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REVIEW

Greenhouse gases in the Earth system: a palaeoclimate perspective

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While the trends in greenhouse gas concentrations in recent decades are clear, their significance is only revealed when viewed in the context of a longer time period. Fortunately, the air bubbles in polar ice cores provide an unusually direct method of determining the concentrations of stable gases over a period of (so far) 800 000 years. Measurements on different cores with varying characteristics, as well as an overlap of ice-core and atmospheric measurements covering the same time period, show that the ice-core record provides a faithful record of changing atmospheric composition. The mixing ratio of CO₂ is now 30 per cent higher than any value observed in the ice-core record, while methane is more than double any observed value; the rate of change also appears extraordinary compared with natural changes. Before the period when anthropogenic changes have dominated, there are very interesting natural changes in concentration, particularly across glacial/interglacial cycles, and these can be used to understand feedbacks in the Earth system. The phasing of changes in temperature and CO₂ across glacial/interglacial transitions is consistent with the idea that CO₂ acts as an important amplifier of climate changes in the natural system. Even larger changes are inferred to have occurred in periods earlier than the ice cores cover, and these events might be used to constrain assessments of the way the Earth could respond to higher than present concentrations of CO₂, and to a large release of carbon: however, more certainty about CO₂ concentrations beyond the time period covered by ice cores is needed before such constraints can be fully realized.

Keywords: ice cores; carbon dioxide; methane; nitrous oxide; quaternary; pre-industrial

1. Introduction: why do we need a palaeoperspective on greenhouse gases?

The continuous measurement series started by Keeling *et al.* [1] at Mauna Loa in 1958 shows clearly that the mixing ratio of CO₂ in the atmosphere has risen from 316 ppmv (parts per million by volume) to 389 ppmv in the last 52 years. However, there were no regular or reliable measurements of the background atmosphere, away from local sources or sinks, before that date. Data from the palaeorecord

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(for CO₂ and other radiatively active gases) are therefore essential in providing a full picture of the recent increase, and therefore of the radiative forcing the additional atmospheric burden provides. They also offer a perspective on how unusual such an increase is over different time scales.

Over time scales in which large natural changes in climate and biogeochemistry occurred (glacial/interglacial cycles), the palaeorecord offers an insight into natural cycles, and especially into the climate-trace gas feedbacks that occurred: these are feedbacks that might operate in the future, and that therefore need to be understood. Going back further still, we reach periods in which the CO₂ content of the atmosphere was substantially higher than today—to the extent that we can infer the climate and atmospheric composition of such times, and we can assess whether high CO₂ climates, and the impacts of such climates, were as predicted by models. Finally, we can search the palaeorecord for evidence of large releases of carbon in the past, which might serve as partial analogues for the current experiment being carried out on the Earth's atmosphere and climate system.

Generally speaking, palaeorecords are based on proxies that can be crudely interpreted in terms of an environmental parameter of interest. However, as we will see, in the case of the trace gases we are extremely fortunate to have, in ice cores, an archive of preserved ancient air that allows us to directly measure atmospheric mixing ratios for the last few hundred thousand years. Most of this paper will be dedicated to discussing the ice-core records of trace gases and what we have learnt from them. The paper ends with a brief discussion of the findings of less direct methods for determining past CO₂ levels in deeper time.

2. Air in ice cores

Ice cores from the polar regions contain multiple sources of information. The isotopic content of the water molecules provides information about past changes in atmospheric temperature (e.g. [2,3]). Impurities trapped in snowflakes and on the snow surface provide information about environmental parameters, such as the occurrence of volcanic eruptions [4], and other aspects of the aerosol content of the atmosphere [5]. However, perhaps the most famous and unique ice-core records come from the atmospheric samples trapped in air bubbles.

Snowflakes that fall onto the cold polar ice sheets are overlaid by succeeding snowfalls. As they are buried deeper in the firn column, they metamorphose and form networks of ice crystals that become less permeable, until eventually they form a totally impermeable ice matrix in which bubbles of air are trapped. This so-called close-off depth occurs only at between about 60 and 100 m (depending on the site). The trapped bubbles are an almost perfect sample of the overlying air, and their contents can be analysed for major as well as trace components. The sampling is only 'almost perfect' for three reasons: (i) gases that have a short lifetime such as photochemically produced radicals are of course missing from the air bubbles; (ii) the air at the close-off depth typically has an age of a few decades owing to the time it takes for air to diffuse to this depth, so the trapped air is older than the air above the snow surface, but much younger than the ice that encloses it; and (iii) fractionation occurs in the firn column, mainly owing to gravitational effects that concentrate heavier molecules at the bottom of the column: this small fractionation is negligible for concentration

measurements (of the order of 0.5% for CO₂), although it can be important (and must be corrected for (e.g. [6]) when studying the per mil (‰) level variations in isotopic ratios of trace gases. Deeper in the ice sheet, the prevailing pressure and temperature allow the bubbles to transform into clathrate hydrate crystals (e.g. [7]); the air from these can be extracted in the normal way, but care must be taken, particularly in the transition zone, where different components of the air may be preferentially fractionated into either hydrates or bubbles.

