

# Ice core records of atmospheric carbon dioxide\*

Thomas K. Bauska<sup>1</sup>

<sup>1</sup>British Antarctic Survey, High Cross, Madingley Road, Cambridge, UK, CB3 0ET

## Abstract

Beneath the surface of Antarctica lies a near perfect record of changes in the atmosphere composition over hundreds of thousands of years. This unique archive allows us to reconstruct atmospheric CO<sub>2</sub> prior to the onset of modern atmospheric monitoring in the 1950s, with an accuracy of just a few parts per million. The data reveal natural variations in atmospheric CO<sub>2</sub> on glacial-interglacial, millennial, and centennial time scales and thus provide reliable reconstructions of the radiative forcing over time. Additionally, the stable isotopes of CO<sub>2</sub> can be measured at sufficient accuracy to quantify the sources and sinks of CO<sub>2</sub> over these same timescales. In combination, the concentration and isotope composition of CO<sub>2</sub> allow us to constrain both the past climate sensitivity (i.e., how climate responds to a change in CO<sub>2</sub>) and carbon-climate feedbacks (i.e., how the carbon cycle responds to a change in climate).

## Contents

<b>1</b>	<b>Introduction: What have ice core CO<sub>2</sub> data ever done for us?</b>	<b>2</b>
1.1	Key Points . . . . .	2
<b>2</b>	<b>Overview of ice core CO<sub>2</sub></b>	<b>2</b>
2.1	From the atmosphere to the bubbles: The reliability of ice core CO <sub>2</sub> . . . . .	5
<b>3</b>	<b>The Last Millennium: From the pre-Industrial to the Anthropocene</b>	<b>6</b>
3.1	The industrial rise . . . . .	6
3.2	The pre-Industrial . . . . .	7
3.3	Multi-decadal scale variability: humans or climate? . . . . .	7
<b>4</b>	<b>The Holocene: CO<sub>2</sub>, civilization, and the carbonate cycle</b>	<b>9</b>
<b>5</b>	<b>The Last Deglaciation: CO<sub>2</sub> as both forcing and feedback</b>	<b>10</b>
5.1	Constraints from CO <sub>2</sub> Concentration . . . . .	10
5.2	Constraints from Carbon Isotopes . . . . .	12
5.3	Mechanisms in brief . . . . .	12
<b>6</b>	<b>The Pleistocene: Tracing the heartbeat of The Ice Age</b>	<b>13</b>
6.1	Glacial-interglacial variability . . . . .	13
6.2	Millennial- and centennial-scale variability . . . . .	15
<b>7</b>	<b>The Pleistocene and beyond: Atmospheric CO<sub>2</sub> from surface outcrops and buried pockets of ancient ice</b>	<b>17</b>
<b>8</b>	<b>Outlook</b>	<b>17</b>

---

\*Please cite as Bauska, T.K., Encyclopedia of Quaternary Science, 3rd Edition, <https://doi.org/10.1016/B978-0-323-99931-1.00264-6>

# 1 Introduction: What have ice core CO<sub>2</sub> data ever done for us?

In 1958, when modern measurements of the concentration of atmospheric CO<sub>2</sub> began, CO<sub>2</sub> was near 315 ppm (Keeling et al. 2001). In 2021, atmospheric CO<sub>2</sub> surpassed a significant milestone when it reached 415 ppm, thus marking a 100 ppm increase in just 63 years. CO<sub>2</sub> is currently rising at about 2.5 ppm per year and will do so at similar rates unless significant steps are taken to curb fossil fuel emissions (Friedlingstein et al. 2023).

When confronted with such data a basic question to ask is whether or not the levels we see today or the rapidity of the recent rise is unprecedented in earth history? Prior to the late 1950s we rely on paleo-archives of atmospheric CO<sub>2</sub>, mostly in the form of proxies. The gold standard among these archives are ice core reconstructions which faithfully record the concentration of atmospheric CO<sub>2</sub> with accuracies of a few parts per million. Currently, the oldest continuous ice core record spans the past 800,000 years but snapshots of even more ancient times (over 2 million years ago) have been recovered from discontinuous outcrops of old ice.

Critically, high-accuracy measurements of atmospheric CO<sub>2</sub> (along with CH<sub>4</sub> and N<sub>2</sub>O: see respective chapters) enable quantification of the past radiative forcing of the earth in great detail over multiple glacial-interglacial cycles. The stable isotopic composition of carbon in CO<sub>2</sub> ( $\delta^{13}\text{C-CO}_2$ ) allows us to, in part, trace the sources and sinks of CO<sub>2</sub> over time and thus hone in on the mechanisms that alter the natural carbon cycle and drive the observed changes in CO<sub>2</sub>. Together, ice core CO<sub>2</sub> studies underpin our constraints on climate sensitivity and the climate-carbon cycle sensitivity.

## 1.1 Key Points

- **Ice cores provide reliable records of past changes in atmospheric CO<sub>2</sub>**
- **The current levels of atmospheric CO<sub>2</sub> are unprecedented over at least the last 800,000 years having never risen above ~300 ppm prior to the Industrial Revolution. The current rate of change in atmospheric CO<sub>2</sub> is similarly unprecedented.**
- **Ice core CO<sub>2</sub> records shows variability on timescales ranging from glacial-interglacial (60-90ppm), millennial (10-30ppm), and centennial (5-15ppm).**
- **The stable isotopes of CO<sub>2</sub> help fingerprint the sources and sinks responsible for this variability.**

## 2 Overview of ice core CO<sub>2</sub>

Ice core CO<sub>2</sub> data are not a palaeoclimate proxy in the traditional sense whereby a given climate state is indirectly inferred from a geologically preserved, measurable variable (e.g., the magnesium content of a shell is controlled by temperature at which it formed and thus acts a proxy for ocean temperature) (Henderson 2002). The air parcels captured in polar ice are, with a few exceptions discussed below, pristine relics of the ancient atmosphere (Figure 1. This ancient air was slowly isolated from the atmosphere as snow is compacted first into firn and then into ice (see chapter on the firn). The depth-scales and time-scales over which this occurs varies depending on the temperature and accumulation at the site, but broadly speaking, the transition for porous firn to fully occluded bubbles occurs from anywhere between 40 and 120 meters below the surface (Herron and Langway 1980; Schwander et al. 1993). At this point, the massive ice sheets that blanket the polar regions, namely Greenland and Antarctica, still retain a significant volume of air. By volume, at standard temperature and pressure, the air content of ice after the bubbles fully close is about 10% (i.e., 10 mL of air per 100 mL of ice) but this varies with the overlying atmospheric pressure and thus elevation (Martinerie et al. 1992)(see chapter on total air content). By mass, the air content is about 0.01% (i.e., grams of air per grams

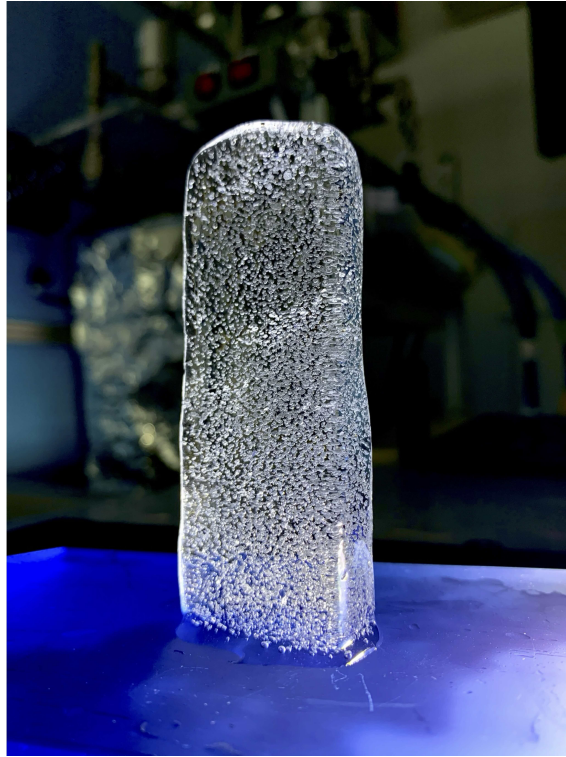


Figure 1: An ice core sample showing the bubbles that contain near pristine samples of ancient atmosphere

of ice), a small amount of air, but enough that the  $\text{CO}_2$  content can be measured with as little as 10 grams (g) of ice, to precisions of less than 1 parts per million ppm (Ahn, Brook, and Howell 2009; Bereiter, Stocker, and Fischer 2013). The concentration of  $\text{CO}_2$  in ice cores is measured as the dry mole fraction of  $\text{CO}_2$  in the total amount of air released during extraction (reported as part per million or ppm).

The stable isotopes of  $\text{CO}_2$  can also be measured in similarly small amounts of air to a high-degree of precision ( $\sim 0.05\text{-}0.1\text{‰}$ ) (Leuenberger, Eyer, et al. 2003; Schmitt, Schneider, and Fischer 2011; Jenk et al. 2016) but are markedly improved with samples up to a few hundred grams of ice that yield tens of millilitres of air (Francey et al. 1999; Bauska, Brook, Mix, et al. 2014) or by applying advanced laser spectroscopy techniques (Bereiter, Tuzson, et al. 2020; Mächler et al. 2023). The isotopic composition of carbon ( $\delta^{13}\text{C}\text{-CO}_2$ ) or oxygen ( $\delta^{18}\text{O}\text{-CO}_2$ ) is reported as the parts per thousands (per mil or ‰) deviation from an internationally accepted standard, either Vienna Pee Dee Belemnite (VPDB) or, in the case of oxygen isotopes, Vienna Standard Mean Ocean Water (VSMOW).

The carbon isotopes are a powerful constraint on the sources and sinks for  $\text{CO}_2$ . Three major processes fractionate carbon isotopes: less  $^{13}\text{C}$  is taken up by plant material during photosynthesis; more  $^{13}\text{C}$  is taken up by the ocean during air-sea gas exchange; and on average, no more or no less  $^{13}\text{C}$  is taken up by reefs, shells and other  $\text{CaCO}_3$  material during the formation of  $\text{CaCO}_3$  from seawater. The net effect is that the major reservoirs of carbon are measurably different in their  $\delta^{13}\text{C}$  values (Figure2). The pre-Industrial atmosphere ranges between  $-6$  and  $-7\text{‰}$  (VPDB). Organic carbon stocks are lighter than the atmosphere including: C3 plant material ( $-20$  to  $-35\text{‰}$ ), C4 plant material ( $-12$  to  $-18\text{‰}$ ), a mixture of both C3 and C4 in the form of soil carbon, long-dead plant material in the form of fossil fuels ( $-20$  to  $-35\text{‰}$ ) and marine plankton ( $-18$  to  $-30\text{‰}$ ). Inorganic stocks are heavier than the atmosphere with seawater ranging between  $0$  and  $+2\text{‰}$ , marine  $\text{CaCO}_3$  covering a very similar range; and volcanic emissions, which reflect a combination of both  $\text{CaCO}_3$ -rich substrates (e.g., limestone) and organic-rich substrates (e.g., shales) typically range between  $-3$  and  $-5\text{‰}$ .

