 1999). During the interglacial periods, CO₂ concentration is relatively high, generally between 250–300 ppm. At the end of the interglacial periods, notably lagging the start of the Antarctic glacial cooling (Petit et al., 1999), CO₂ concentrations start to decrease slowly, to values of about 180 ppm at the glacial maxima, which correspond with ice volume maxima and sea level minima. During the 8 glacial-interglacial periods, CO₂ concentrations remain within upper and lower boundaries of ~280 and ~180 ppm, reflecting effective boundaries on the climate system (Galbraith and Eggleston, 2017). At the end of the glacial periods, atmospheric CO₂ increases rapidly from the glacial period level to the interglacial level. These transitional periods are called the glacial terminations.

Among glacial periods, the last glacial period has been carefully investigated in Antarctic ice cores. Millennial-scale variability of atmospheric CO₂ are closely linked to major variations of isotopic records of Antarctic temperature (Ahn and Brook, 2014; Bereiter et al., 2012), varying on the order of 10–20 ppm during the major Antarctic temperature peaks (Bereiter et al., 2012). During the smallest Antarctic isotope maxima events, smaller CO₂ variability is observed, generally less than 5 ppm (Ahn and Brook, 2014; Bereiter et al., 2012). During these smaller changes, the magnitude of atmospheric CO₂ variation does not match the magnitude of temperature variation in Antarctica.

CO₂ variations are relatively stable during the interglacial periods as compared to glacial periods. For example, during the Holocene period atmospheric CO₂ shows multi-centennial to millennial variability of ~2–9 ppm (Ahn et al., 2012; Flückiger et al., 2002; Indermühle, A., et al. (1999); Marcott et al., 2014; Monnin et al., 2004).

This section is essentially devoted to:

- The history of the reconstruction of the long glacial-interglacial ice core record of atmospheric greenhouse gases
- The assessment of the interplay between atmospheric CO₂ and Climate at the glacial-interglacial time scale
- Underlining the variety of the interglacial periods
- Presenting a high resolution CO₂ record from the West Antarctic Ice Sheet (WAIS) Divide ice core in order to discuss more specifically the interplay between atmospheric CO₂ and Temperature during the last deglaciation.

4.1 Ice core records of atmospheric greenhouse gases

4.1.1. Vostok ice core, the cornucopia and the four last ice age cycles

The story of long ice core records of greenhouse gases starts with the long venture of drilling operations at Vostok, the Antarctic Soviet station on the high East Antarctic Plateau (see figure 6).

*** Insert Figure 6 ***

Caption: Map of Antarctica showing the localisation of Antarctic ice core sites mentioned in chapter 2:

East Antarctica: Dome Fuji (DF), EPICA Dome C (EDC), Law Dome (LD), Vostok (VK)

West Antarctica: WAIS Divide (WD)

The map also shows the contours of surface topography.

Credit: Bedmap2 for surface topography. Free access.

The term *Cornucopia* was attributed to the Vostok ice core by the British scientific journal *Nature* (Campbell 1987, Stauffer 1999), essentially because the reconstruction of the history of two major greenhouse trace gases (CO_2 and CH_4) from measurements performed on the Vostok ice core appeared to be of wide interest among a large scientific community and decision makers, well beyond the relatively small community of those interested in the past history of our climate.

In 1987, *Nature*, in its October 1st issue, published three articles presented by a French-Soviet collaboration on the Vostok ice core (Barnola et al. 1987, Genthon et al. 1987, Jouzel et al. 1987). At this time the Vostok ice core, recovered by the Soviet Antarctic Expeditions in East Antarctica, was 2,083m long, the deepest to have been drilled, and the published records extended through the last glaciation, the last interglacial and the preceding glaciation back to about 160,000 years ago (Jouzel et al. 1987), i.e. a full ice age cycle. The CO_2 record (Barnola et al. 1987) measured using the dry extraction method exhibits two dramatic shifts from about 190 to 280 ppm which correspond to the two deglacial transitions, not only confirming both the prediction of Arrhenius and the pioneering works of 1980, but for the first time showing a high correlation between

CO₂ concentrations and Antarctic climate with significant oscillatory behaviour of CO₂ between high levels during interglacial periods and low levels during glacial periods. Besides the major cycle of about 100,000 years, the record seemed to also exhibit a cyclic change with a period close to 21,000 years, suggesting that the global climate system and carbon cycle are highly interactive (Genthon et al. 1987, Lorius et al. 1990).

*** Insert Figure 7 ***

Caption: **Vostok ice core** (from Barnola et al., 1987)

The first record of atmospheric CO₂ variations over a full glacial interglacial cycle. The record shows a high correlation between CO₂ and Antarctic temperatures (derived from the ice isotopic composition) with a marked oscillatory behaviour of CO₂ between high levels during interglacial periods and low levels during glacial periods.

Credit: Barnola et al., Nature, 1987

About 10 years after the publication of the Vostok records covering the last 160,000 years, the drilling operation at Vostok reached a depth of 3,623 m and allowed the extension of the ice record of atmospheric composition and climate to the past four glacial-interglacial cycles (Petit et al. 1999). This highly cited paper confirms that the close correlation already obtained during the last climatic cycle between temperature and atmospheric concentrations of CO₂ and CH₄ at the scale of glacial-interglacial changes hold also during the past four cycles. Thus, changes in these greenhouse trace-gases are notably an inherent phenomenon of change between glacial and interglacial periods.