There are a number of different methods used for extracting air from ice samples; once extracted, the air can be analysed in similar ways to those used on flasks of air collected in the present-day atmosphere. For components such as CH₄ and N₂O, a melt–freeze technique can be used (e.g. [8]); however, for CO₂, which strongly interacts with liquid water, dry extraction techniques are used (e.g. [9,10]). In one method, a cube of ice (typically 8 g) is placed in a cooled vacuum apparatus, and the surrounding air is pumped out. The ice sample is then crushed into tiny pieces using needles, releasing all the air from bubbles and hydrates; the air can then be transferred to the analytical system (for example, a laser infrared absorption analyser might be used for CO₂). Sublimation methods have also been used to ensure the extraction of all hydrate CO₂, and the similarity [11] of results using the two methods (sublimation and crushing) shows both that the crushing methods are generally adequate and that there is no ‘hidden’ CO₂ in the ice lattice.

Ice containing melt layers must be avoided, but there is an additional potential artefact for CO₂ that can lead to apparently unreasonable interhemispheric concentration differences and to unfeasibly fast changes within Greenland data [12]. The problem seems to be confined to Greenland ice (as shown by the similarity of data from Antarctic sites with different characteristics, discussed later) and to be related to the high concentrations of other impurities in Greenland ice, especially during the glacial period [13]. Although it remains somewhat unclear whether the excess CO₂ arises from reactions of acid and carbonate, or from oxidation of organic material [13], the problem is simply avoided by using only Antarctic ice, which has much lower concentrations of other impurities (this issue is relevant only for CO₂; no such problem inhibits the use of Greenland ice for CH₄).

Before presenting the data, one further issue has to be discussed: that of the way the enclosure process affects the age distribution of air in a given layer of an ice core. As already discussed, the air bubbles are sealed from the firn column and the atmosphere only at a depth of typically 60–100 m (depending on the characteristics of the site). Furthermore, bubbles are closed over a finite depth range (of the order of 12 m), so that a given depth contains bubbles with an age distribution [14]. At sites with a very low snow accumulation (e.g. EPICA site at Dome C, Antarctica, 25 kg m⁻² a⁻¹, i.e. 2.8 cm a⁻¹ ice), the ice at the close-off depth will already be over 2000 years old (under current climate) [15], while the newly enclosed air will have an age equivalent only to the diffusion time for air through the firn column (typically a few decades); the differences between the ice age and the gas age at a given depth are referred to as the Δ -age, and it is the uncertainty in Δ -age for past times that causes uncertainty in assessing the phasing of changes in temperature and in trace gas concentrations in the past. The age distribution within a given (Holocene) layer at Dome C will be typically 400 years [14], and this is what controls the resolution that can be achieved. At the

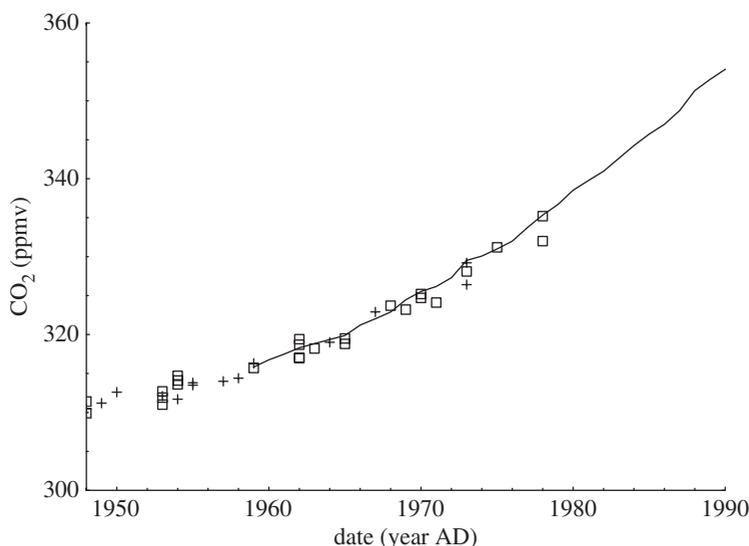


Figure 1. CO₂ mixing ratio for recent decades measured in air and in ice cores. The line represents atmospheric data from South Pole (data available at <http://www.esrl.noaa.gov/gmd/ccgg/iadv/>); the symbols are from the Law Dome (Antarctica) ice cores: crosses, MacFarling Meure *et al.* [10]; squares, Etheridge *et al.* [16].