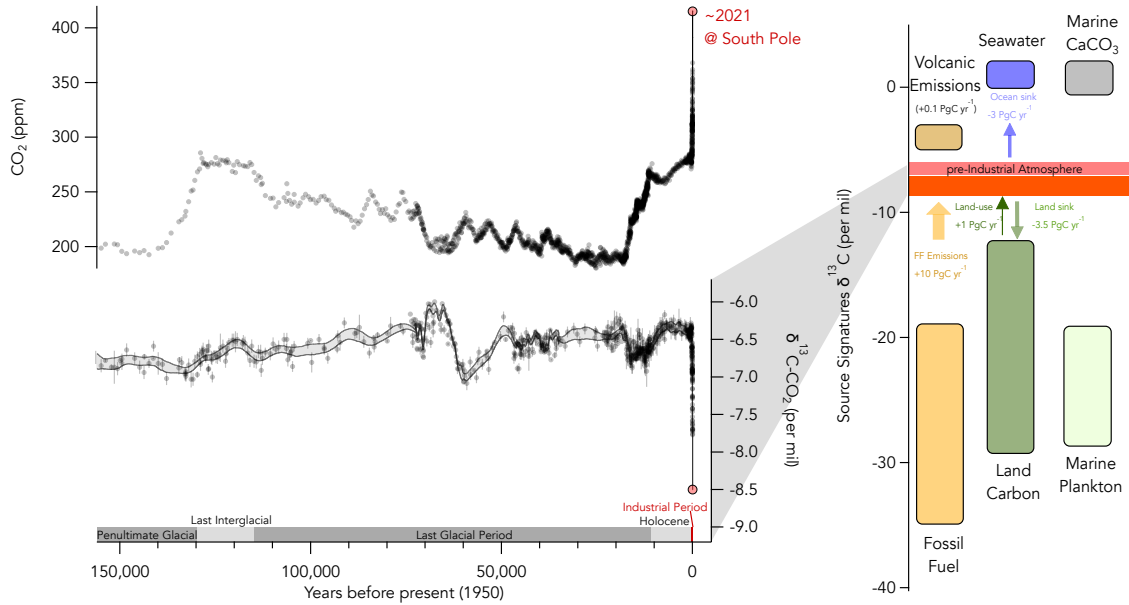


Figure 2: Left panel: The concentration and isotopic composition of atmospheric CO<sub>2</sub> from near the present day to the penultimate glacial period. The instrumental data is sourced from South Pole Station measured as part of the Scripps Institution of Oceanography atmospheric monitoring programme (Keeling et al. 2001). The concentration data are shown undifferentiated by core or reference and come from a large variety of sources including: (Monnin, Steig, et al. 2004; Lourantou, Chappellaz, et al. 2010; Ahn, Brook, Mitchell, et al. 2012; Marcott et al. 2014; Bereiter, Lüthi, et al. 2012; Rubino, Etheridge, Thornton, et al. 2019; Bauska, Marcott, and Brook 2021). The plot also shows all the available isotopic data on CO<sub>2</sub> which can constrain some of the sources and sinks of CO<sub>2</sub> (Elsig et al. 2009; Lourantou, Lavrič, et al. 2010; Schmitt, Schneider, Elsig, et al. 2012; Bauska, Baggenstos, et al. 2016; Bauska, Brook, Marcott, et al. 2018; Eggleston et al. 2016; Rubino, Etheridge, Thornton, et al. 2019; Menking et al. 2022). Right panel: a plot showing an approximate isotopic range of the major sources of CO<sub>2</sub>. The arrows between the various reservoirs and atmosphere represent net fluxes of CO<sub>2</sub> from a simplified version of the recent carbon budget based on data from the Global Carbon Project (Friedlingstein et al. 2023)

The magnitude of isotopic fractionation (i.e., the fractionation factor) for each mechanism can vary with several parameters. Most notably, the combination of equilibrium and kinetic fractionation factors that lead to preferential transfer of  $^{13}\text{C}$  to the ocean from the atmosphere (and likewise preferential transfer of  $^{12}\text{C}$  to the atmosphere from ocean) will decrease with increasing sea surface temperature. Thus, a warming of the ocean will drive more  $\text{CO}_2$  out the ocean due to decreased solubility, but also “pull” the atmospheric  $\delta^{13}\text{C}\text{-CO}_2$  ( $-6\text{‰}$ ) closer to the mean surface ocean value ( $\sim 0\text{‰}$ ), thus increasing atmospheric  $\delta^{13}\text{C}\text{-CO}_2$ . The oxygen isotopes, on the other hand, reflect the exchange of oxygen between the  $\text{CO}_2$  and the surrounding water ice and are thus set by a combination of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  and temperature (Friedli, Moor, et al. 1984; Siegenthaler, Friedli, et al. 1988; Bauska, Brook, Mix, et al. 2014). The only exception to this is firn air samples and possibly very young ice core samples that have not had enough time to come into equilibrium with the entombing ice (Assonov, Brenninkmeijer, and Jöckel 2005). Finally, the radiocarbon content of  $\text{CO}_2$  has also been determined on samples up to a few kilograms (Wilson, 1995) but these data do not reliably record atmospheric values and instead are heavily overprinted by in situ production of  $^{14}\text{C}$  by cosmic rays (Lal et al. 1990; Petrenko et al. 2016).

## 2.1 From the atmosphere to the bubbles: The reliability of ice core $\text{CO}_2$

To first order, the concentration of  $\text{CO}_2$  measured in ice core samples are directly comparable to atmospheric records. However, we know of a few processes that can slightly modify the gas composition of the bubbles relative to the atmosphere. Firstly, the air at the base of the firn is slightly older than the overlying atmosphere ( $\sim$ decades) and is enriched in the heavier gases (Craig, Horibe, and Sowers 1988; Etheridge et al. 1996).  $\text{CO}_2$  (44.01 g/mol) is heavier than bulk air (28.96 g/mol) and is thus preferentially enriched by gravitationally settling as the air slowly diffuses within the firn (i.e., a slightly higher concentration). Similarly, the minor isotopologue of  $\text{CO}_2$ , containing the stable isotope of carbon ( $^{13}\text{C}$ ), is heavier than the major isotopologue by one neutron ( $\sim$ atomic mass unit [amu]) and is thus also preferentially enriched (i.e., a slightly more positive isotopic ratio).

This enrichment can be determined independently to a high degree of accuracy by measuring the isotopic variations in gases that do not vary in the atmosphere over geologic time. Most commonly this is determined using the isotopes of  $\text{N}_2$  (the  $^{15}\text{N}^{14}\text{N}$ -to- $^{14}\text{N}^{14}\text{N}$  ratio) - a gas with a lifetime of  $\sim 10^4$  years (Mariotti 1983) and a mass difference of  $\sim 1$  amu — the same mass difference as  $^{13}\text{C}\text{-CO}_2$ . The gravitationally settling effect varies with the temperature and accumulation at the site, is proportional to the depth of the firn column, and varies anywhere from 0.2 to 0.6‰. This equates to enrichments of the exact same magnitude for  $\delta^{13}\text{C}\text{-CO}_2$  and between about 0.8 and 2.5 ppm artificially elevated values for  $\text{CO}_2$  concentration.

The slow diffusion of gases within the firn ( $\sim$ a decade) and gradual trapping of bubbles ( $\sim$ decades to a few hundreds of years depending on accumulation) also acts as a low-pass filter, smoothing out any variability that is higher-frequency than the overall width of gas age distribution. The exact degree of smoothing remains a matter of debate (Mitchell et al. 2015) — particularly at low accumulation sites (Fourteau et al. 2017). Broadly speaking, the shortest resolvable signal at high-accumulation sites is about one decade (Trudinger, Etheridge, et al. 2002). At the lowest accumulation sites, centennial-scale features are markedly smoothed but still resolvable (Nehrbass-Ahles et al. 2020). It is thus not straightforward to directly compare the rates observed from direct atmospheric measurements with some of the low-accumulation site ice core data without a firm understanding of the firn smoothing.

Other firn-induced effects include a diffusive fractionation because lighter isotopes diffuse more rapidly than the heavier isotopes. This is only significant when the  $\text{CO}_2$  concentration is changing rapidly enough in the atmosphere such that a substantial concentration gradient is established in the firn (Trudinger, Enting, Etheridge, et al. 1997). This correction is crucial for determining the precise variations in  $\delta^{13}\text{C}\text{-CO}_2$  across the rise

in CO<sub>2</sub> since the onset of the Industrial Revolution, with corrections on the order 0.2‰ (Rubino, Etheridge, Thornton, et al. 2019), but is inconsequential during the more gradual, natural changes observed in the past (Buizert, Sowers, and Blunier 2013). Theoretically, thermal fractionation (Severinghaus et al. 1998) will also impact  $\delta^{13}\text{C-CO}_2$  but this has yet to be measured in the lab or observed in natural settings.

A number of other processes can significantly deteriorate the quality of the ice core data. The presence of any liquid water, in the form of melt or rain, that comes into contact with the atmosphere will lead to large amounts of CO<sub>2</sub> dissolving into the melt. Upon (re)freezing within the snowpack, a substantial portion of the CO<sub>2</sub> will remain dissolved within the ice matrix. This dissolved CO<sub>2</sub> can then diffuse across the sharp concentration gradient surrounding the melt layer and into the otherwise pristine bubbles. The dissolved CO<sub>2</sub> can also be liberated during the extraction of the air. The net effect is artificially high CO<sub>2</sub> observed across melt layers. These melt layers are rare in most of the polar ice cores in which CO<sub>2</sub> has been measured and readily identifiable by visual inspection in bubbly ice or via other gas methods in clear, clathrate ice and thus easily avoidable. When analysed at high-resolution they can provide important empirical constraints on the diffusion rate of CO<sub>2</sub> in polar ice (Ahn, Headly, et al. 2008).

After bubble closure, the concentration of CO<sub>2</sub> can be artificially raised by in situ production, particularly in acidic ice with large amounts of carbonate dust, as is observed in Greenland ice (Delmas 1993; Anklin et al. 1997). Conversely, the concentration can also be theoretically artificially lowered in basic ice. Contamination by organic material is also possible but has yet to be well documented. The best example to date is in basal ice from the oldest ice core samples recovered from the Allan Hills blue ice site where the carbon isotopic signature clearly demonstrated the presence of organic CO<sub>2</sub> at high levels (Yan et al. 2019).

Finally, post-coring gas loss during storage is known to affect many gases (Bender, Sowers, and Lipenkov 1995) but is thought to have a minor effect on CO<sub>2</sub>, on the order of 1 ppm, as long as the outermost part of the core is removed prior to measurement (Bereiter et al., 2009). The diffusion rate of the CO<sub>2</sub> within the ice matrix is currently not well known and is an active area of research as this could lead to an artificial smoothing out of the atmospheric signal in very old ice under warm, basal ice conditions (Bereiter, Fischer, et al. 2014).

### **3 The Last Millennium: From the pre-Industrial to the Anthropocene**

#### **3.1 The industrial rise**

One of the most salient findings of ice core science is the unprecedented impact the Industrial Revolution has had on atmospheric CO<sub>2</sub> (Raynaud and Barnola 1985; Neftel, Moor, et al. 1985; Pearman et al. 1986; Etheridge et al. 1996; Siegenthaler, Monnin, et al. 2005; MacFarling Meure et al. 2006; Ahn, Brook, Mitchell, et al. 2012). Figure 3 shows many of the ice cores records that span the last millennium and dramatic rise in CO<sub>2</sub> starting around 1800 C.E. Accompanying the sharp rise in CO<sub>2</sub> is a similarly rapid decrease in  $\delta^{13}\text{C-CO}_2$  (Friedli, Löttscher, et al. 1986; Francey et al. 1999; Bauska, Joos, et al. 2015; Rubino, Etheridge, Thornton, et al. 2019). This shift to more <sup>13</sup>C-depleted values is consistent with the release of photosynthetically fixed carbon (i.e., organic carbon) as the main source of CO<sub>2</sub> to the atmosphere (Joos and Bruno 1998). Together with radiocarbon records, which fingerprint this organic material as long-dead (Stuiver and Quay 1981), the combined <sup>13</sup>C and <sup>14</sup>C records provide some of the key evidence that the rise in atmospheric CO<sub>2</sub> is almost entirely driven by the burning of fossil fuels (i.e., ancient organic carbon). Accordingly, the data unequivocally rule out that the recent CO<sub>2</sub> rise comes from volcanic sources, which have very similar source signature (-3 to -5‰) to the

pre-Industrial atmosphere and would not cause the  $\delta^{13}\text{C-CO}_2$  to decrease. The data also exclude major sources from rising ocean temperature as this would be accompanied by a decrease in the equilibrium isotopic fractionation during air-sea gas exchange and thus would cause  $\delta^{13}\text{C-CO}_2$  to increase rather than decrease.

To date, only the Law Dome ice core overlaps with the instrumental record of  $\text{CO}_2$  (Figure 3), although many firn air reconstructions also bridge this gap (Rubino, Etheridge, Thornton, et al. 2019). The excellent agreement between the ice core-based reconstruction and the instrumental record has been crucial to establishing the reliability of the ice core record. Additionally, multiple ice core records, measured at different laboratories with different methods, record remarkably similar pre-Industrial values (Figure 3). In the context of the Industrial Rise, any differences between the various records are indistinguishable.