Due to their different lifetime in the atmosphere and to the different sources and sinks responsible for their natural changes, CO₂ and CH₄ depict significant differences of trends at shorter time scales than glacial-interglacial changes. Namely, methane shows abrupt changes of millennial or centennial-scale nature which parallel temperature changes as recorded in Greenland ice. These changes are characterized by rapid increases of up to 200 ppb within only 100 to 200 years, followed by slow decreases (Delmotte et al., 2004 ; Chappellaz et al., 2013 ; Baumgartner et al., 2014). For CO₂, more progressive changes are generally observed, mimicking the evolution of Antarctic temperature (Bauska et al., 2018).

4.1.2 More information on CH₄, N₂O, and on the carbon isotopic ratio (¹³C/¹²C) of CO₂

Three years later than CO₂, a companion Vostok record of CH₄ covering the last 160,000 years was completed (Chappellaz et al., 1990). The methane measurements also revealed substantial changes over the past 160,000 years, which are associated with climate changes and interpreted as resulting from variations of wetland areas notably in tropical regions. Analyses of N₂O in ice cores proved to be possible in the early 1990s. The first glacial-interglacial investigation was conducted on the Byrd ice core (Leuenberger and Siegenthaler, 1992) and showed values 30% lower during glacial conditions. Afterwards, N₂O was measured in the Vostok ice core as well (Sowers, 2001). It revealed the presence of large artefacts in ice formed during glacial conditions but it also confirmed the high values observed during interglacial periods. Although the highest and lowest values in the CO₂, CH₄ and N₂O records are found during the warmest and coldest conditions respectively, the difference between the 3 signals should reflect the predominant sources, which are different for each of these three greenhouse trace-gases. For CO₂, analyses of its stable carbon isotopic ratio (¹³C/¹²C) indicate that the transfer of old carbon from the deep ocean to the atmosphere during glacial-interglacial transitions probably contributed the most to the concomitant ~40% increase of its atmospheric concentration (Lourantou et al., 2010, Schmitt et al., 2012). The decomposition of permafrost carbon at the start of deglaciations could have contributed in addition (Crichton et al., 2016). Regarding CH₄, investigations of its dual carbon and hydrogen stable isotopic composition as well as of the inter-polar gradient indicate that tropical wetlands most probably controlled most of its past changes (Bock et al., 2017), with only minor contributions from geological sources. Lastly for N₂O, isotopic investigations on nitrogen and oxygen atoms of the molecule indicate that terrestrial and marine sources contributed equally during deglaciations while terrestrial sources were probably the main contributors to millennial-scale changes of this trace gas (Schilt et al., 2014).

The results also show that methane and nitrous oxide have probably contributed, like carbon dioxide to glacial-interglacial temperature changes, but with a much more reduced amplitude.

4.1.3 Extension of the record back to 800,000 years ago.

The close correlation shown at Vostok between CO₂ and CH₄ on one side and Antarctic and Northern Hemisphere temperature for the last four climatic cycles has now been shown to be valid even further in the past with the EPICA DC records extending the CO₂ (Siegenthaler et al., 2005; Lüthi et al., 2008 as recently revised and updated (Bereiter et al., 2015) and CH₄ records (Loulergue et al., 2008) back to 800,000 years ago (figure 8). A major conclusion of these records is that present atmospheric CO₂ and CH₄ mixing ratios have, most likely, never been reached during the past 800,000 years.

*** Insert Figure 8 ***

Caption: The ice core (Vostok and EPICA DC) record of atmospheric CO₂ (Petit et al., 1999; Siegenthaler et al., 2005; Lüthi et al., 2008; Bereiter et al., 2015) and CH₄ (Loulergue et al., 2005) covering the last 800,000 years, in comparison with the isotopic (D/H) ice core (EPICA DC) record (Jouzel et al., 2007) taken as a proxy for Antarctic temperature. The records are plotted on the AICC2012 age model.

Horizontal dashed lines are drawn as values considered typical of the preindustrial atmosphere (CO₂: 280 ppm; CH₄ 700 ppb).

Marine Isotope Stages MIS 11 and MIS 19 are two interglacial periods cited in the text.

Credit: References in caption

Interglacial diversity

Interglacial periods, including the current Holocene period, are warm end-member of glacial cycles. An extensive review on interglacials of the last 800,000 years has recently been published (PAGES, 2016).

Figure 8 shows the diversity of the eleven interglacial periods recorded during the last 800,000 years in Antarctic ice. A striking observation is the change in strength of interglacial periods at 450 ka, which is apparent in atmospheric CO₂ and CH₄ as well as in Antarctic temperature. It also appears in deep ocean temperature records, although it is missing in many other oceanic and continental records (PAGES, 2016).