other extreme, sites with very high snow accumulation rates have a very small ice age/gas age difference (and hence a very small age uncertainty); Law Dome site DE08 ($1100 \text{ kg m}^{-2} \text{ a}^{-1}$) has a Δ -age estimated at just 30 years [16], and an age distribution (hence resolution) of about a decade [17].

3. The ice-core record of trace gases—the recent past

Because of its very high snow accumulation rate, Law Dome is ideal for studying changes over the last few centuries. In particular, it has been possible to compare data from the ice just below the close-off depth with atmospheric measurements (from South Pole) over recent decades; since the ice measurements fall on the atmospheric curve, we can be confident that the ice enclosure process itself does not induce any unexpected artefacts (figure 1). However, measurements of CO₂ have been made at several Antarctic sites for this period (figure 2). We can make several deductions from this figure: firstly, the increasing trend seen in the atmospheric datasets actually began in the early nineteenth century; secondly, the increase from the typical value of the AD 1000–1800 period to the present is nearly 40 per cent; thirdly, there were small variations, of a few ppmv on centennial time scales, before the Industrial Era; and, finally, the fact that data from four very different sites, from Law Dome (a coastal site with a mean annual temperature of -19°C and relatively high concentrations of some impurities) to the EPICA Dronning Maud Land site (a high-altitude inland site with a mean annual temperature of -44.6°C and very low impurity concentrations), show the same concentrations and trends also rules out any artefacts that affect the concentration after enclosure.

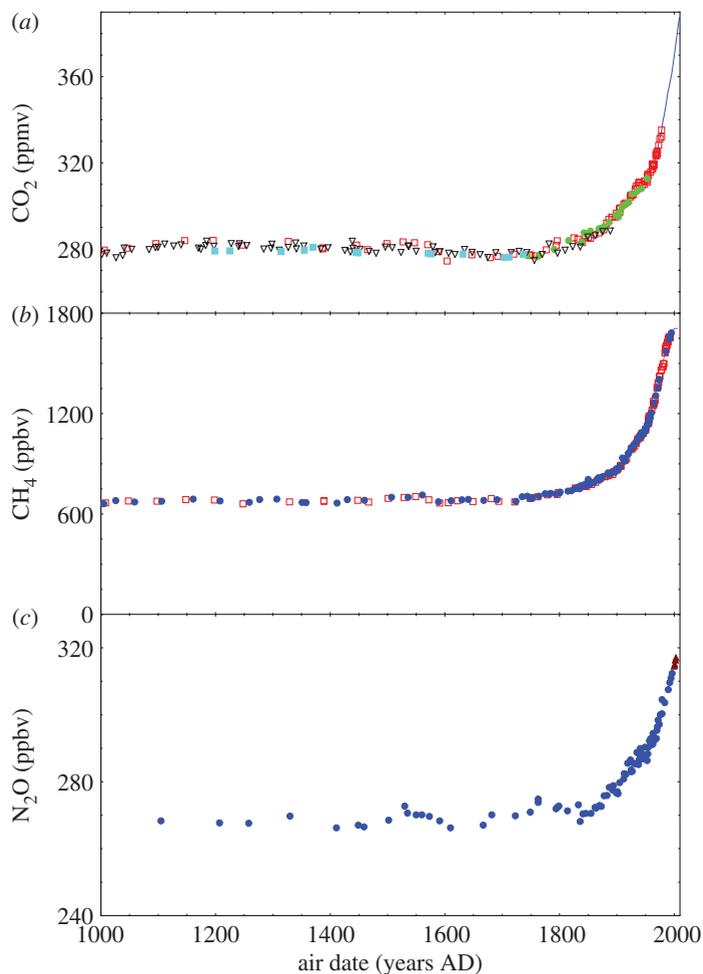


Figure 2. Trace gas mixing ratios over the last 1000 years from ice cores and atmospheric measurements. (a) CO₂; the solid line is Mauna Loa annual average atmospheric data; red squares are from Law Dome [16]; green circles from Siple [18]; black triangles from the EPICA DML site; turquoise squares from South Pole [19]. (b) CH₄ on the CSIRO calibration scale; line is annual averages of flask samples from Cape Grim Observatory (CGO), Tasmania; ice-core data from Law Dome are shown by blue circles [10] and red squares [20]. (c) N₂O; brown triangles are annual averages from CGO flask samples; blue circles represent data from Law Dome ice cores [10].