### 3.2 The pre-Industrial

Figure 3 shows these records in detail, prior to the Industrial Rise, between 800 and 1800 C.E (Siegenthaler, Monnin, et al. 2005; Ahn, Brook, Mitchell, et al. 2012; Bauska, Joos, et al. 2015; Rubino, Etheridge, Thornton, et al. 2019). Comparing the three major records of Law Dome, WAIS Divide and EDML by first interpolating to a common timestep ( $dt = 10$  years) and then common histogram bins (Figure 3C), reveals small but significant differences. Data from the relatively low-accumulation EDML ice core (6.4 cm water equivalent per year) measured at the University of Bern average to 281.8 ppm, data from Law Dome ice core measured at Commonwealth Scientific and Industrial Research Organisation average to 280.3 ppm, and data from the WAIS Divide ice core measured at Oregon State University average to 283.0 ppm. If the three major records are weighted equally, the overall average is 281.5 ppm. Preliminary laboratory intercomparison studies suggest that these differences are not due to contrasting methods or reference schemes and thus most likely reflect the effect of small artefactual preservation in the ice (Ahn, Brook, Mitchell, et al. 2012). Note such differences cannot be due to atmospheric gradients in  $\text{CO}_2$  over Antarctica as the gas is very well-mixed on the continental-scale. Until further intercomparison work can be carried out, a conservative conclusion is that the *absolute value* of ice core-derived atmospheric  $\text{CO}_2$  cannot be determined to within 3 ppm. Although a measurable error, within the context of current atmospheric levels ( $\sim 140$  ppm higher than the pre-Industrial) and the major swings of the past ( $\sim 100$  ppm lower than the pre-Industrial), the error represents at most a 3% uncertainty. For  $\delta^{13}\text{C-CO}_2$ , the case is different, with significant differences in the mean value of the pre-Industrial between Law Dome (Rubino, Etheridge, Thornton, et al. 2019) and WAIS Divide (Bauska, Joos, et al. 2015) (Figure 3). On average the difference is about 0.1‰ or about 5% of the 2‰ shift across the Industrial Rise in  $\text{CO}_2$ . The root cause of this discrepancy is currently unknown but is more likely to arise due to the methodological differences

### 3.3 Multi-decadal scale variability: humans or climate?

In the Common Era, the ice core  $\text{CO}_2$  records reveal many common modes of variability (Figure 3). First, a rise of 5-6 ppm occurs from 950 to 1100 C.E followed by a gradual decrease of similar magnitude to a minimum around 1700 C.E. This trend is punctuated by a relatively rapid rise in  $\text{CO}_2$  around 1450 C.E., followed soon thereafter by the most dramatic change in  $\text{CO}_2$  of the pre-Industrial with a rapid drop in  $\text{CO}_2$  around 1600 C.E. The magnitude of this drop varies across different cores. It is largely absent in low-accumulation records from the DML core (Rubino, Etheridge, Trudinger, Allison, Rayner, et al. 2016), about 7 ppm in WAIS Divide, 8 ppm in Skytrain Ice Rise and very sharp at over 10 ppm in Law Dome (King et al. 2024). Broadly speaking, these variations in  $\text{CO}_2$  are negatively correlated with changes in the  $\delta^{13}\text{C-CO}_2$ . Deconvolution studies, using simple carbon cycle box models, have shown that these variations are consistent with changes in land carbon as the primary driver (Trudinger, Enting, Rayner, et al. 2002;

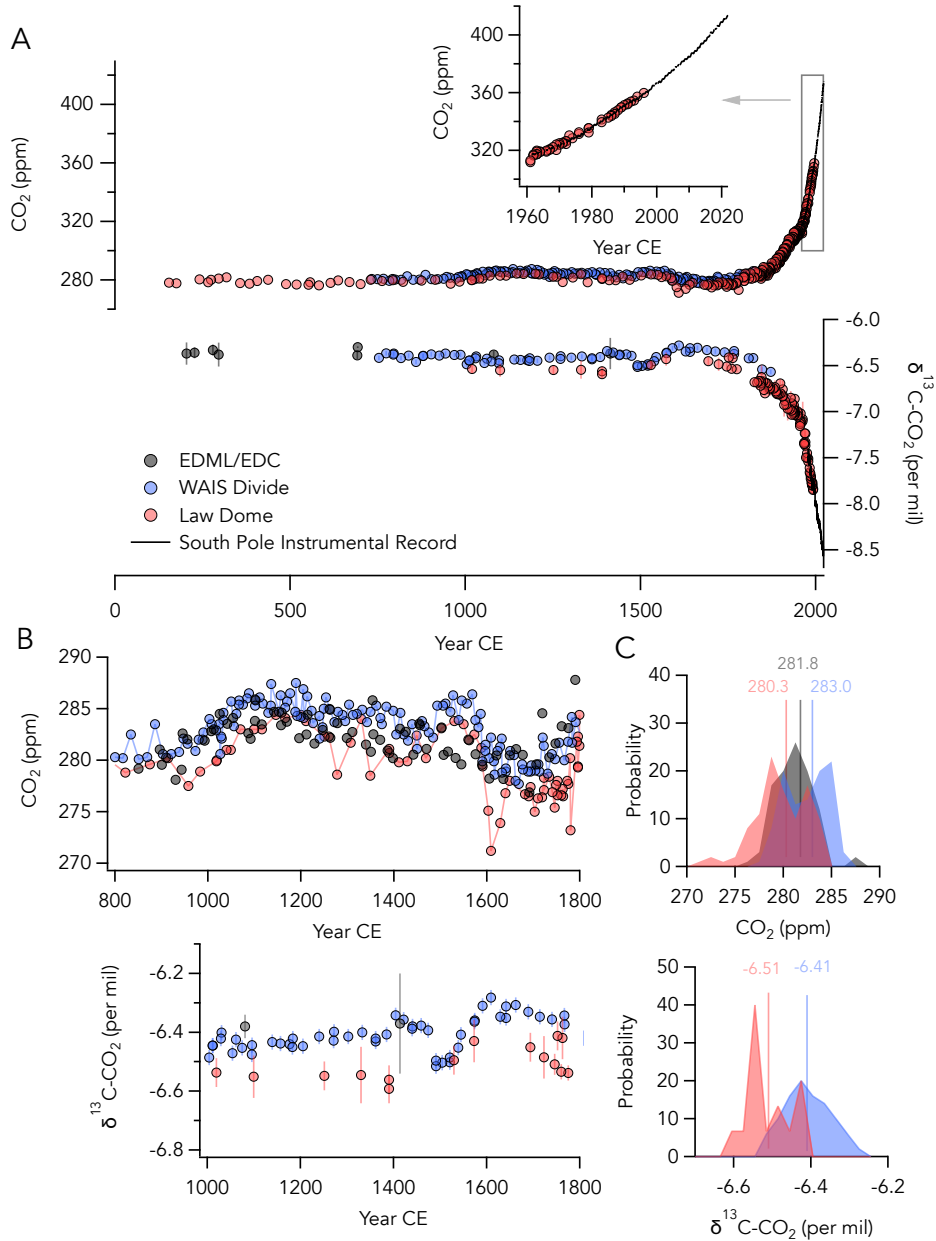


Figure 3: Panel (A): The concentration and isotopic composition of atmospheric CO<sub>2</sub> over the past two millennia. As in Figure 2, the instrumental data (black line) is sourced from South Pole Station measured as part of the Scripps Institution of Oceanography atmospheric monitoring program (Keeling et al. 2001) and is also shown in detail in the upper inset. Data sources are as follows: a combination of EPICA cores (Siegenthaler, Monnin, et al. 2005; Elsig et al. 2009) (grey); WAIS Divide Ahn, Brook, Mitchell, et al. 2012; Bauska, Joos, et al. 2015) (blue); and Law Dome (Rubino, Etheridge, Thornton, et al. 2019) (red). Panel (B): A zoom of the above showing just the variability prior to 1800 CE. Panel (C): Histograms of the pre-1800 CE data for both CO<sub>2</sub> and  $\delta^{13}\text{C-CO}_2$ . Narrow bars indicate the mean and show the overall offsets between the various records.

Rubino, Etheridge, Trudinger, Allison, Battle, et al. 2013).

The mechanisms behind multidecadal variability are currently debated (Kaplan 2015). The leading hypotheses involve human-driven land-use change or climate-driven land carbon feedbacks — or a combination of the two. In the case of land-use change, some models with high per-capita land-use suggest that variations in population can drive multi-decadal changes in CO<sub>2</sub>. The CO<sub>2</sub> increase between 950 and 1100 CE can plausibly be attributed to an increase in population in Asia associated with the rise of the Song Dynasty whilst the CO<sub>2</sub> drop at 1600 CE could be driven by large population decreases in the New World (up to 90%) following devastating epidemics (Kaplan et al. 2011; King et al. 2024).

In the case of climate-land carbon feedbacks, it has been suggested that variations in temperature on land, particularly the Arctic, controls soil respiration rates (Bauska, Joos, et al. 2015). Thereby, increases in temperature lead to greater carbon losses from soils. Although the pattern of regional temperature varies greatly, it has been suggested warming temperature around 900 CE, the so-called Medieval Warm Period, drive a loss of carbon. Conversely, cooling into the so-called Little Ice Age drives land carbon uptake. The combination of land temperature reconstruction and ice core data have been used to estimate the magnitude of the overall CO<sub>2</sub>-climate feedback Cox and Jones 2008; Frank et al. 2010) as well as parsing out the land carbon-climate sensitivity (Bauska, Joos, et al. 2015; Rubino, Etheridge, Thornton, et al. 2019). Both estimates support current estimates of the carbon-climate sensitivity in IPCC class models (Arora et al. 2020) but the systematic error introduced from the still unknown influence of humans precludes a precise determination. Moreover, comprehensive earth system models forced with realistic boundary conditions of the last millennium fail to simulate the variability seen in the ice cores (Goosse et al. 2022).

## 4 The Holocene: CO<sub>2</sub>, civilization, and the carbonate cycle

Starting about 11,600 years ago, the earth entered an extended period of relatively warm and stable climate conditions known as the Holocene. This period saw the development of human civilisation with the agricultural revolution driving large-scale land-use change. Over the same period, ice core records, primarily from lower-accumulation cores EDC and Taylor Dome (Monnin, Steig, et al. 2004), show CO<sub>2</sub> slowly varying: initially decreasing from about 270 to 260 ppm from 11,000 to 7,000 year BP and then slowly rising to 280 ppm prior to the onset of the Industrial Revolution ( Figure 4). Carbon isotope records show that the early decrease is accompanied by a steady increase of 0.3‰ and the subsequent rise is characterized by stable values with a hint of a slight decreasing trend (Elsig et al. 2009). Early, low-resolution data, which suggested large swings in  $\delta^{13}\text{C-CO}_2$ , have been ruled out as erroneous (Smith et al. 1999). Recent studies have also examined the CO<sub>2</sub> response on the millennial-scale in the early Holocene and found evidence for the fluctuations of 2–4 ppm that punctuate the initial 10 ppm drop (Shin, Ahn, et al. 2022), including a muted response to the 8.2 ka event (Ahn, Brook, and Buizert 2014).

Four major factors are thought to affect the carbon cycle during the Holocene: (1) regrowth of the terrestrial biosphere, in particular growth of extensive northern hemisphere peatlands; (2) reef building; (3) deep-water CaCO<sub>3</sub> deposition due to CaCO<sub>3</sub> compensation and (4) anthropogenic land-use change (Brovkin et al. 2019). Additionally, more speculative work has highlighted the possibility that other factors contributed such as increased volcanism (Huybers and Langmuir 2009) or continued changes in ocean circulation/biology following from deglaciation (Studer et al. 2018; Barker et al. 2019; Riechelsohn et al. 2024).

The gradual drawdown of CO<sub>2</sub> from about 11,000 to 7,000 years BP is thought to be due in large part to the regrowth of the terrestrial biosphere following the deglaciation in the Northern Hemisphere and the general climate amelioration. This is supported by both top-down constraints from the stable carbon isotopes which follow an increasing

trend (Elsig et al. 2009) and bottom-up constraints from carbon cycle models and peatland reconstructions (Stocker et al. 2017). Most likely, this is not the only process driving the changes as other processes are required to counteract this sink and maintain the CO<sub>2</sub> near interglacial levels. These likely include the shallow-water deposition of carbonate during the formation of the major modern reef systems, deep-water deposition of carbonate as the ocean became less acidic following the ventilation of waters with a high amount of dissolved CO<sub>2</sub>, and possibly increased volcanism that would have propped up CO<sub>2</sub> level in the early Holocene.

The exact causes of the rise in CO<sub>2</sub> after about 7,000 years BP remain largely elusive and hotly debated. The close coincidence of the rise and the development of agriculture lead to the provocative hypothesis that anthropogenic land-use change drove the CO<sub>2</sub> increase (Ruddiman 2003) (the so-called “early anthropogenic” or “Ruddiman hypothesis”). This has subsequently been supported by some bottom-up quantitative models of land-use (Kaplan et al. 2011) but not by others (Stocker et al. 2017) and thus remains an open question. Carbon isotope data, which would fingerprint the source of CO<sub>2</sub> as coming from the land, has largely ruled out humans as the sole driver of the CO<sub>2</sub> rise given the steady values. However, that data cannot rule out a human-driven terrestrial source as being fortuitously compensated by another naturally driven terrestrial sink. The leading culprit for such a sink is the regrowth of peatlands (Yu et al. 2014). Current evidence, based on a combination of ice core data, peatland reconstruction and modelled land-use change scenarios suggest that land-use emissions may have played a role as early as 3,000 years ago (Stocker et al. 2017).