Based on model experiments, the glacial threshold, i.e. the end of an interglacial, depends not only on insolation but also on atmospheric CO₂ level (Archer and Ganapolski, 2005). Understanding the role of the carbon cycle in the dynamics of interglacial periods becomes essential, and knowledge of the length of the pre-Holocene interglacials is important to understand how natural processes, modified by human influence on atmospheric greenhouse gases, will control the future evolution of the Holocene. On this respect, glacial inceptions at the end of past interglacials, which occurred near summer insolation minimum - i.e. under an astronomically-forced insolation configuration rather close to the current one - are of interest. This is the case of the interglacial periods MIS11 and MIS19 (see figure 8), around respectively 400,000 and 780,000 years ago. Although they have similar insolation configurations, MIS 11, an exceptionally long interglacial, last much longer (about 30ka) than MIS 19 (about 13 ka) (PAGES 2016). The explanation is likely due to lower CO₂ concentrations (about 240 ppm) during MIS 19, compared to MIS 11 (close to 280 ppm, like the pre-industrial level). This is in line with model results suggesting that in the current astronomical configuration (weak minimum in summer insolation) glacial inception would require CO₂ concentrations below the pre-industrial level (PAGES, 2016, and references herein). So, our current interglacial, given concentrations of atmospheric CO₂ much higher - because of human activity - than during the last 11 interglacial periods, is expected to be longer than any of those observed during the last 800,000 years.

4.2. Phase relationship (leads and lags) between atmospheric CO₂ and temperature in the ice core record.

4.2.1. Why calculate leads and lags?

The unique record of past atmospheric composition in Antarctic ice cores leads to an intriguing question: how did CO₂ concentrations in the past interact with global and regional temperatures?

Several climate processes can link these two variables. The first, and most obvious, is the greenhouse effect. Increasing CO₂ concentrations should lead to higher global temperatures, as is the case for current warming. However, the release of CO₂ from oceanic and terrestrial reservoirs into the atmosphere can itself be provoked by

mechanisms associated with changing temperature. Changes in Antarctic temperature can be related to changes in the heat transport related to oceanic circulation, which itself controls the upwelling of CO₂-rich waters in the Southern Ocean. Temperature changes can also provoke changes in land surface vegetation, changing the terrestrial carbon stock. The operation of these CO₂-climate feedbacks during past climatic changes is still mostly unexplored. One of the simplest ways to begin to characterize the relationship between these two strongly coupled variables is to precisely understand their relative timings, or leads and lags, during large-scale climatic changes.

The warming interval occurring from 22,000 to 11,500 years before present (BP; years before 1950) is known as the last deglaciation, or Termination 1 (T1). This interval offers a case study for a period of global mean surface temperature increase across the globe by 3 and 8 ° C (Masson-Delmotte et al., 2013). The last deglaciation is well-recorded in ice cores, with high resolution CO₂ and isotopic temperature proxy measurements, and relatively low dating uncertainty with respect to older periods of global-scale climatic change.

In Antarctica, the isotopic temperature record is marked by four visually evident changes in trend during the last deglaciation (as shown in Figure 9)--and these overall trends are visible in many paleoclimate records from the Southern Hemisphere (Pedro et al., 2016). At around 18,000 years BP, temperature began to increase consistently, at what we refer to as the deglaciation onset, or T1 onset. This trend was interrupted at around 14,500 years BP, when Antarctic temperature decreased and then stabilized until around 12,500 years BP, during what we refer to as the Antarctic Cold Reversal, or ACR. At the end of the ACR, the deglacial temperature increase resumed, with the end of T1 occurring at around 11,500 years BP.

Interestingly, temperature in the northern hemisphere did not follow the same patterns during the deglaciation. The initial deglacial warming was much more limited. At roughly the same time as the Antarctic Cold Reversal, the Northern Hemisphere experienced an abrupt warming, followed by a period of warm, stable to slightly decreasing temperatures known as the Bølling-Allerød. As Antarctica warmed after 12,500 years BP, the Northern Hemisphere entered a cold period known as the Younger Dryas, finally beginning to warm at around 11,500 years BP. This anti-phased behavior

of Northern and Southern Hemisphere climate on millennial timescales is often referred to as the bipolar seesaw. Variations in methane, which approximately track Northern Hemisphere climate during T1, represent these Northern Hemisphere trends in Figure 9.

4.2.2. How to calculate leads and lags?

To calculate leads and lags between Antarctic Temperature and CO₂, it is essential to have an accurate chronology of the ice and gas in an ice core, ideally with low relative uncertainty between the two. Since temperature proxies are contained in the ice, we can only estimate leads or lags in terms of probabilities, to within the relative age uncertainty between the air and the ice.

Two simple methods have been traditionally used to calculate leads and lags between time series. The first estimates a fixed lag across the entire time interval of the two series, by calculating the lag at which the correlation between the two series is largest. The second method calculates leads and lags between coherent change points—times at which the overall trends of the series change. This allows for the leads and lags to change over time, reflecting changing climate mechanisms. Since the deglacial records of CO₂ and Antarctic Temperature can be approximated by a series of straight lines, with changing slope, several studies have used piecewise linear fits to estimate the probabilities of the locations of change points.

4.2.3. A history of leads and lags results during the last deglaciation

Using measurements from the EPICA Dome C ice core, Monnin et al. (2001) reported that at the onset of the last deglaciation, around 18,000 years ago, CO₂ lagged temperature by 800 ± 600 years. This estimate was widely cited, and was briefly popular among deniers of global climate change, who argued that since CO₂ was not the initial driver of warming during the last deglaciation, it could not be held responsible for current warming.