The Law Dome site has also been used to produce profiles of other atmospheric gases, for which the continuous instrumental record is even shorter. Figure 2 shows the CH₄ record; the mixing ratio of this gas also rose above its millennial norm in the early nineteenth century, and now stands 140 per cent above that value. Table 1 summarizes the magnitude of the increases that the ice-core and atmospheric records have revealed (for the most valid comparison, South Pole atmospheric data are shown). Measurements of ¹³CO₂ [21] and ¹³CH₄ [22,23] over the last millenium are consistent with the view that the recent increases are due mainly to fossil fuel input for CO₂, and to mixed biogenic/fossil sources for CH₄, although the ¹³C data alone are not enough to constrain the sources without

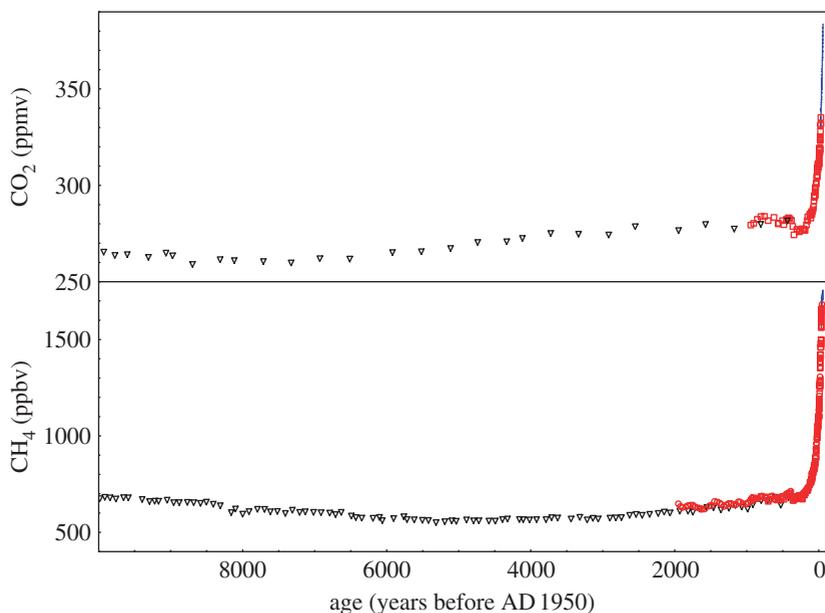


Figure 3. CO_2 and CH_4 mixing ratios over the last 10 kyr. The blue lines represent atmospheric measurements from flasks collected at South Pole; the red squares are from Law Dome ice cores [10,16]; the black triangles are from Dome C ice cores [25]. Note that Dome C has a much wider age distribution for each sample (see text) and therefore shows a smoothed signal compared with Law Dome.

Table 1. Pre-industrial concentrations of trace gases in comparison with 2008 averages.

gas	pre-industrial (Law Dome, average of 1000–1750)	present day (South Pole, 2008 annual average)
CO_2	280 ppmv	383 ppmv
CH_4	680 ppbv	1740 ppbv
N_2O	269 ppbv	320 ppbv

further information such as emission inventories, the dilution of ^{14}C by ^{14}C -free fossil sources seen in tree rings until the first nuclear bomb tests (Suess effect), and changes in the O_2/N_2 ratio of the atmosphere [24].

Finally, in assessing the recent increases, we can also view them in the context of the entire Holocene period (figure 3). Here, we can observe a slow increase in CO_2 over the last 8 kyr, and in CH_4 over 6 kyr. While insignificant in amplitude and rate compared with the changes of the last 200 years, there is a very active ongoing debate about whether these increases are actually the result of early anthropogenic activities—land clearance and the growth of rice cultivation [26,27]. Several lines of argument have been used to counteract this proposal: that human activity was simply not intense enough in earlier millennia to have such a large effect; that the hypothesis is not consistent with carbon isotopic

data; that reasonable natural explanations for the increasing concentrations are available [6,28–30]. Resolving the cause of change is important because it has additionally been proposed that the rise in CO₂ during the Holocene may have been responsible for staving off the inception of the next glacial stage [26].