## 5 The Last Deglaciation: CO<sub>2</sub> as both forcing and feedback

### 5.1 Constraints from CO<sub>2</sub> Concentration

Starting about 20,000 years ago, the earth began transitioning from the most recent glacial period into the current warm period. The glacial termination was accompanied by a substantial rise in atmospheric CO<sub>2</sub> (Figure 4). Pioneering measurements on the Byrd ice core (Berner, Oeschger, and Stauffer 1980; Delmas, Ascencio, and Legrand 1980; Neftel, Oeschger, et al. 1982) constrained the magnitude of CO<sub>2</sub> change but could not precisely define the timing. High-quality data from EDC demonstrated that the deglacial CO<sub>2</sub> rise (76 ppm) occurred over four distinct stages (Monnin, Indermühle, et al. 2001). The chronology of EDC is complicated by large and variable delta-ages during the deglaciation (2,000 in the Holocene to 5,500 years in the LGM). Although the original chronology was inaccurate in detail, these broad trends have been preserved in subsequent revisions (Parrenin et al. 2013). First, CO<sub>2</sub> quickly rose from approximately 18 to 16.1 ka (sometimes referred to as Heinrich stadial 1b) followed by a more gradual rise until the onset of the Bölling-Allerod (B/A) at 14.6 ka. CO<sub>2</sub> then plateaued during the Antarctic Cold Reversal (ACR) before resuming a relatively fast rise during the Younger-Dryas (YD : 12.9 to 11.5 ka) until the onset of the pre-Boreal.

This pattern of two major ramps and one plateau mimics changes in Antarctic temperature. The two changes are nearly synchronous with no clear lead or lag with the critical exception that the initial rise in Antarctic temperature preceded the rise in CO<sub>2</sub> (Chowdhry Beeman et al. 2019). On a global scale, the opposite is the case. Global temperatures clearly lag the changes in CO<sub>2</sub> and thus solidifies the role of CO<sub>2</sub> in driving of the deglaciation alongside changes in insolation, ice sheets and dust (Shakun et al. 2012; Osman et al. 2021).

The EDC record also showed that both the onset of the B/A and the pre-Boreal are associated with centennial-scale “jumps” in the CO<sub>2</sub> record. At the time, these jumps were resolved by only two data points and near the cut-off edge of resolvable variability given the high degree of firn-smoothing. It was thus unclear if the jumps could be significantly faster or even larger in magnitude (Köhler et al. 2011). Results from the higher-accumulation

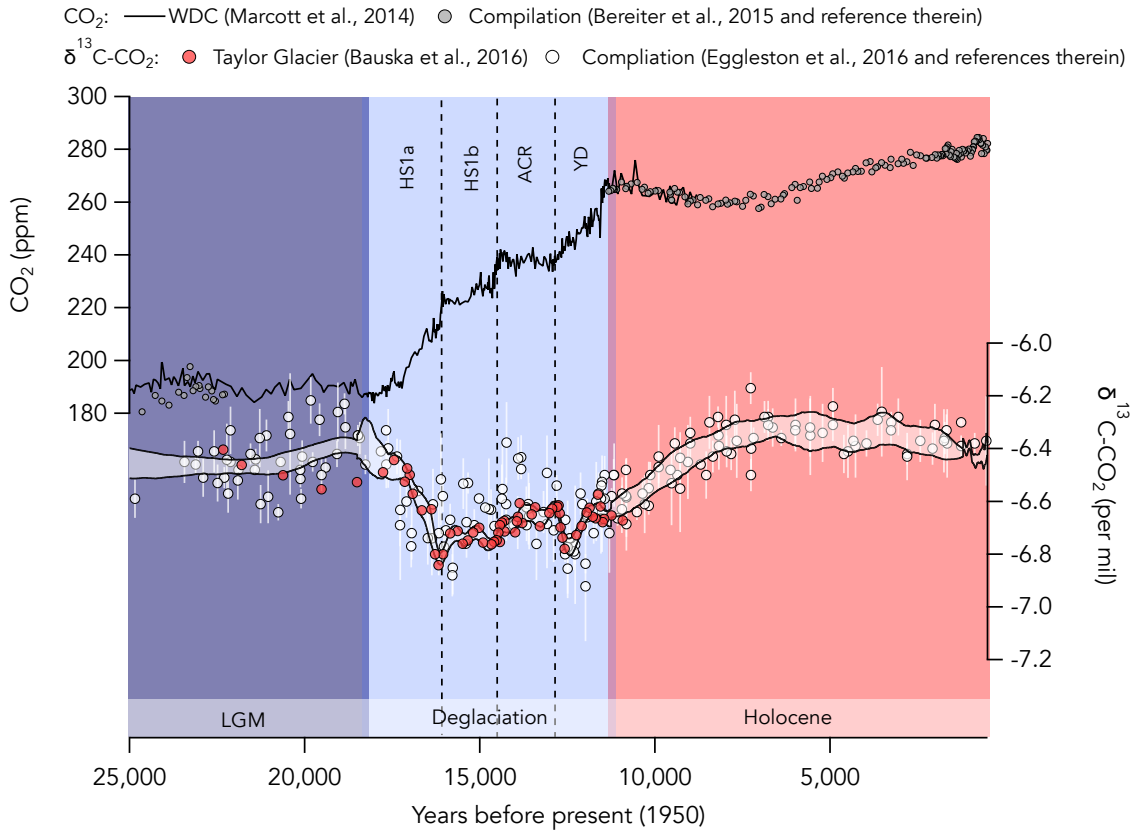


Figure 4: The concentration and isotopic composition of atmospheric CO<sub>2</sub> spanning the Last Glacial Maximum (LGM), Last Deglaciation and Holocene (prior the Industrial period). CO<sub>2</sub> data in grey come from a compilation of data primarily from (Monnin, Steig, et al. 2004; Ahn and Brook 2008; Bereiter, Eggleston, et al. 2015); CO<sub>2</sub> data in black come solely from the WAIS Divide Ice Core Marcott et al. 2014; Bauska, Marcott, and Brook 2021).  $\delta^{13}\text{C-CO}_2$  in white comes from a variety of sources compiled in Eggleston et al. 2016). Data in red come from the Taylor Glacier blue ice core (Bauska, Baggenstos, et al. 2016). Dashed lines show the boundaries between key intervals referenced in the main text: Heinrich Stadial 1a (HS1a); Heinrich Stadial 1b (HS1b); Antarctic Cold Reversal (ACR); and the Younger-Dryas (YD).

Siple Dome ice core hinted that faster rates of change were possible, but generally scattered CO<sub>2</sub> data obscured some of the critical variability (Ahn, Wahlen, et al. 2004). The WAIS Divide ice core provided both a well-dated CO<sub>2</sub> (delta age 200 years in the Holocene –500 years in the LGM) with high enough resolution to reveal centennial-scale changes (Marcott et al. 2014). The two CO<sub>2</sub> jumps at the onset of the B/A ( $12 \pm 1$  ppm within  $200 \pm 30$  years) and pre-Boreal ( $13 \pm 1$  ppm within  $100 \pm 40$  years) were confirmed and determined to be precisely in-phase with rises in CH<sub>4</sub>. Additionally, a second mode of centennial-scale variability was observed at 16.3 ka ( $12 \pm 1$  ppm within  $100 \pm 20$  years). This jump also demarcates the previously identified switch to a much slower rate of CO<sub>2</sub> rise (Monnin, Indermühle, et al. 2001), which in WAIS Divide is even more dramatic with a small plateau in CO<sub>2</sub> immediately following the jump.

## 5.2 Constraints from Carbon Isotopes

Pioneering measurements from the last glacial maximum (Leuenberger, Siegenthaler, and Langway 1992) and these across the last deglaciation (Smith et al. 1999) revealed a broad minimum of “U” shape indicating a switch in source of CO<sub>2</sub> during the deglacial transition. Higher-resolution yet relatively low-precision data from EDC showed some rapid fluctuations, possibly at the onset of the B/A and YD (Lourantou, Lavrič, et al. 2010). Thus the “U” became more of a “W”. EDC was later refined with the inclusion of higher-precision measurements from a sublimation-based extraction which dampened the “W” back towards a “U” (Schmitt, Schneider, Elsig, et al. 2012). (Figure 4 shows primarily this data). Crucially, the data showed that the initial CO<sub>2</sub> rise (18-16 ka) was associated with a 0.3‰ drop in  $\delta^{13}\text{C-CO}_2$  —in other words that the first drop to the bottom of the “U” was very sharp. More recently, high-precision measurements using large volume samples from Taylor Glacier confirmed the “U” and provided strong constraints on centennial-scale features (Bauska, Baggenstos, et al. 2016). The CO<sub>2</sub> jumps at the onset of the B/A and pre-Boreal showed only minor changes or slight shifts towards enriched values in carbon isotopes whereas the CO<sub>2</sub> jump at 16.3 ka was associated with a sharp minimum well below the 0.3‰ drop. A similar minimum was found at the onset of the YD. In the simplest terms, the “U” remains the major feature of the deglaciation but superimposed on this is a lowercase “w” with local minima at 16.3 and 12.9 ka.

## 5.3 Mechanisms in brief

Following on decades of research across a broad range of palaeoclimate disciplines, the list of possible carbon cycle mechanisms responsible for the CO<sub>2</sub> rise during the deglaciation has become relatively well defined and nearly exhaustive. However, it remains to be quantified precisely when and to what magnitude a given mechanism contributed to the deglacial rise. The list includes: (1) rising ocean temperature (a source); (2) decreasing ocean salinity (a sink); (3) gradual regrowth of the terrestrial biosphere (a slow sink); (4) rapid releases of terrestrial carbon (a transient source); (5) reef building (a source); (6) CaCO<sub>3</sub> compensation as a feedback from the transfer of CO<sub>2</sub> from the ocean to the atmosphere and terrestrial biosphere (a source); (7) increased upwelling of respired carbon in the Southern Ocean (a source from a “bottom-up” weakening of the biological pump); (8) decreased productivity in the Southern Ocean (a source from a “top-down” weakening of the biological pump); (9) AMOC shutdowns (a complicated process but probably an overall source from a weakening of the biological pump); and (10) reductions in Antarctic sea-ice (a source). These ten or more mechanisms can be grouped into five categories that can be partially delineated using paired measurements of CO<sub>2</sub> and  $\delta^{13}\text{C-CO}_2$ : (i) the solubility pump; (ii) the biological pump; (iii) the alkalinity pump; (iv) the disequilibrium carbon pump; and (v) terrestrial carbon storage.

Parsing the specific carbon cycle through time with ice core data alone is a highly under-constrained problem. Despite this, progress has been made by synthesizing ice core

data with other palaeoclimate records and model results. A brief overview follows. Firstly, the initial increase in CO<sub>2</sub> from 18 to 16.1 ka is associated almost exclusively with a release of organic carbon — most likely from a weakening of the biological pump. It is currently debated whether this weakening comes from “below” via upwelling (Schmitt, Schneider, Elsig, et al. 2012) or from “above” via iron fertilization (Bauska, Baggenstos, et al. 2016) or some combination of the two. This crucial period, when CO<sub>2</sub> is rising quickly, ends with an abrupt release of CO<sub>2</sub> to the atmosphere that must come from transient sourced light carbon – possibly from the terrestrial biosphere (Bauska, Baggenstos, et al. 2016) or from a rapid ventilation of an intermediate water mass (Menviel et al. 2018). After 16 ka, as the CO<sub>2</sub> increase slows down, the effect of rising ocean temperatures begins to play a bigger role indicating that positive feedbacks in the carbon cycle are beginning to operate. These continue throughout the rest of the deglaciation and indeed, rising ocean temperatures may be partially responsible for the CO<sub>2</sub> jumps during the warming at B/A and the end of the YD. The second ramp up in CO<sub>2</sub> during the YD is most likely a smaller version of increase during HS1 that is additionally superimposed upon slowly evolving positive feedbacks from rising ocean temperatures, reef building, and CaCO<sub>3</sub> compensation, as well as negative feedbacks from increased terrestrial carbon storage. In summary, the ice core data show that the initial trigger for the CO<sub>2</sub> rise is most likely a small set of mechanisms related the biological pump whereas the rise that follows is caused by a complex set of feedbacks that may only be activated when the earth fully transitions out of a glacial period.

However, there are a number of unresolved questions. What is the role for changes in air-sea gas exchange and sea-ice during the deglaciation? What is the relationship between the rapid rise in mean ocean temperature (Bereiter, Shackleton, et al. 2018) during the initial CO<sub>2</sub> rise given that the carbon isotopes indicate a minimal role for changes in solubility? Precisely to what degree did CaCO<sub>3</sub> feedbacks or volcanic emissions play a role in establishing interglacial levels?

## 6 The Pleistocene: Tracing the heartbeat of The Ice Age

The first indication of CO<sub>2</sub> variability across a complete glacial-interglacial came from pioneering measurements on the Vostok ice core (Barnola et al. 1987). It was immediately recognized that CO<sub>2</sub> closely tracks Antarctic temperature, as indicated in stable water isotope records (see chapter on water isotopes). This same pattern of near one-to-one coupling has been replicated in many cores (Figure 5), extended further back in time to 800,000 years ago (Petit et al. 1999; Siegenthaler, Stocker, et al. 2005; Lüthi et al. 2008; Bereiter, Eggleston, et al. 2015) and further refined with higher-resolution data which show the tight coupling is present at the millennial-scale Stauffer et al. 1998; Ahn and Brook 2008; Bereiter, Lüthi, et al. 2012; Shin, Nehrbass-Ahles, et al. 2020. This one-to-one coupling probably only breaks down on centennial-scales (Ahn and Brook 2014; Nehrbass-Ahles et al. 2020; Bauska, Marcott, and Brook 2021).