This argument was wrong for three reasons. First, Antarctic temperature is not representative of global temperature. Rather, it reflects a specific set of processes in the climate system—in particular, the transport of heat to and from the Southern

Hemisphere via oceanic and atmospheric circulation, which can be further modulated by regional-scale circulation.

Second, CO₂ certainly acted as an amplifier of global temperature change during the last deglaciation, regardless of whether or not an increase in Antarctic temperature preceded its initial release. Shakun et al. (2012), using a stack of temperature proxy records from across the globe, showed that global temperature lagged CO₂ during the last deglaciation by 460±340 years. The magnitude of temperature change during the deglaciation would not have been possible without the greenhouse forcing of CO₂.

Third, the age difference between the ice and air in the EPICA Dome C ice core was incorrectly estimated at the time of the Monnin et al. (2001) study. Parrenin et al. (2013) were able to better constrain this difference, using the ratio of ¹⁵N/¹⁴N, which depends on the height of the firn column, to revise the air age scale. Using piecewise linear fits to CO₂ and a stack of five isotopic temperature records, the authors assessed the probabilities of leads and lags at four key change points: the deglaciation onset (~18,000 years BP), at the beginning and end of the Antarctic cold reversal, a period during which Southern Hemisphere temperature cooled and then stabilized (from ~14,500 to ~12,500 years BP) and finally at the end of the termination, corresponding with the onset of the Holocene period (~11,500 years BP). The authors found the CO₂ and Antarctic temperature to be synchronous within 200 years, with the exception of the termination end, where temperature appeared to lead CO₂ by 500±90 years.

These estimates, indicating a tighter synchrony between CO₂ and Antarctic temperature, agreed with the results of Pedro et al. (2012), who had assessed the phase relationship using CO₂ series from the Siple Dome and Byrd ice cores, and an independently developed stack of Antarctic temperature. Using cross-correlation between the series to assess leads and lags, the authors found the two series to be synchronous within 400 years.

4.2.4. New Results from WAIS Divide

The West Antarctic Ice Sheet Divide (WAIS Divide) ice core, for which drilling was finished in 2011, provided a new opportunity to assess leads and lags between CO₂ and Antarctic Temperature. The chronology of the WAIS Divide core is based on annual layer

counting in the ice phase (an accurate dating method) and well-constrained firn modeling in the air phase (Sigl et al., 2016) during the last termination.

Chowdhry Beeman et al. (2019) used a new CO₂ record of unprecedented resolution from WAIS Divide (Marcott et al., 2014) and a stack of five Antarctic δ¹⁸O records, aligned to the much more precise WAIS Divide chronology using volcanic events recorded in the ice (Buizert et al., 2018) to recalculate leads and lags during T1. Using updated statistical methods, the number and timing of key change points in the two series are found by exploring the full range of the time series, rather than assumed *a priori* as in earlier studies (figure 9).

*** Insert Figure 9 ***

Caption: : Antarctic temperature, atmospheric CO₂ and CH₄ during the last deglaciation (adapted from Chowdhry Beeman et al., 2019)

From top to bottom: the d18O stack of Buizert et al., denoted ATS3 (2018), representing mean Antarctic temperature variations during the deglaciation; the CO₂ record from WAIS Divide (Marcott et al., 2014); and the WAIS Divide Methane record (Rhodes et al., 2015) which provides an analog for Northern Hemisphere and low latitude climate. The approximate timings (95% probability) of the four major coherent changes for Antarctic Temperature and CO₂ identified by Chowdhry Beeman et al. (2019) are shown as grey bars.

Credit: adapted from Chowdhry Beeman et al. (2019)

The four key changes identified by Parrenin et al. (2013)—the Deglaciation onset, Antarctic Cold Reversal onset, Antarctic Cold Reversal end, and Deglaciation end—were all confirmed to be present in both records, with two overall patterns of phasing: tight synchrony of CO₂ with the Antarctic Temperature stack during the Antarctic cold Reversal and a temperature lead on the order of 500 years at the Deglaciation onset and Deglaciation end. Synchrony is within the 95% central probability intervals for each of the changes except the Deglaciation end (where Parrenin et al., as well, identified a likely about 500 year temperature lead).

The precise volcanic synchronization of Buizert et al. (2018) also allows for an assessment of change point timings for the individual δ¹⁸O series. Though the four major

temperature changes were coherent across the Antarctic continent, their timings indeed varied. This is especially true for the WAIS Divide $\delta^{18}\text{O}$ series, representing temperature in West Antarctica, which is climatically distinct from East Antarctica even on long timescales.

The overall conclusion is that Antarctic Temperature and atmospheric CO_2 were near synchronous, and very closely linked, during the last deglaciation. This is likely because of the important role of oceanic circulation in both heat transport and CO_2 outgassing. Nevertheless, phasing varied in time. This indicates that explanations of the close coupling of CO_2 and Antarctic temperature during the deglaciation must allow for external changes to the circulation mechanisms that control heat transport and CO_2 outgassing, and/or internal feedbacks in the climate-carbon cycle. Pinpointing these changes and feedbacks will allow us to better understand the mechanisms of CO_2 release during deglacial periods.