A major plank of the argument in favour of an early human impact is the observation that the Holocene is unusual with respect to other interglacials. In most other recent interglacials, CO₂ and CH₄ concentrations declined in phase with northern summer insolation [27]; in the Holocene, both gases started to increase while insolation was still falling. For CO₂, recent papers [6,31] have presented natural (non-anthropogenic) explanations that are compatible with the Holocene increase in CO₂ and the rather flat profile of ¹³CO₂ that is observed; in its published form the early anthropogenic hypothesis [26] is not consistent with the isotopic data [6]. The research challenge of the next few years is to present a natural hypothesis that convincingly replicates both the Holocene rise and the falls of previous interglacials in these gases, while also being consistent with the associated isotopic data.

4. The longer perspective—glacial/interglacial cycles

(a) Carbon dioxide

Ice-core records of trace gases are now available over the full 800 kyr extent of ice-core records. This time period is characterized most clearly by the succession of long, cold glacial periods, interspersed with short, warm interglacial periods [3,32]. The pattern recurs with approximately a 100 kyr frequency, and is seen in terrestrial and marine as well as ice-core records. CO₂ shows exactly the same pattern [9] (figure 4), and indeed has remarkably similar characteristics to Antarctic temperature as recorded in the deuterium/hydrogen ratios of water in ice cores. The correlation of CO₂ with deduced Antarctic temperature has an r^2 of 0.82. In particular, CO₂ is low (typically 170–200 ppmv) during glacial maxima, and relatively high (ranging from 240 to 300 ppmv) during interglacials; it has lower concentrations during the weaker interglacials (between 800 and 450 ka) than in the later, generally stronger, interglacials. Although the strong correlation suggests an almost constant and linear relationship, it actually appears as if the earliest part of the record (before about 650 ka) had lower mixing ratios (both absolutely and in comparison with Antarctic temperature) than other sections of the record [9]. When taking account of fast feedbacks (such as water vapour and sea ice changes) resulting from the forcing (but not astronomical or ice sheet changes), CO₂ seems to be responsible for around 30–50% of the observed variability seen in climate records [33,34] (also P. Holden 2009, personal communication).

The similarity between the CO₂ mixing ratio and Antarctic temperature extends to the smaller multi-millennial-scale variations during glacial periods [35] and to the pattern of change during terminations [36]. In this respect, CO₂ millennial variability mirrors that of Antarctic temperature but not the stronger and sharper variations seen in Greenland and many other Northern Hemisphere records, enhancing the view that much of the control on CO₂ is driven from the Southern Ocean. The exact mechanisms controlling glacial/interglacial CO₂ change remain unresolved. A number of mechanisms are reasonably