### 6.1 Glacial-interglacial variability

The mode of variability with the largest range are the glacial-interglacial cycles that exhibit a roughly 100,000 year cyclicality with the classic “sawtooth” pattern that characterizes global swings in temperature and ice volume during the late Pleistocene. In detail, the range spans about 190 to 280 ppm during the most recent four cycles but is markedly smaller during earlier cycles – between about 190 to and 250 ppm (Figure 5). This mode switch occurs as part of the so-called mid-Brunhes transition, which is an enigmatic shift between MIS 13 and MIS 11, primarily in the magnitude for glacial-interglacial variability seen in many different climate reconstructions (Barth et al. 2018). Over the entire ice core record, the lowest CO<sub>2</sub> value ever measured in a deep ice core 173.7 ppm at ~670 ka and the highest value, prior to the Industrial Revolution, is 300 ppm at 334 ka.

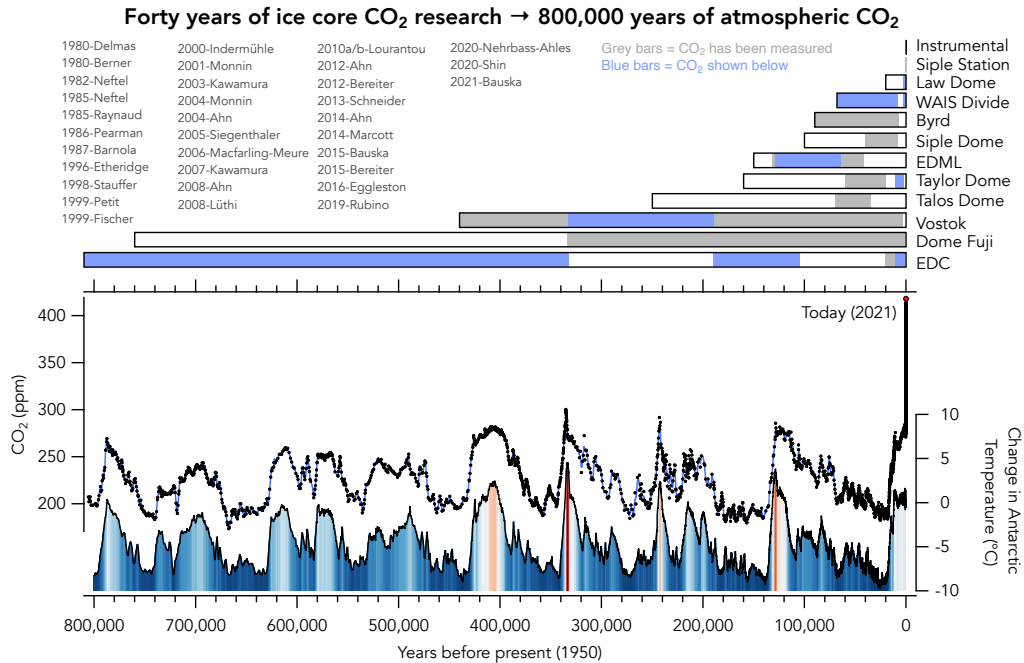


Figure 5: The complete record of atmospheric CO<sub>2</sub> from the present day to the oldest ice ever recovered from a deep, continuous ice core (black markers with blue smoothing spline). The bars on the top extending back in time indicate the span of ages of ice recovered in a given ice core with the grey bars indicating zones where CO<sub>2</sub> has been measured, but not shown in this compilation due to superior data from other cores, and the blue bars indicating zones where CO<sub>2</sub> has also been measured and displayed below. Alongside the CO<sub>2</sub> data is a temperature stack from Antarctica as compiled by Parrenin et al. 2013. The color bars below the curve are varied from warm temperatures (red) to cold temperature (blue) with an asymmetric red-to-white-to-blue color ramp. CO<sub>2</sub> data source include: (Ahn, Brook, Mitchell, et al. 2012; Ahn and Brook 2008; Ahn and Brook 2014; Barnola et al. 1987; Bauska, Joos, et al. 2015; Bauska, Marcott, and Brook 2021; Bereiter, Lüthi, et al. 2012; Bereiter, Eggleston, et al. 2015; Berner, Oeschger, and Stauffer 1980; Delmas, Ascencio, and Legrand 1980; Eggleston et al. 2016; Etheridge et al. 1996; Fischer, Wahlen, et al. 1999; Indermühle et al. 2000; Kawamura, Nakazawa, et al. 2003; Kawamura, Parrenin, et al. 2007; Lourantou, Chappellaz, et al. 2010; Lourantou, Lavrič, et al. 2010; Lüthi et al. 2008; MacFarling Meure et al. 2006; Monnin, Indermühle, et al. 2001; Monnin, Steig, et al. 2004; Neftel, Oeschger, et al. 1982; Neftel, Moor, et al. 1985; Nehrbass-Ahles et al. 2020; Pearman et al. 1986; Petit et al. 1999; Raynaud and Barnola 1985; Rubino, Etheridge, Thornton, et al. 2019; Shin, Nehrbass-Ahles, et al. 2020; Siegenthaler, Stocker, et al. 2005; Stauffer et al. 1998)

As opposed to the deglaciation, where we have radiocarbon dated proxy records, defining the lead-lag between temperature and CO<sub>2</sub> over the entire glacial-interglacial record is much more challenging. Some insights can be gained by comparing directly to the Antarctic temperature records (shown as a compilation of records in Figure 5). As the earth first re-enters a glacial period (e.g., MIS5e to 5d or ~120 to 100 ka), Antarctic temperatures tend to drop earlier and to a much greater extent than CO<sub>2</sub>. This apparent lag may be due to a gradual release of terrestrial carbon and lingering effects of the penultimate deglaciation via CaCO<sub>3</sub> compensation that maintain CO<sub>2</sub> at interglacial levels despite the nascent glacial conditions (Schneider et al. 2013). Additionally, the processes that draw-down CO<sub>2</sub> to the lowest level during full glacial (e.g., MIS 5a to MIS4 or ~75-65 ka) are highly complex and probably involve most of the mechanisms responsible for a deglaciation but in the opposite sense and in a different sequence of events Eggleston et al. 2016; Menking et al. 2022). Most notably, paired measurements of CO<sub>2</sub> and  $\delta^{13}\text{C-CO}_2$  indicate that there are potentially large swings in air-sea gas disequilibrium, most likely driven by changes in Antarctic sea-ice, under glacial conditions.

## 6.2 Millennial- and centennial-scale variability

Most of our knowledge of millennial-scale variability comes from studies of the last glacial period (Ahn and Brook 2008; Ahn and Brook 2014; Bereiter, Lüthi, et al. 2012; Bauska, Marcott, and Brook 2021; Wendt et al. 2024), although progress has recently been made to extend high-resolution datasets into older glacial period (Nehrbass-Ahles et al. 2020; Shin, Nehrbass-Ahles, et al. 2020). The most salient observation is that CO<sub>2</sub> is positively correlated with Antarctic temperature in a very similar pattern to the longer glacial-interglacial mode of variability (Figure 6). These triangular wave-like variations are sometimes referred to as carbon dioxide maxima (CDM) and can vary between 10 and 30 ppm. The rising limbs are usually associated with coldest stadial conditions and the descending limbs associated with the interstadial phases. Although carbon isotope data remain scarce, available data suggest that dominant mechanisms at play are changes in strength of biological pump with minimal feedbacks from global changes in ocean temperature (Bauska, Brook, Marcott, et al. 2018). Multiple-lines of evidence point to the Southern Ocean as a route by which the CO<sub>2</sub> escapes from the deep ocean to the atmosphere, implicating the bi-polar seesaw as a crucial driver of this variability. The initial trigger and/or the specific climate state that precondition the carbon cycle to this mode of variability is unresolved and probably will remain so until a theory of the millennial-scale climate changes becomes more complete.

On the centennial-scale this strong relationship between Antarctic temperature and CO<sub>2</sub> tends to breakdown (Ahn and Brook 2014; Bauska, Marcott, and Brook 2021). Firstly, following the onset of an interstadial (a warming) in Greenland (sometimes inferred from a large increase in CH<sub>4</sub>), CO<sub>2</sub> continues to rise or even rapidly increases (see Figure 6 for examples during Last Glacial Period). This variability is akin to rapid jumps during the B/A and end of the YD during the deglaciation discussed earlier and have been referred to as carbon dioxide jumps plus (CDJ+) (Nehrbass-Ahles et al. 2020). They are pervasive during the last glacial period and have been identified in some high-resolution section in older glacials. They also occur at the onset of some interglacials as dramatic “overshoots” with CO<sub>2</sub> reaching some of the highest levels observed prior to the Industrial Period (300 ppm) – most notably at 426, 334, 242 and 129 ka. Limited isotope data suggests that rapid rises at DO8, B/A and end of the YD are not dominated by terrestrial carbon releases (Bauska, Baggenstos, et al. 2016; Bauska, Brook, Marcott, et al. 2018); conversely DO19 – which occurs during a period of intermediate ice volume -could be explained by a pulse of terrestrial carbon (Menking et al. 2022). It thus remains an open question as to whether these overshoots are, at least in part, driven by rapid destabilisation of terrestrial carbon. Crucially, the dramatic “overshoots” at the onset of the older interglacials have yet to be fingerprinted.

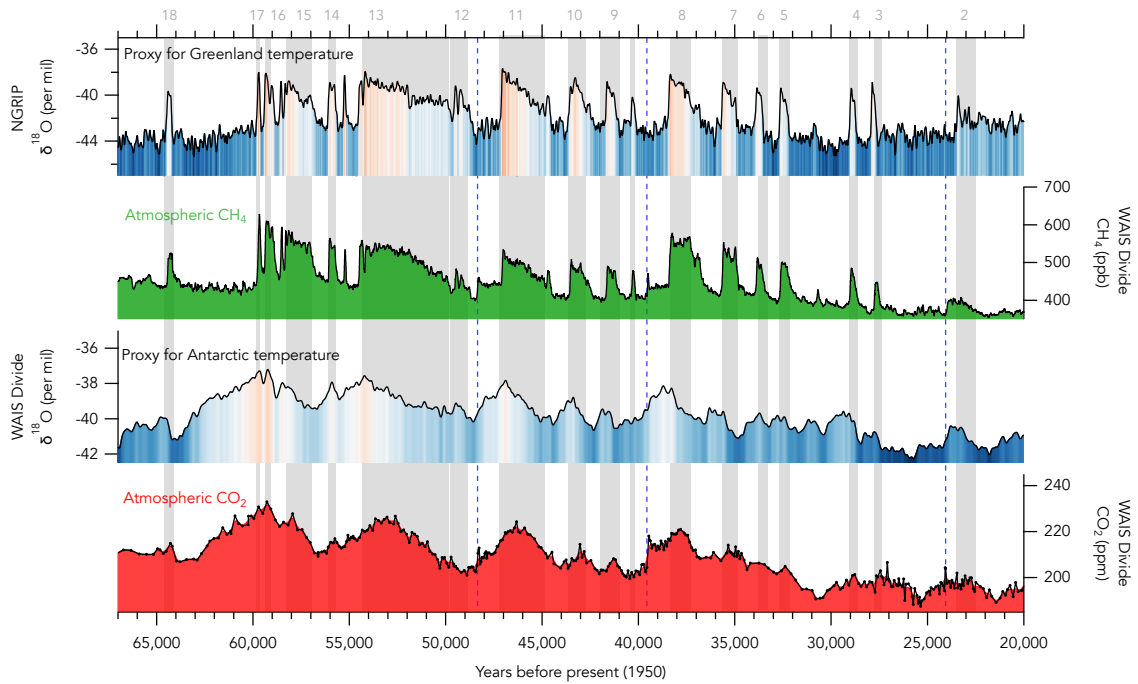


Figure 6: A simple synthesis of climate and carbon cycle variability during a portion (67–20 ka) of the Last Glacial Period. The four time-series are as follows: (1) a proxy for Greenland temperature based on NGRIP oxygen isotopes (Andersen et al. 2004) with the age model adjusted by 1.0063 as per (Buizert, Cuffey, et al. 2015) with a red (warm)-to-blue (cold) color ramp as fill; (2) the continuous CH<sub>4</sub> records from WAIS Divide (Rhodes et al. 2015) with a green fill; (3) a proxy for Antarctic temperature from the WAIS Divide oxygen isotopes (Buizert, Adrian, et al. 2015) with a similar red-to-blue fill; and (4) the WAIS Divide record of atmospheric CO<sub>2</sub> (Bauska, Marcott, and Brook 2021) with a red fill. Grey bars show interstadial periods; blue bars shows some of the major Heinrich Events.