5. Conclusions

5.1 The Carbon cycle and Climate: lesson from the ice core record of CO₂ and other Greenhouse Gases

Just after the measurements by the groups in Grenoble and in Bern on gases bound in polar ice cores provided the first tantalizing data for atmospheric CO₂ concentrations substantially lower than present values during the last glacial period (Delmas et al., 1980; Berner et al., 1980), Wallace Broecker, a prominent geochemist, proposed to explore the cause of this change (Broecker 1982). Later, Broecker and Peng (1986) estimated that the hottest topic for those interested in the earth's carbon cycle is the change in atmospheric CO₂ content between glacial and interglacial time. Since then, numerous studies have been performed to assess the degree of integrity of the Antarctic record of CO₂ and other greenhouse trace gases and validate the glacial-interglacial cycles. Although the two fundamental questions asked by Broecker and Peng: "What causes the glacial-interglacial CO₂ changes? What is their role in glacial cycles?" are not yet fully understood, however the lesson from the ice core record of greenhouse gases is important. This non-exhaustive list highlights critical components of our current understanding of the carbon cycle that are all essentially based on the analysis of gases trapped in Antarctic ice cores:

- The current atmospheric concentration in CO₂ and CH₄ are likely unprecedented during the last 800,000 years.
- The close correlation between greenhouse gases and climate over glacial-interglacial cycle attests to the tight coupling between climate and carbon cycle during the late Pleistocene.
- Insolation changes driven by Earth's orbital and axial oscillations (Milankovich astronomical cycles) are pacemakers of the glacial cycles. But radiative forcing of greenhouse gases (3W/m²) together with extent and decay of the northern ice sheets (3W/m²) are the main key drivers of glacial-interglacial cycles.
- Antarctic temperature and atmospheric CO₂ are near synchronous and very closely linked during the last deglaciation. This is likely because of the important role of oceanic circulation in both heat transport and CO₂ outgassing. The study

of the last deglaciation allows us to better understand the mechanisms of CO₂ release during deglacial periods.

- Changes in climate and CO₂ reconstructed from ice cores offer a benchmark against which climate and carbon cycle models can be tested.

5.2 The enigma of the Mid-Pleistocene Transition: a stimulating project

The long-term Antarctic ice core record of CO₂ and other greenhouse gases has much more to reveal not only at the millennial scale of variability but also at the scale of the Milankovich cycles. During the Pleistocene, roughly the last 2.5 million years, the Earth's surface has experienced a series of glacial-interglacial cycles stimulated by changes in the distribution of the solar radiation reaching the Earth's surface, themselves driven by the periodicities of the Earth's motion around the sun (about 100 and 400 ka) and of changes in the tilt (41 ka) and direction (23 and 19ka) of Earth's rotation axis. These oscillations are well imprinted in the long deep-sea sediment records (Lisiecki and Raymo 2005) but surprisingly, they indicate a systematic change in the predominant periodicity from about 40 to about 100ka around one million years ago, although there is no marked change in the insolation signal driven by the Earth's orbital and axial parameters. This is called the Mid-Pleistocene Transition (MPT) and is a major, if not the key Pleistocene enigma yet to be solved. Most hypotheses for the origin of the MPT invoke a response to a long-term cooling possibly induced by decreasing atmospheric CO₂ concentrations (Clark et al., 2006, and reference herein). Assuming that the Pliocene cooling played a major role in the establishment of the MPT, we have to assess the potential contribution of atmospheric CO₂ to this cooling trend and to the MPT shift between obliquity and eccentricity as the dominant signal in the paleo-record. Clearly, the most direct and reliable archive of long-term atmospheric CO₂ has to be searched in Antarctica. Unfortunately, as mentioned in this chapter, no long vertical ice core offers, up to date, a continuous chronological sequence reaching one Ma or more. To recover such a core is one of the major and exciting challenges in ice core science for the near future (Fischer et al., 2013).

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References

Ahn, J., and E. J. Brook, 2008: Atmospheric CO₂ and climate on millennial time scales during the last glacial period. *Science*, **322**, 83–85.

Ahn, J., et al. (2012): "Atmospheric CO₂ over the last 1000 years: A high-resolution record from the West Antarctic Ice Sheet (WAIS) Divide ice core", *Global Biogeochemical Cycles*, **26**.

Ahn, J. and Brook, E. J. (2014): "Siple Dome ice reveals two modes of millennial CO₂ change during the last ice age", *Nature Communications*, **5**, 3723.

Archer, D., and Ganopolski, A. (2005). "A movable trigger: Fossil fuel CO₂ and the onset of the next glaciation." *Geochemistry, Geophysics, Geosystems* 6.5.

Arrhenius, S. (1896). "On the influence of carbonic acid in the air upon the temperature of the ground." *The London, Edinburgh, and Dublin Philosophical Magazine* **41**(251): 237-275.

Barnola, J.-M., et al. (1991). "CO₂ climate relationship as deduced from the Vostok ice core: a re-examination based on new measurements and on a re-evaluation of the air dating." *Tellus B* **43**: 83-91.