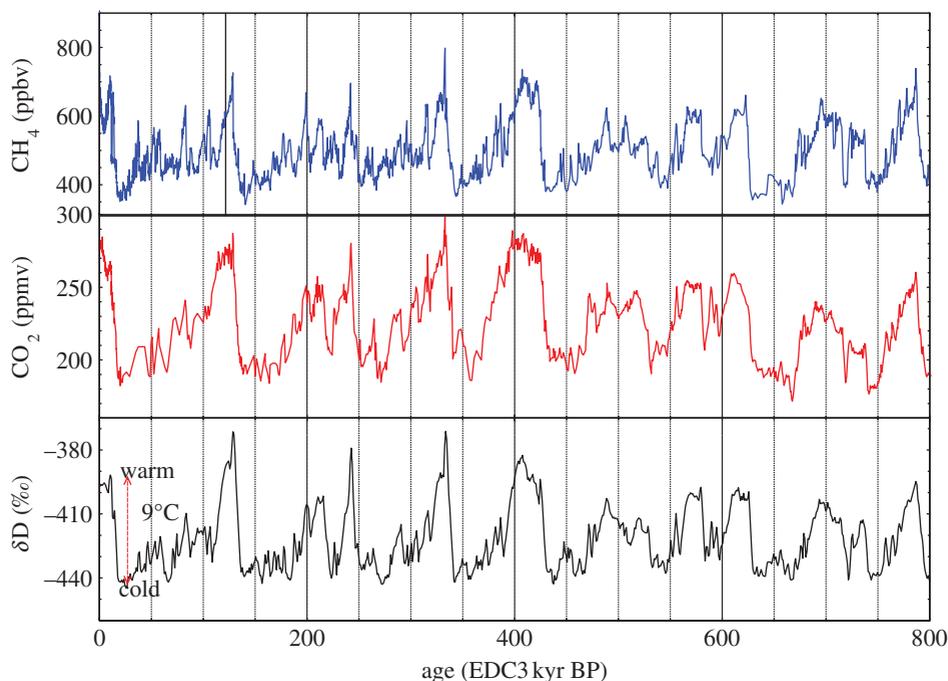


Figure 4. CO_2 and CH_4 mixing ratios over the last 800 kyr. Also shown for comparison is the Dome C deuterium profile [3], which acts as an Antarctic temperature proxy. CO_2 is from Dome C and Vostok ([9] and references therein); CH_4 is from Dome C ([8] and references therein). Note that the plots are shown with time running from right to left and that the increased values of the last 200 years are not included. The black vertical line on the CH_4 plot is the period of known warmth above present in the last interglacial in Greenland (referred to in §5*a*).

well understood (e.g. [37,38]): the increase in terrestrial vegetation in interglacials acts to remove CO_2 , while the increase in sea surface temperatures leads to less solubility in the ocean and an increase in atmospheric CO_2 ; taken together with the effects of changing sea level, these better quantified effects probably almost cancel each other out, leaving a change of about 100 ppmv still to explain. Most of the proposed explanations centre either on changes in ocean circulation (and ventilation of the deep ocean) or on ocean biogeochemistry (removal of carbon through sinking as a result of enhanced biological productivity). Both modelling and observation allow limits to be placed on some mechanisms; for example, the impact of one mechanism, fertilization by Fe in certain regions of the ocean, has been constrained both by model studies [39] and by observation of periods in the ice-core record when dust concentrations were low but CO_2 remained low [40]. The current view is that no single mechanism will explain the changes seen, but that quantifying the different processes involved will improve modelling of the mechanisms that may be expected to partition increased CO_2 between the atmosphere, land and ocean under future conditions.

Three further remarks need to be made about these long ice-core records of CO_2 . Firstly, it is again the case, at least over the last 100 kyr, that different ice-core sites with very different physical and chemical characteristics [34–36,41]

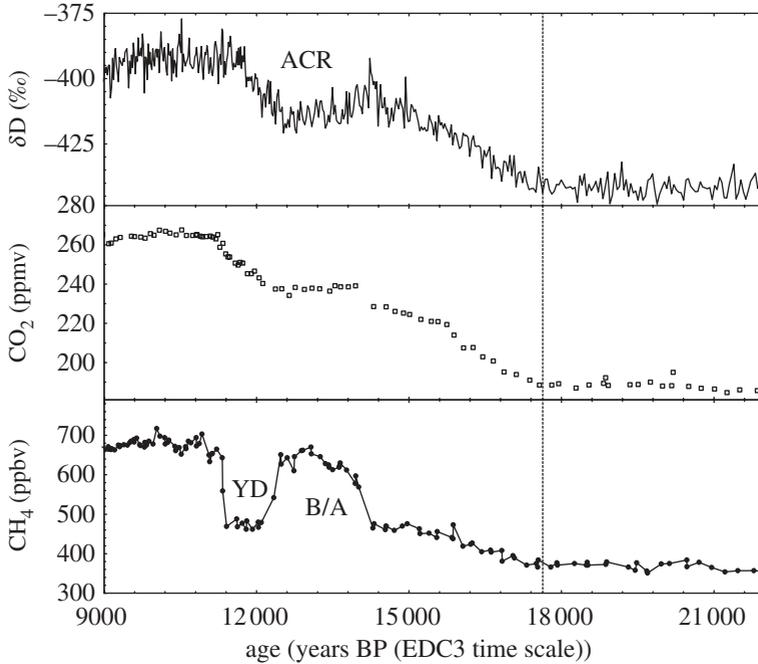


Figure 5. Phasing of changes in CO_2 , CH_4 and deuterium across the last glacial termination. This figure uses data from Dome C and is based on that shown by Monnin *et al.* [36], but all data have been placed on the newer EDC3 age scale [43]. Deuterium represents Antarctic climate. The vertical dashed line is drawn at the start of the rise in deuterium as defined by the RAMPFIT statistical tool [44]. The Antarctic Cold Reversal (ACR) and the Northern Hemisphere Younger Dryas (YD) and Bolling/Allerod (B/A) periods are marked.

show the same concentrations and patterns of change; this provides the best possible evidence that any remaining artefacts are negligible, and that these ice-core records give a true representation of the past atmospheric mixing ratios.