Secondly, the most rapid natural increase in CO<sub>2</sub> occurs within a stadial (cold phase) in Greenland and is always associated with a Heinrich Event (Marcott et al. 2014). To date, the largest increase is found at Heinrich Event 4 (39.5 ka) and is characterized by a 14–15 ppm rise in as little as 100 years (Bauska, Marcott, and Brook 2021)(Figure 6)). Again, there is a straightforward analogy found within the last deglaciation at 16.1 ka (Heinrich Event 1) as described previously (Figure 4). These have been termed carbon dioxide jumps minus (CDJ-) and coincident with a small increase in CH<sub>4</sub> closely associated with Heinrich Events - the so-called “Rhodes’ Bumps” (Rhodes et al. 2015). Carbon isotope evidence suggests the source of these jumps could be terrestrial in origin, although it cannot be ruled out that large changes in air-sea gas exchange combined with rapid ocean ventilation could be at play (Bauska, Brook, Marcott, et al. 2018; Wendt et al. 2024).

Both types of events suggest that the carbon cycle can respond quickly to abrupt climate change. In particular, reactions to rapid increases in Arctic temperatures and shifts in tropical precipitation may force carbon cycle responses on timescales that are relevant to policy makers, greenhouse gas emissions reductions strategies, and future climate--carbon feedbacks.

## 7 The Pleistocene and beyond: Atmospheric CO<sub>2</sub> from surface outcrops and buried pockets of ancient ice

Prior to 800 ka, the ice core record of atmospheric gases becomes discontinuous, yet still yields critical information about radiative forcing and carbon cycle dynamics from “snapshots” of CO<sub>2</sub> recovered from blue ice areas. Most notably, recent discoveries of ice as old as 3 million years old at the Allan Hills site in East Antarctica have provided reliable CO<sub>2</sub> measurements back to 2 million years ago (Higgins et al. 2015; Yan et al. 2019) (Figure 7). Critically, these records now extend through the mid-Pleistocene Transition (MPT) – the transition between the “40 k world” characterized by shorter, smaller magnitude glacial-interglacial cycles to the “100 k world” characterized by longer, larger magnitude cycles (Clark et al. 2006; Lisiecki and Raymo 2005). Because the ice at these sites is often out of stratigraphic order where the oldest ice is only found near the bedrock-ice interface (tens of meters above the bed), the ages of individual gas samples must be determined using co-registered measurements of <sup>40</sup>Ar-based ages and then binned into bulk ages with wide ranges ( $\pm \sim 10\%$  of the absolute age). Note that some samples recovered appear to be contaminated by in situ production of CO<sub>2</sub> from organic carbon as indicated by implausibly negative  $\delta^{13}\text{C-CO}_2$  values and have subsequently been excluded.

Information gleaned from the covariation of the atmospheric CO<sub>2</sub> data with other gas records (notably CH<sub>4</sub>) and climate proxies (notably water isotopes) suggest that climate-carbon cycle systematics do not deviate from relationships, nor exceed the range of variability, observed over the past 800,000 years. However, prior to the MPT, there is notable absence of CO<sub>2</sub> data with concentrations that fall on the lower end of the glacial-interglacial spectrum. This suggests that the transition from the 40 k to 100 k world was accompanied by a shift towards lower glacial CO<sub>2</sub> concentration but potentially invariant interglacial CO<sub>2</sub> concentrations. Numerous international efforts are currently underway to recover continuous records of CO<sub>2</sub> from traditional deep ice cores that should reveal the precise nature of the MPT (Fischer, Severinghaus, et al. 2013).

## 8 Outlook

Ice core records of atmospheric CO<sub>2</sub> have revealed multiple modes of natural variability in the carbon cycle that, first and foremost, clearly distinguish the rise in CO<sub>2</sub> since Industrial Revolution as unprecedented. The data have also demonstrated the tight coupling between CO<sub>2</sub> and climate over a wide variety of timescales and have thus identified the presence of strong, natural feedbacks between the climate system and the carbon cycle.

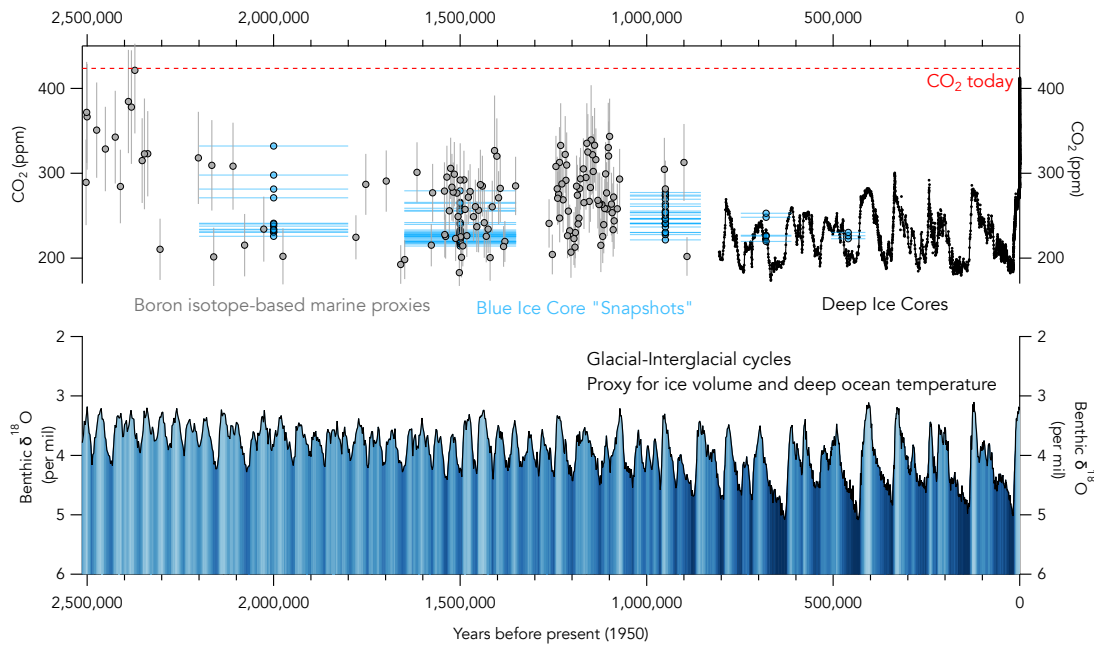


Figure 7: The complete record of atmospheric CO<sub>2</sub> from the present day to the oldest ice ever recovered as in Fig. 4 but with the additional of data from blue ice sites (Higgins et al. 2015; Yan et al. 2019) (light blue markers) along with boron isotope-based proxies for CO<sub>2</sub> (Chalk et al. 2017; Dyez, Hönisch, and Schmidt 2018) (grey markers). Also shown is the canonical record of glacial-interglacial variability from a stack of benthic oxygen isotope data – a proxy for global ice volume and deep ocean temperature (Lisiecki and Raymo 2005).

The root causes of much of the CO<sub>2</sub> variability remain elusive; as does a complete understanding of the mechanisms that couple climate to the carbon cycle. Despite recent progress in analytical techniques (particularly the isotopic composition of CO<sub>2</sub>), improvements in resolution (particularly high-accumulation cores with accurate gas chronologies), and advances in carbon cycle modelling (particularly isotope-enabled models), several key questions persist.

1. What causes glacial-interglacial changes in CO<sub>2</sub> and thus what role do carbon cycle feedbacks play in pacing the glacial-interglacial cycles?
2. Are oceanic or terrestrial sources responsible for the rapid jumps in CO<sub>2</sub> observed during glacial conditions?
3. What role did humans play, if any, in driving the gradual increase in CO<sub>2</sub> over the last 7,000?
4. Finally, given the presence of both positive and negative feedbacks between the climate and the carbon cycle, can ice cores inform us how quickly CO<sub>2</sub> will decrease if and when anthropogenic emissions drop to a net sum of zero?

These questions, as well as many others, will hopefully be answered by integrating ice core data with other paleoclimate proxy information through the use of earth system models.

## Glossary

**Carbon-12** <sup>12</sup>C — A stable isotope of carbon with six protons and six neutrons that is the most abundant form of carbon on earth at about 99%. 18

**Carbon-13**  $^{13}\text{C}$  — A stable isotope of carbon with seven neutrons which is the second most abundant form of carbon at about 1%. Reported as parts per thousand, per mil (‰) deviation on the VPDB reference scale using the delta ( $\delta$ ) notation.. 18

**Carbon-14**  $^{14}\text{C}$  — A radioactive isotope (i.e., “radiocarbon”) with eight neutrons and half-life of 5700 years occurring at the parts per trillion level.. 18

**Deconvolution methods** A class of numerical techniques whereby different atmospheric fluxes (typically land and ocean fluxes) are separated out from common signal (typically  $\delta^{13}\text{C-CO}_2$  in the case of “single deconvolution” or both  $\text{CO}_2$  and  $\delta^{13}\text{C-CO}_2$  in the case of a “double deconvolution”). These are most often performed directly with a carbon cycle model or with a simplified emulator of a carbon cycle model. 18

**Fractionation factor** The isotopic difference between two reservoirs that is established by either two-way processes that have reached a chemical equilibrium (equilibrium fractionation), one-way processes (kinetic fractionation), or a combination of the two.. 18

**VPDB** “Vienna Pee Dee Belemnite” A virtual anchor point which defines the per mil (‰) scale used to report the stable isotopes of atmospheric  $\text{CO}_2$ . The anchor is zero per mil by definition. Several primary references then define the scale. For atmospheric gases, typically the directly referenced materials measured routinely in laboratories are secondary standards produced from atmospheric mixtures.. 18

## References

- Ahn, Jinho, Edward J Brook, and Christo Buizert (2014). “Response of atmospheric  $\text{CO}_2$  to the abrupt cooling event 8200 years ago”. In: *Geophysical Research Letters* 41.2. eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2013GL058177>, pp. 604–609. DOI: <https://doi.org/10.1002/2013GL058177>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2013GL058177>.
- Ahn, Jinho and Edward J. Brook (2008). “Atmospheric  $\text{CO}_2$  and Climate on Millennial Time Scales During the Last Glacial Period”. In: *Science* 322.5898. eprint: <https://www.science.org/doi/pdf/10.1126/science.1160832>, pp. 83–85. DOI: [10.1126/science.1160832](https://www.science.org/doi/abs/10.1126/science.1160832). URL: <https://www.science.org/doi/abs/10.1126/science.1160832>.
- (2014). “Siple Dome ice reveals two modes of millennial  $\text{CO}_2$  change during the last ice age”. In: *Nature Communications* 5.1. Publisher: Nature Publishing Group UK London, p. 3723.
- Ahn, Jinho, Edward J. Brook, and Kate Howell (2009). “A high-precision method for measurement of paleoatmospheric  $\text{CO}_2$  in small polar ice samples”. In: *Journal of Glaciology* 55.191, pp. 499–506. DOI: [10.3189/002214309788816731](https://doi.org/10.3189/002214309788816731).
- Ahn, Jinho, Edward J. Brook, Logan Mitchell, et al. (2012). “Atmospheric  $\text{CO}_2$  over the last 1000 years: A high-resolution record from the West Antarctic Ice Sheet (WAIS) Divide ice core”. In: *Global Biogeochemical Cycles* 26.2. Publisher: Wiley Online Library.
- Ahn, Jinho, Melissa Headly, et al. (2008). “ $\text{CO}_2$  diffusion in polar ice: observations from naturally formed  $\text{CO}_2$  spikes in the Siple Dome (Antarctica) ice core”. In: *Journal of Glaciology* 54.187. Publisher: Cambridge University Press, pp. 685–695.
- Ahn, Jinho, Martin Wahlen, et al. (2004). “A record of atmospheric  $\text{CO}_2$  during the last 40,000 years from the Siple Dome, Antarctica ice core”. In: *Journal of Geophysical Research: Atmospheres* 109 (D13). Publisher: Wiley Online Library.