Barnola, J.-M., et al. (1987). "Vostok ice core provides 160,000-year record of atmospheric CO₂." *Nature* **329**(6138): 408-414.

Baumgartner, M., et al. (2012): "High-resolution inter-polar difference of atmospheric methane around the Last Glacial Maximum." *Biogeosciences* **9**: 3961-3977

Baumgartner, M., et al. (2014). "NGRIP CH₄ concentration from 120 to 10 kyr before present and its relation to a $\delta^{15}\text{N}$ temperature reconstruction from the same ice core." *Climate of the Past* **10**(2): 903-920.

Bauska, T., et al. (2018). "Controls on millennial-scale atmospheric CO₂ variability during the last glacial period." *Geophysical Research Letters* **45**(15): 7731-7740.

Bender, M., et al. (2006). "Gas age-ice age differences and the chronology of the Vostok ice core, 0-100ka." *J. Geophys. Res.* **111**(D21).

Bereiter, B. (2012). « Atmospheric CO₂ reconstructions using polar ice cores : development of a new dry extraction device and insights from highly resolved records. » PhD Thesis, University of Bern.

Bereiter, B., et al. (2012): "Mode change of millennial CO₂ variability during the last glacial cycle associated with a bipolar marine carbon seesaw", *Proceedings of the National Academy of Sciences* **109**, 9755-9760.

Bereiter, B., S. Eggleston, J. Schmitt, C. Nehrbass-Ahles, T. F. Stocker, H. Fischer, S. Kipfstuhl, and J. Chappellaz (2015), Revision of the EPICA Dome C CO₂ record from 800 to 600 kyr before present, *Geophys. Res. Lett.*, **42**, 542–549, doi:10.1002/2014GL061957.

Berner, W., et al. (1980). "Information on the CO₂ cycle from ice core studies." *Radiocarbon* **22**: 227-235.

Bock M., et al. (2017). "Glacial/interglacial wetland, biomass burning, and geological methane emissions constrained by dual stable isotopic CH₄ ice core records." Proceedings of the National Academy of Sciences of the USA, **114** (29), E5778-E5786, 2017.

Broecker, W. S. (1982). "Glacial to Interglacial Changes in Ocean Chemistry." Progress in Oceanography **11**: 151-197.

Broecker, W. S. and T.-H. Peng (1986). "Glacial to interglacial changes in the operation of the global carbon cycle." Radiocarbon **28** (2A): 309-327.

Buizert, Christo, et al. (2018). "Abrupt ice-age shifts in southern westerly winds and Antarctic climate forced from the north." Nature **563**: 681.

Campbell, P. (1987). "The Antarctic cornucopia." Nature **329**: 387.

Chappellaz, J., et al. (1990). "Ice-core record of atmospheric methane over the past 160,000 years." Nature **345**(6271): 127-131.

Chappellaz J., et al. (1997). "Changes in the atmospheric CH₄ gradient between Greenland and Antarctica during the Holocene." Journal of Geophysical Research **102**, 15987-15997.

Chappellaz, J., et al. (2013). "High-resolution glacial and deglacial record of atmospheric methane by continuous-flow and laser spectrometer analysis along the NEEM ice core." Climate of the Past **9**(6) : 2579-2593.

Chowdhry Beeman, J., et al. (2019). "Antarctic temperature and CO₂: near-synchrony yet variable phasing during the last deglaciation." Clim. Past **15**(3): 913-926.

Clark, P. U., et al. (2006). "The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric pCO₂." Quaternary Science Reviews: doi:10.1016/j.quascirev.2006.1007.1008.

Craig, H., et al. (1988). "Gravitational separation of gases and isotopes in polar ice caps." Science **242**: 1675-1678.

Crichton K.A., et al. (2016). "Permafrost carbon as a missing link to explain CO₂ changes during the last deglaciation ». Nature Geoscience **9**: 683-686.

Delmas, R. J., et al. (1980). "Polar ice evidence that atmospheric CO₂ 20 000 BP was 50% of the present." Nature **284**: 155-157.

Delmotte, M., et al. "Atmospheric methane during the last four glacial-interglacial cycles: Rapid changes and their link with Antarctic temperature." Journal of Geophysical Research: Atmospheres **109**.D12 (2004).

EPICA-COMMUNITY-MEMBERS (2004). "Eight glacial cycles from an Antarctic ice core." Nature **429**(6992): 623-628.

Etheridge, D. M., et al. (1996). "Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firn." Journal of Geophysical Research **101**: 4115-4128.

Fischer, H., et al. (2010): "The role of Southern Ocean processes in orbital and millennial CO₂ variations—A synthesis", Quaternary Science Reviews, **29**, 193-205.

Fischer H., Severinghaus J., Brook E., Wolff E., Albert M., Alemany O., Arthern R., Bentley C., Blankenship D., Chappellaz J., Creyts T., Dahl-Jensen D., Dinn M., Frezzotti M., Fujita S., Gallee H., Hindmarsh R., Hudspeth D., Jugie G., Kawamura K., Lipen- kov V., Miller H., Mulvaney R., Parrenin F., Pattyn F., Ritz C., Schwander J., Steinhage D., van Ommen T., Wilhelms F. (2013). Where to find 1.5 million yr old ice for the IPICS «Oldest-Ice» ice core, Climate of the Past **9** : 2489–2505.