Secondly, it is very important to note that the highest concentration seen in the entire 800 kyr record [9] is 300 ppmv—compared with the increase to 389 ppmv in the last two centuries. The resolution of the data from ice cores is insufficient to absolutely rule out that a similarly high value remains unsampled somewhere in the 800 kyr dataset, but it can be asserted with high confidence that no such values occurred at any time in the last 50 kyr [42]. We are thus well out of the natural range, and do not have an analogue to explore the likely results of the current CO_2 increase anywhere in the ice-core era. The fastest multicentennial rate of increase seen in the well-resolved record of the last glacial termination is about 20 ppmv in a millennium: the CO_2 mixing ratio rose by 20 ppmv in just 11 years before 2010.

Finally, there has been much discussion about the phasing between changes in temperature and CO_2 during the large changes of glacial terminations (figure 5). As already pointed out, it is difficult to pin down this phasing with existing records because of uncertainties in calculating Δ -age, and we must also note that comparisons are generally made with Antarctic temperature, which of course may

have a regional overlay onto the globally forced signal. However, the best estimate [36] shows Antarctic temperature and CO_2 moving in remarkably close harmony over the approximately 6 kyr period of increase, including the hiatus known as the Antarctic Cold Reversal. Antarctic temperature appears to start to increase about 400 years before any increase in CO_2 occurs. The existence of this lead has been questioned [45] and is close to the uncertainty; however, accepting it as the current best estimate, it implies that Antarctic temperature might have increased by a few tenths of a degree before CO_2 responded. This is entirely consistent with the notion that other factors initiated the climate warming in the natural case, but that a mutual amplification (positive feedback) then occurred, in which the temperature change caused a release of CO_2 (probably primarily through ocean processes discussed above), and the increased CO_2 caused further warming. As a test of the ‘hypothesis’ that changing CO_2 causes climate change, note that there is no evidence for any period of significant change in CO_2 concentration in the ice-core record that is not accompanied by changes in Antarctic temperature. Difficulties with data synchronization make it harder to make such a definite statement for CO_2 concentration relative to global temperature, but a similar statement is probably true.

(b) *Methane and nitrous oxide*

A more detailed review of the changes in these gases was published relatively recently [46] and here I will provide only a summary. CH_4 also varies strongly between glacial and interglacial periods (figure 4), with values of typically 350–400 ppbv during glacial maxima, and 600–800 ppbv during interglacials [8]. Again, cooler interglacials (as defined by the Antarctic ice-core record) tend to have lower mixing ratios than warmer ones. The similarity in this case, however, is not so strong with Antarctic temperature at the millennial scale; instead, methane shows sharp millennial changes (of the order of 200 ppbv) [47] that parallel the rapid millennial Dansgaard–Oeschger events that are most clearly observed in Greenland ice cores. By use of measurements of ^{15}N in N_2 , which acts as a proxy for rapid temperature changes within the air bubbles, it has been shown that these rapid changes in methane begin within 30–70 years of the start of the rapid climate warmings observed in Greenland [47,48], and are completed within about a century (see examples in figure 5). The changes in methane, while significant, are such as to make them a minor player in terms of changes in radiative forcing over glacial/interglacial time scales [42].

The natural concentration of CH_4 in the atmosphere is driven by changes in a range of sources (most notably wetlands, either boreal or tropical, biomass burning, and perhaps the release of methane hydrates from the seafloor) or by changing sinks (most notably the concentration of the OH radical in the atmosphere). The partitioning of change between these different causes can be constrained by isotopic data, by measuring the concentrations in Greenland and Antarctica to derive inter-polar gradients, and by modelling of vegetation emissions and atmospheric chemistry. Isotopic evidence (deuterium and $^{14}\text{CH}_4$) was recently used to show that the role of methane hydrates in explaining the CH_4 increase at the last glacial termination is most likely very limited [49–51]. An increase in wetland emissions is generally considered to be the most likely dominant influence [52], although this statement carries considerable uncertainty.

The range of mixing ratios observed in the 800 kyr record is 340–800 ppbv, showing that the increase to 1740 ppbv (at South Pole) in the last two centuries has been extraordinary.

N₂O (not shown in figure 4) also shows lower values in cold periods (as low as approx. 200 ppbv) than in interglacials (up to 280 ppbv) [53], although the record is patchy because artefacts do occur that make the records in some sections of ice unreliable. N₂O shows significant millennial scale variability with higher values during Dansgaard–Oeschger warm periods but a more complex and gradual response in comparison with CH₄ [47]. N₂O derives partly from terrestrial and partly from oceanic emissions. The range of values so far observed does not come close to the recent increase up to 320 ppbv (table 1).