- Andersen, K. K. et al. (Sept. 1, 2004). “High-resolution record of Northern Hemisphere climate extending into the last interglacial period”. In: *Nature* 431.7005, pp. 147–151. ISSN: 1476-4687. DOI: [10.1038/nature02805](https://doi.org/10.1038/nature02805). URL: <https://doi.org/10.1038/nature02805>.
- Anklin, M. et al. (1997). “CO<sub>2</sub> record between 40 and 8 kyr B.P. from the Greenland Ice Core Project ice core”. In: *Journal of Geophysical Research: Oceans* 102 (C12). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/97JC00182>, pp. 26539–26545. DOI: <https://doi.org/10.1029/97JC00182>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/97JC00182>.
- Arora, V. K. et al. (2020). “Carbon–concentration and carbon–climate feedbacks in CMIP6 models and their comparison to CMIP5 models”. In: *Biogeosciences* 17.16, pp. 4173–4222. DOI: [10.5194/bg-17-4173-2020](https://doi.org/10.5194/bg-17-4173-2020). URL: <https://bg.copernicus.org/articles/17/4173/2020/>.
- Assonov, S. S., C. A. M. Brenninkmeijer, and P. Jöckel (2005). “The <sup>18</sup>O isotope exchange rate between firm air CO<sub>2</sub> and the firm matrix at three Antarctic sites”. In: *Journal of Geophysical Research: Atmospheres* 110 (D18). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2005JD005769>. DOI: <https://doi.org/10.1029/2005JD005769>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2005JD005769>.
- Barker, Stephen et al. (2019). “Early Interglacial Legacy of Deglacial Climate Instability”. In: *Paleoceanography and Paleoclimatology* 34.8. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2019PA003661>, pp. 1455–1475. DOI: <https://doi.org/10.1029/2019PA003661>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2019PA003661>.
- Barnola, J. M. et al. (Oct. 1, 1987). “Vostok ice core provides 160,000-year record of atmospheric CO<sub>2</sub>”. In: *Nature* 329.6138, pp. 408–414. ISSN: 1476-4687. DOI: [10.1038/329408a0](https://doi.org/10.1038/329408a0). URL: <https://doi.org/10.1038/329408a0>.
- Barth, A. M. et al. (2018). “Climate evolution across the Mid-Brunhes Transition”. In: *Climate of the Past* 14.12, pp. 2071–2087. DOI: [10.5194/cp-14-2071-2018](https://doi.org/10.5194/cp-14-2071-2018). URL: <https://cp.copernicus.org/articles/14/2071/2018/>.
- Bauska, Thomas K., Daniel Baggenstos, et al. (2016). “Carbon isotopes characterize rapid changes in atmospheric carbon dioxide during the last deglaciation”. In: *Proceedings of the National Academy of Sciences* 113.13. \_eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.1513868113>, pp. 3465–3470. DOI: [10.1073/pnas.1513868113](https://doi.org/10.1073/pnas.1513868113). URL: <https://www.pnas.org/doi/abs/10.1073/pnas.1513868113>.
- Bauska, Thomas K., Edward J. Brook, Shaun A. Marcott, et al. (2018). “Controls on Millennial-Scale Atmospheric CO<sub>2</sub> Variability During the Last Glacial Period”. In: *Geophysical Research Letters* 45.15. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2018GL077881>, pp. 7731–7740. DOI: <https://doi.org/10.1029/2018GL077881>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2018GL077881>.
- Bauska, Thomas K., Edward J. Brook, Alan C. Mix, et al. (2014). “High-precision dual-inlet IRMS measurements of the stable isotopes of CO<sub>2</sub> and the N<sub>2</sub>O/CO<sub>2</sub> ratio from polar ice core samples”. In: *Atmospheric Measurement Techniques* 7.11, pp. 3825–3837. DOI: [10.5194/amt-7-3825-2014](https://doi.org/10.5194/amt-7-3825-2014). URL: <https://amt.copernicus.org/articles/7/3825/2014/>.
- Bauska, Thomas K., Fortunat Joos, et al. (May 1, 2015). “Links between atmospheric carbon dioxide, the land carbon reservoir and climate over the past millennium”. In: *Nature Geoscience* 8.5, pp. 383–387. ISSN: 1752-0908. DOI: [10.1038/ngeo2422](https://doi.org/10.1038/ngeo2422). URL: <https://doi.org/10.1038/ngeo2422>.
- Bauska, Thomas K., Shaun A. Marcott, and Edward J. Brook (Feb. 1, 2021). “Abrupt changes in the global carbon cycle during the last glacial period”. In: *Nature*

- Geoscience* 14.2, pp. 91–96. ISSN: 1752-0908. DOI: [10.1038/s41561-020-00680-2](https://doi.org/10.1038/s41561-020-00680-2). URL: <https://doi.org/10.1038/s41561-020-00680-2>.
- Bender, M., T. Sowers, and V. Y. Lipenkov (1995). “On the concentrations of O<sub>2</sub>, N<sub>2</sub>, and Ar in trapped gases from ice cores”. In: *Journal of Geophysical Research: Atmospheres* 100 (D9). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/94JD02212>, pp. 18651–18660. DOI: <https://doi.org/10.1029/94JD02212>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/94JD02212>.
- Bereiter, B., H. Fischer, et al. (2014). “Diffusive equilibration of N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> mixing ratios in a 1.5-million-years-old ice core”. In: *The Cryosphere* 8.1, pp. 245–256. DOI: [10.5194/tc-8-245-2014](https://doi.org/10.5194/tc-8-245-2014). URL: <https://tc.copernicus.org/articles/8/245/2014/>.
- Bereiter, B., T. F. Stocker, and H. Fischer (2013). “A centrifugal ice microtome for measurements of atmospheric CO<sub>2</sub> on air trapped in polar ice cores”. In: *Atmospheric Measurement Techniques* 6.2, pp. 251–262. DOI: [10.5194/amt-6-251-2013](https://doi.org/10.5194/amt-6-251-2013). URL: <https://amt.copernicus.org/articles/6/251/2013/>.
- Bereiter, B., B. Tuzson, et al. (2020). “High-precision laser spectrometer for multiple greenhouse gas analysis in 1 mL air from ice core samples”. In: *Atmospheric Measurement Techniques* 13.11, pp. 6391–6406. DOI: [10.5194/amt-13-6391-2020](https://doi.org/10.5194/amt-13-6391-2020). URL: <https://amt.copernicus.org/articles/13/6391/2020/>.
- Bereiter, Bernhard, Sarah Eggleston, et al. (2015). “Revision of the EPICA Dome C CO<sub>2</sub> record from 800 to 600 kyr before present”. In: *Geophysical Research Letters* 42.2. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2014GL061957>, pp. 542–549. DOI: <https://doi.org/10.1002/2014GL061957>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2014GL061957>.
- Bereiter, Bernhard, Dieter Lüthi, et al. (2012). “Mode change of millennial CO<sub>2</sub> variability during the last glacial cycle associated with a bipolar marine carbon seesaw”. In: *Proceedings of the National Academy of Sciences* 109.25. \_eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.1204069109>, pp. 9755–9760. DOI: [10.1073/pnas.1204069109](https://doi.org/10.1073/pnas.1204069109). URL: <https://www.pnas.org/doi/abs/10.1073/pnas.1204069109>.
- Bereiter, Bernhard, Sarah Shackleton, et al. (Jan. 1, 2018). “Mean global ocean temperatures during the last glacial transition”. In: *Nature* 553.7686, pp. 39–44. ISSN: 1476-4687. DOI: [10.1038/nature25152](https://doi.org/10.1038/nature25152). URL: <https://doi.org/10.1038/nature25152>.
- Berner, Werner, Hans Oeschger, and Bernhard Stauffer (1980). “Information on the CO<sub>2</sub> Cycle from Ice Core Studies”. In: *Radiocarbon* 22.2, pp. 227–235. DOI: [10.1017/S0033822200009498](https://doi.org/10.1017/S0033822200009498).
- Brovkin, V. et al. (2019). “What was the source of the atmospheric CO<sub>2</sub> increase during the Holocene?” In: *Biogeosciences* 16.13, pp. 2543–2555. DOI: [10.5194/bg-16-2543-2019](https://doi.org/10.5194/bg-16-2543-2019). URL: <https://bg.copernicus.org/articles/16/2543/2019/>.
- Buizert, Christo, Betty Adrian, et al. (Apr. 1, 2015). “Precise inter-polar phasing of abrupt climate change during the last ice age”. In: *Nature* 520.7549, pp. 661–665. ISSN: 1476-4687. DOI: [10.1038/nature14401](https://doi.org/10.1038/nature14401). URL: <https://doi.org/10.1038/nature14401>.
- Buizert, Christo, Todd Sowers, and Thomas Blunier (2013). “Assessment of diffusive isotopic fractionation in polar firn, and application to ice core trace gas records”. In: *Earth and Planetary Science Letters* 361, pp. 110–119. ISSN: 0012-821X. DOI: <https://doi.org/10.1016/j.epsl.2012.11.039>. URL: <https://www.sciencedirect.com/science/article/pii/S0012821X12006577>.
- Buizert, Christo., K. M. Cuffey, et al. (2015). “The WAIS Divide deep ice core WD2014 chronology Part 1: Methane synchronization (68–31 ka BP) and the gas age–ice age

- difference”. In: *Climate of the Past* 11.2, pp. 153–173. DOI: [10.5194/cp-11-153-2015](https://doi.org/10.5194/cp-11-153-2015). URL: <https://cp.copernicus.org/articles/11/153/2015/>.
- Chalk, Thomas B. et al. (2017). “Causes of ice age intensification across the Mid-Pleistocene Transition”. In: *Proceedings of the National Academy of Sciences* 114.50. \_eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.1702143114>, pp. 13114–13119. DOI: [10.1073/pnas.1702143114](https://doi.org/10.1073/pnas.1702143114). URL: <https://www.pnas.org/doi/abs/10.1073/pnas.1702143114>.
- Chowdhry Beeman, J. et al. (2019). “Antarctic temperature and CO<sub>2</sub>: near-synchrony yet variable phasing during the last deglaciation”. In: *Climate of the Past* 15.3, pp. 913–926. DOI: [10.5194/cp-15-913-2019](https://doi.org/10.5194/cp-15-913-2019). URL: <https://cp.copernicus.org/articles/15/913/2019/>.
- Clark, Peter U. et al. (2006). “The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric pCO<sub>2</sub>”. In: *Quaternary Science Reviews* 25.23, pp. 3150–3184. ISSN: 0277-3791. DOI: <https://doi.org/10.1016/j.quascirev.2006.07.008>. URL: <https://www.sciencedirect.com/science/article/pii/S0277379106002332>.
- Cox, Peter and Chris Jones (2008). “Illuminating the Modern Dance of Climate and CO<sub>2</sub>”. In: *Science* 321.5896. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.1158907>, pp. 1642–1644. DOI: [10.1126/science.1158907](https://doi.org/10.1126/science.1158907). URL: <https://www.science.org/doi/abs/10.1126/science.1158907>.
- Craig, H., Y. Horibe, and T. Sowers (1988). “Gravitational Separation of Gases and Isotopes in Polar Ice Caps”. In: *Science* 242.4886. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.242.4886.1675>, pp. 1675–1678. DOI: [10.1126/science.242.4886.1675](https://doi.org/10.1126/science.242.4886.1675). URL: <https://www.science.org/doi/abs/10.1126/science.242.4886.1675>.
- Delmas, Robert J. (1993). “A natural artefact in Greenland ice-core CO<sub>2</sub> measurements”. In: *Tellus B: Chemical and Physical Meteorology* 45.4. Publisher: Taylor & Francis \_eprint: <https://doi.org/10.3402/tellusb.v45i4.15737>, pp. 391–396. DOI: [10.3402/tellusb.v45i4.15737](https://doi.org/10.3402/tellusb.v45i4.15737). URL: <https://doi.org/10.3402/tellusb.v45i4.15737>.
- Delmas, Robert J., Jean-Marc Ascencio, and Michel Legrand (Mar. 1, 1980). “Polar ice evidence that atmospheric CO<sub>2</sub> 20,000 yr BP was 50% of present”. In: *Nature* 284.5752, pp. 155–157. ISSN: 1476-4687. DOI: [10.1038/284155a0](https://doi.org/10.1038/284155a0). URL: <https://doi.org/10.1038/284155a0>.
- Dyez, Kelsey A., Bärbel Hönlisch, and Gavin A. Schmidt (2018). “Early Pleistocene Obliquity-Scale pCO<sub>2</sub> Variability at 1.5 Million Years Ago”. In: *Paleoceanography and Paleoclimatology* 33.11. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2018PA003349>, pp. 1270–1291. DOI: <https://doi.org/10.1029/2018PA003349>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2018PA003349>.
- Eggleston, S. et al. (2016). “Evolution of the stable carbon isotope composition of atmospheric CO<sub>2</sub> over the last glacial cycle”. In: *Paleoceanography* 31.3. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2015PA002874>, pp. 434–452. DOI: <https://doi.org/10.1002/2015PA002874>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2015PA002874>.
- Elsig, Joachim et al. (Sept. 1, 2009). “Stable isotope constraints on Holocene carbon cycle changes from an Antarctic ice core”. In: *Nature* 461.7263, pp. 507–510. ISSN: 1476-4687. DOI: [10.1038/nature08393](https://doi.org/10.1038/nature08393). URL: <https://doi.org/10.1038/nature08393>.
- Etheridge, D. M. et al. (1996). “Natural and anthropogenic changes in atmospheric CO<sub>2</sub> over the last 1000 years from air in Antarctic ice and firn”. In: *Journal of Geophysical*