Fourteau, K., et al. (2017). "Analytical constraints on layered gas trapping and smoothing

of atmospheric variability in ice under low-accumulation conditions." Climate of the Past **13**: 1815-1830.


Flückiger, J., et al. (2002): "High-resolution Holocene N₂O ice core record and its relationship with CH₄ and CO₂." Global Biogeochemical Cycles, **16**, 10-11-10-18.

Galbraith, E. and Eggleston, S. (2017): "A lower limit to atmospheric CO₂ concentrations over the past 800,000 years." Nature Geoscience, **10**: 295.

Genthon, C., et al. (1987). "Vostok ice core: climatic response to CO₂ and orbital forcing changes over the last climatic cycle." Nature **329**: 414-418.

Indermühle, A., et al. (1999): "Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica." Nature, **398**: 121.

Jouzel, J., et al. (1987). "Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years)." Nature **329**(6138): 403-408.

Kawamura, K. et al. (2003) Atmospheric CO₂ variations over the last three glacial-interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique. Tellus **B 55**, 126–137. 

Kawamura, K., et al. (2007). "Northern Hemisphere forcing of climatic cycles in Antarctica over the past 360,000 years." Nature **448**: 912-916.

Kobashi, T., et al. (2015). "Post-bubble close-off fractionation of gases in polar firn and ice cores: effects of accumulation rate on permeation through overloading pressure." Atmos. Chem. Phys. **15**: 13895-13914.

Lisiecki, L. E. and M. E. Raymo (2005). "A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}\text{O}$ records." Paleoceanography **20**: PA1003,doi:10.1029/2004PA001071.

Lorius, C., et al. (1990). "The ice-core record: climate sensitivity and future greenhouse warming." Nature **347**(6289): 139-145.

Loulergue L., et al. (2008). Orbital and millennial-scale features of atmospheric CH₄ over the past 800,000 years. Nature **453** : 383-386.

Lourantou A., et al. (2010). "Constraint of the CO₂ rise by new atmospheric carbon isotopic measurements during the last deglaciation." Global Biogeochemical Cycles, **24**: 545.

Lüthi, D., et al. (2010). "CO₂ and O₂/N₂ variations in and just below the bubble-clathrate transformation zone of Antarctic ice cores." Earth and Planetary Science Letters **297**: 226-233.

Lüthi, D., et al. (2008). "High-resolution carbon dioxide concentration record 650,000-800,000 years before present." Nature **453**: 379-382.

MacFarling Meure, C., et al. (2006). "Law Dome CO₂, CH₄ and N₂O ice records extended to 2000 years BP." Geophysical Research Letters **33**(L14810): doi:10.1029/2006GL026152.

Marcott, S. A., et al. (2014). "Centennial-scale changes in the global carbon cycle during the last deglaciation." Nature **514**: 616-619.

Masson-Delmotte, V., et al. (2013). Information from Paleoclimate Archives. Climate Change 2013: The Physical Science Basis. T. edited by: Stocker, Qin, D., Plattner, G.-K., Tignor, M., Allen, S., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. Cambridge, UK and New York, NY, Cambridge University Press: 383–464.

Miteva, V., et al. (2016). "Geochemical and Microbiological Studies of Nitrous Oxide Variations within the New NEEM Greenland Ice Core during the Last Glacial Period, ." Geomicrobiology Journal **33**(8): 647-660.

Monnin, Eric, et al. (2001). "Atmospheric CO₂ concentrations over the last glacial termination." Science **291** (5501): 112-114.

Neff, P. D. (2014). "A review of the brittle ice zone in polar ice cores." Annals of Glaciology **55**(68): 72-82.

Neftel, A., et al. (1985). "Evidence from polar ice cores for the increase in atmospheric CO₂ in the past two centuries." Nature **315**: 45-47.

Parrenin, F., et al. (2013). "Synchronous change of atmospheric CO₂ and Antarctic temperature during the last deglacial warming." Science **339**(6123): 1060-1063.

PAGES (2016). "Interglacials of the last 800,000 years." Rev. Geophys. **54**: 162-219.

Pedro, J. B., et al. (2016). "The spatial extent and dynamics of the Antarctic Cold Reversal." Nature Geoscience **9**: 51-55.

Pedro, J. B., et al. (2012). "Tightened constraints on the time-lag between Antarctic temperature and CO₂ during the last deglaciation." Clim. Past **8**: 1213–1221.

Petit, J. R., et al. (1999). "Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica." Nature **399**: 429-436.

Raynaud, D. (2012). "The integrity of the ice record of greenhouse gases with a special focus on atmospheric CO₂." Ice and Snow **2**: 5-14.

Raynaud, D., et al. (2005). "The record for marine isotopic stage 11." Nature **436**(7047): 39-40.

Raynaud, D., et al. (1993). "The ice record of greenhouse gases." Science **259**: 926-933.

Rhodes, R. H., et al. (2015). "Enhanced tropical methane production in response to iceberg discharge in the North Atlantic." Science **348**(6238): 1016-1019.