5. What can we learn from warmer climates and deeper time?

(a) *The last interglacial and methane*

The last interglacial warm period, running from about 135–110 ka, provides an important case study in relation to polar processes, because it appears that each polar region was significantly warmer than present for at least a part (though not necessarily the same part) of the period. In particular, there is good evidence that the Arctic [54] experienced summer warmth up to 5° above that of today, and specifically for Greenland [55] that warmer annual temperatures (of the order of 5° above present) persisted for at least 3 kyr around 120 ka. There have been concerns that persistent warmth of such a scale in the future could cause instability of permafrost or methane hydrates; the CH₄ data for the last interglacial, however, show no significant jumps (figure 4), implying that any such releases were slow and did not lead to elevated concentrations (indeed the concentration at this time remained considerably below those of the pre-industrial period).

(b) *The Late Pliocene and carbon dioxide*

Beyond the period for which ice-core data are available, atmospheric CO₂ mixing ratios have been inferred by a number of methods. These methods are highly indirect and give a wide range of results. Nevertheless, over the Phanerozoic Eon (542 Ma), glaciation (and colder temperature) seems to have occurred only when CO₂ is inferred to be at the lower end of its range [56, fig. 6.1, 57]. However, there are substantial difficulties in defining not only the CO₂ regime but also the palaeogeography and climate of these earlier times, in order to use this information quantitatively to constrain future climate.

More definite conclusions can be drawn for the interval approaching the Quaternary. It is thought that extensive glaciation of Greenland began in the Late Pliocene, about 3 Ma, and several causes have been proposed. However, a recent modelling study found that, under inferred Pliocene CO₂ concentrations of around 400 ppmv (i.e. slightly higher than those of today), three popular proposed causes (tectonic uplift, closure of the Panama seaway and termination of permanent El Niño conditions) failed to initiate such extensive glaciation [58]. Only by reducing CO₂ from 400 to 280 ppmv did this study succeed in initiating the full-scale glaciation of Greenland. This provocative result clearly raises concerns for the future health of the Greenland ice sheet, but mainly highlights the urgent need

to confirm by multiple methods what the CO₂ content of the atmosphere was before and after the inception of Greenland glaciation.

(c) *The Palaeocene–Eocene thermal maximum*

There is very clear evidence from marine sediments that, 55 Ma, Earth experienced a planet-wide abrupt (within 1–10 kyr) warming of several degrees, that lasted about 100 kyr (e.g. [59,60]). A large accompanying excursion in ¹³C values suggests that there was a large release of carbon with low ¹³C into the atmosphere and ocean; an accompanying dissolution of seafloor carbonates [61] suggests that acidification of the ocean also occurred. The amount of C released has been estimated to be of similar magnitude to, or even greater than (e.g. [62]), the amount expected from anthropogenic carbon release in the next century. The cause of the release remains a matter of discussion [63]; however, as information about this event increases, it offers a potentially useful analogue for the effects of such a rapid release, and the time period required for recovery of the Earth system.

6. Conclusion

Because ice cores provide such a direct measure of past atmospheric composition, they have been an invaluable resource for putting our knowledge of the ancient atmosphere on a firm footing. Most potential artefacts can confidently be dismissed on the basis of existing experiments and measurements, allowing unequivocal statements about the extraordinary and unusual magnitude and rate of change of CO₂, CH₄ and (with slightly less certainty) N₂O in the last two centuries to be made. Similarly, unprecedented changes in radiative forcing can therefore be inferred.

Nonetheless, there are significant changes in mixing ratios of all three gases on glacial/interglacial and millennial time scales. These are not yet fully understood, and the challenge of understanding these natural cycles has to be met in order to give us adequate knowledge of feedbacks (especially with respect to ocean carbon and wetland methane).

Finally, periods in the past of greater warmth, or of unusual natural carbon releases, may provide good testbeds for events that may be predicted for the next century and beyond. It may prove possible to extend the ice-core record somewhat further back in time: International Partnerships in Ice Core Sciences has outlined plans to go as far as 1.5 Ma (http://www.pages-igbp.org/ipics/data/ipics_oldaa.pdf). However, this is probably a practical limit, and extension into older periods of interest demands that the reliability of other methods of inferring past CO₂ concentrations must be rigorously tested and replicated so that progress can be made.

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