Rhodes, R. H., et al. (2016). "Local artifacts in ice core methane records caused by layered bubble trapping and in situ production: a multi-site investigation." Clim. Past, **12**, 1061-1077.

Rubino, M., et al. (2019). "Revised records of atmospheric trace gases CO₂, CH₄, N₂O, and δ¹³C-CO₂ over the last 2000 years from Law Dome, Antarctica." Earth Syst. Sci. Data **11**: 473-492.

Schaefer, H., et al. (2011). "On the suitability of partially clathrated ice for analysis of concentration and δ¹³C of palaeo-atmospheric CO₂." Earth and Planetary Science Letters **307.3-4**: 334-340.

Scholander, P. F., et al. (1956). "Gases in Icebergs." Science **123**(3186): 104-105.


Scholander, P. F., et al. (1961). "Composition of gas bubbles in Greenland icebergs." Journal of Glaciology **3**(29): 813-822.

Schmitt J., et al. (2012). "Carbon isotope constraints on the deglacial CO₂ rise from ice cores." Science **336**: 711-714.

Schwander, J. (1989). The transformation of snow to ice and the occlusion of gases. The Environmental Record in Glaciers and Ice Sheets. H. Oeschger and C. C. Langway Jr., John Wiley, New York: 53-67.

Schilt, A., et al. (2014). "Isotopic constraints on marine and terrestrial N₂O emissions during the last deglaciation." Nature **516**: 234.

Shakun, J. D., et al. (2012). "Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation." Nature **484**: 49-54.

Siegenthaler, U., et al., (2005): Stable carbon cycle-climate relationship during the late Pleistocene. *Science*, **310**, 1313–1317. 

Sigl, M., et al. (2016). "The WAIS Divide deep ice core WD2014 chronology–Part 2: Annual-layer counting (0–31 ka BP). ." *Climate of the Past* **12**(3): 769-786.

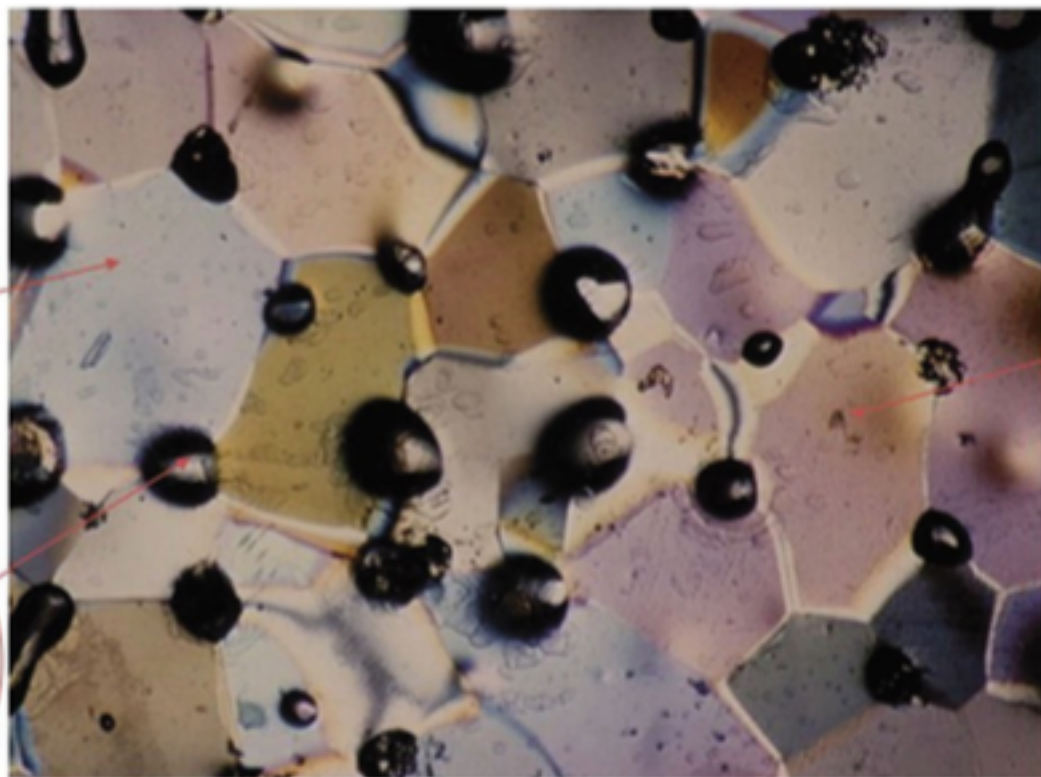
Sowers, Todd (2001). "N₂O record spanning the penultimate deglaciation from the Vostok ice core." *Journal of Geophysical Research: Atmospheres* **106**(D23): 31903-31914.

Stauffer, B. (1999). "Cornucopia of ice core results." *Nature* **399**: 412-413.

Stauffer, B., et al. (1981). "Atmospheric CO₂ history from ice core studies." *Zeitschrift für Gletscherkunde und Glazialgeologie* **17**(1): 1-15.

Water
H₂O
H₂¹⁸O
HDO

Air
CO₂
CH₄
δ¹⁵N
δ⁴⁰Ar
δ¹⁸O...



Impurities
dust,
sea salt,
¹⁰Be
Trace elem.
pollution,
volcanism