- Research: Atmospheres* 101 (D2). \_eprint:  
<https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/95JD03410>, pp. 4115–4128.  
 DOI: <https://doi.org/10.1029/95JD03410>. URL:  
<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/95JD03410>.
- Fischer, H., J. Severinghaus, et al. (2013). “Where to find 1.5 million yr old ice for the IPICS “Oldest-Ice” ice core”. In: *Climate of the Past* 9.6, pp. 2489–2505. DOI: [10.5194/cp-9-2489-2013](https://doi.org/10.5194/cp-9-2489-2013). URL: <https://cp.copernicus.org/articles/9/2489/2013/>.
- Fischer, Hubertus, Martin Wahlen, et al. (1999). “Ice Core Records of Atmospheric CO<sub>2</sub> Around the Last Three Glacial Terminations”. In: *Science* 283.5408. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.283.5408.1712>, pp. 1712–1714. DOI: [10.1126/science.283.5408.1712](https://doi.org/10.1126/science.283.5408.1712). URL: <https://www.science.org/doi/abs/10.1126/science.283.5408.1712>.
- Fourteau, K. et al. (2017). “Analytical constraints on layered gas trapping and smoothing of atmospheric variability in ice under low-accumulation conditions”. In: *Climate of the Past* 13.12, pp. 1815–1830. DOI: [10.5194/cp-13-1815-2017](https://doi.org/10.5194/cp-13-1815-2017). URL: <https://cp.copernicus.org/articles/13/1815/2017/>.
- Francey, R. J. et al. (Jan. 1999). “A 1000-year high precision record of  $\delta^{13}\text{C}$  in atmospheric CO<sub>2</sub>”. In: *Tellus B: Chemical and Physical Meteorology*. DOI: [10.3402/tellusb.v51i2.16269](https://doi.org/10.3402/tellusb.v51i2.16269).
- Frank, David C. et al. (Jan. 1, 2010). “Ensemble reconstruction constraints on the global carbon cycle sensitivity to climate”. In: *Nature* 463.7280, pp. 527–530. ISSN: 1476-4687. DOI: [10.1038/nature08769](https://doi.org/10.1038/nature08769). URL: <https://doi.org/10.1038/nature08769>.
- Friedli, H., H. Löttscher, et al. (Nov. 1, 1986). “Ice core record of the 13C/12C ratio of atmospheric CO<sub>2</sub> in the past two centuries”. In: *Nature* 324.6094, pp. 237–238. ISSN: 1476-4687. DOI: [10.1038/324237a0](https://doi.org/10.1038/324237a0). URL: <https://doi.org/10.1038/324237a0>.
- Friedli, H., E. Moor, et al. (1984). “13C/12C ratios in CO<sub>2</sub> extracted from Antarctic ice”. In: *Geophysical Research Letters* 11.11. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/GL011i011p01145>, pp. 1145–1148. DOI: <https://doi.org/10.1029/GL011i011p01145>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/GL011i011p01145>.
- Friedlingstein, P. et al. (2023). “Global Carbon Budget 2023”. In: *Earth System Science Data* 15.12, pp. 5301–5369. DOI: [10.5194/essd-15-5301-2023](https://doi.org/10.5194/essd-15-5301-2023). URL: <https://essd.copernicus.org/articles/15/5301/2023/>.
- Goosse, Hugues et al. (June 1, 2022). “Changes in atmospheric CO<sub>2</sub> concentration over the past two millennia: contribution of climate variability, land-use and Southern Ocean dynamics”. In: *Climate Dynamics* 58.11, pp. 2957–2979. ISSN: 1432-0894. DOI: [10.1007/s00382-021-06078-z](https://doi.org/10.1007/s00382-021-06078-z). URL: <https://doi.org/10.1007/s00382-021-06078-z>.
- Henderson, Gideon M. (2002). “New oceanic proxies for paleoclimate”. In: *Earth and Planetary Science Letters* 203.1, pp. 1–13. ISSN: 0012-821X. DOI: [https://doi.org/10.1016/S0012-821X\(02\)00809-9](https://doi.org/10.1016/S0012-821X(02)00809-9). URL: <https://www.sciencedirect.com/science/article/pii/S0012821X02008099>.
- Herron, Michael M. and Chester C. Langway (1980). “Firn Densification: An Empirical Model”. In: *Journal of Glaciology* 25.93, pp. 373–385. DOI: [10.3189/S0022143000015239](https://doi.org/10.3189/S0022143000015239).
- Higgins, John A. et al. (2015). “Atmospheric composition 1 million years ago from blue ice in the Allan Hills, Antarctica”. In: *Proceedings of the National Academy of Sciences* 112.22. \_eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.1420232112>, pp. 6887–6891. DOI: [10.1073/pnas.1420232112](https://doi.org/10.1073/pnas.1420232112). URL: <https://www.pnas.org/doi/abs/10.1073/pnas.1420232112>.

- Huybers, Peter and Charles Langmuir (2009). “Feedback between deglaciation, volcanism, and atmospheric CO<sub>2</sub>”. In: *Earth and Planetary Science Letters* 286.3, pp. 479–491. ISSN: 0012-821X. DOI: <https://doi.org/10.1016/j.epsl.2009.07.014>. URL: <https://www.sciencedirect.com/science/article/pii/S0012821X09004166>.
- Indermühle, Andreas et al. (2000). “Atmospheric CO<sub>2</sub> concentration from 60 to 20 kyr BP from the Taylor Dome Ice Core, Antarctica”. In: *Geophysical Research Letters* 27.5. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/1999GL010960>, pp. 735–738. DOI: <https://doi.org/10.1029/1999GL010960>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/1999GL010960>.
- Jenk, T. M. et al. (2016). “A new set-up for simultaneous high-precision measurements of CO<sub>2</sub>, δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> on small ice core samples”. In: *Atmospheric Measurement Techniques* 9.8, pp. 3687–3706. DOI: [10.5194/amt-9-3687-2016](https://doi.org/10.5194/amt-9-3687-2016). URL: <https://amt.copernicus.org/articles/9/3687/2016/>.
- Joos, Fortunat and Michele Bruno (1998). “Long-term variability of the terrestrial and oceanic carbon sinks and the budgets of the carbon isotopes <sup>13</sup>C and <sup>14</sup>C”. In: *Global Biogeochemical Cycles* 12.2. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/98GB00746>, pp. 277–295. DOI: <https://doi.org/10.1029/98GB00746>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/98GB00746>.
- Kaplan, Jed O. (May 1, 2015). “Climate or humans?” In: *Nature Geoscience* 8.5, pp. 335–336. ISSN: 1752-0908. DOI: [10.1038/ngeo2432](https://doi.org/10.1038/ngeo2432). URL: <https://doi.org/10.1038/ngeo2432>.
- Kaplan, Jed O. et al. (2011). “Holocene carbon emissions as a result of anthropogenic land cover change”. In: *The Holocene* 21.5. \_eprint: <https://doi.org/10.1177/0959683610386983>, pp. 775–791. DOI: [10.1177/0959683610386983](https://doi.org/10.1177/0959683610386983). URL: <https://doi.org/10.1177/0959683610386983>.
- Kawamura, Kenji, TAKAKIYO Nakazawa, et al. (Apr. 1, 2003). “Atmospheric CO<sub>2</sub> variations over the last three glacial–interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique”. In: *Tellus B* 55.2. Publisher: John Wiley & Sons, Ltd, pp. 126–137. ISSN: 0280-6509. DOI: [10.1034/j.1600-0889.2003.00050.x](https://doi.org/10.1034/j.1600-0889.2003.00050.x). URL: <https://doi.org/10.1034/j.1600-0889.2003.00050.x> (visited on 03/13/2024).
- Kawamura, Kenji, Frédéric Parrenin, et al. (Aug. 1, 2007). “Northern Hemisphere forcing of climatic cycles in Antarctica over the past 360,000 years”. In: *Nature* 448.7156, pp. 912–916. ISSN: 1476-4687. DOI: [10.1038/nature06015](https://doi.org/10.1038/nature06015). URL: <https://doi.org/10.1038/nature06015>.
- Keeling, C.D. et al. (2001). *Exchanges of atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> with the terrestrial biosphere and oceans from 1978 to 2000*. 01-06. San Diego: Scripps Institution of Oceanography, p. 88. URL: <https://escholarship.org/uc/item/09v319r9>.
- King, Amy C. F. et al. (Mar. 5, 2024). “Reconciling ice core CO<sub>2</sub> and land-use change following New World-Old World contact”. In: *Nature Communications* 15.1, p. 1735. ISSN: 2041-1723. DOI: [10.1038/s41467-024-45894-9](https://doi.org/10.1038/s41467-024-45894-9). URL: <https://doi.org/10.1038/s41467-024-45894-9>.
- Köhler, P. et al. (2011). “Abrupt rise in atmospheric CO<sub>2</sub> at the onset of the Bølling/Allerød: in-situ ice core data versus true atmospheric signals”. In: *Climate of the Past* 7.2, pp. 473–486. DOI: [10.5194/cp-7-473-2011](https://doi.org/10.5194/cp-7-473-2011). URL: <https://cp.copernicus.org/articles/7/473/2011/>.
- Lal, D. et al. (July 1, 1990). “Polar ice ablation rates measured using in situ cosmogenic <sup>14</sup>C”. In: *Nature* 346.6282, pp. 350–352. ISSN: 1476-4687. DOI: [10.1038/346350a0](https://doi.org/10.1038/346350a0). URL: <https://doi.org/10.1038/346350a0>.

- Leuenberger, M. C., M. Eyer, et al. (2003). “High-resolution  $\delta^{13}\text{C}$  measurements on ancient air extracted from less than 10 cm<sup>3</sup> of ice”. In: *Tellus B: Chemical and Physical Meteorology* 55.2. Publisher: Taylor & Francis .eprint: <https://doi.org/10.3402/tellusb.v55i2.16766>, pp. 138–144. DOI: [10.3402/tellusb.v55i2.16766](https://doi.org/10.3402/tellusb.v55i2.16766). URL: <https://doi.org/10.3402/tellusb.v55i2.16766>.
- Leuenberger, Markus, Ulrich Siegenthaler, and Chester Langway (June 1, 1992). “Carbon isotope composition of atmospheric CO<sub>2</sub> during the last ice age from an Antarctic ice core”. In: *Nature* 357.6378, pp. 488–490. ISSN: 1476-4687. DOI: [10.1038/357488a0](https://doi.org/10.1038/357488a0). URL: <https://doi.org/10.1038/357488a0>.
- Lisiecki, Lorraine E. and Maureen E. Raymo (2005). “A Pliocene-Pleistocene stack of 57 globally distributed benthic  $\delta^{18}\text{O}$  records”. In: *Paleoceanography* 20.1. .eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2004PA001071>. DOI: <https://doi.org/10.1029/2004PA001071>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2004PA001071>.
- Lourantou, A., J. Chappellaz, et al. (2010). “Changes in atmospheric CO<sub>2</sub> and its carbon isotopic ratio during the penultimate deglaciation”. In: *Quaternary Science Reviews* 29.17, pp. 1983–1992. ISSN: 0277-3791. DOI: <https://doi.org/10.1016/j.quascirev.2010.05.002>. URL: <https://www.sciencedirect.com/science/article/pii/S027737911000137X>.
- Lourantou, Anna, Jošt V. Lavrič, et al. (2010). “Constraint of the CO<sub>2</sub> rise by new atmospheric carbon isotopic measurements during the last deglaciation”. In: *Global Biogeochemical Cycles* 24.2. .eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2009GB003545>. DOI: <https://doi.org/10.1029/2009GB003545>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2009GB003545>.
- Lüthi, Dieter et al. (May 1, 2008). “High-resolution carbon dioxide concentration record 650,000–800,000 years before present”. In: *Nature* 453.7193, pp. 379–382. ISSN: 1476-4687. DOI: [10.1038/nature06949](https://doi.org/10.1038/nature06949). URL: <https://doi.org/10.1038/nature06949>.
- MacFarling Meure, C. et al. (2006). “Law Dome CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O ice core records extended to 2000 years BP”. In: *Geophysical Research Letters* 33.14. .eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2006GL026152>. DOI: <https://doi.org/10.1029/2006GL026152>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2006GL026152>.
- Mächler, L. et al. (2023). “Laser-induced sublimation extraction for centimeter-resolution multi-species greenhouse gas analysis on ice cores”. In: *Atmospheric Measurement Techniques* 16.2, pp. 355–372. DOI: [10.5194/amt-16-355-2023](https://doi.org/10.5194/amt-16-355-2023). URL: <https://amt.copernicus.org/articles/16/355/2023/>.
- Marcott, Shaun A. et al. (Oct. 1, 2014). “Centennial-scale changes in the global carbon cycle during the last deglaciation”. In: *Nature* 514.7524, pp. 616–619. ISSN: 1476-4687. DOI: [10.1038/nature13799](https://doi.org/10.1038/nature13799). URL: <https://doi.org/10.1038/nature13799>.
- Mariotti, André (June 1, 1983). “Atmospheric nitrogen is a reliable standard for natural <sup>15</sup>N abundance measurements”. In: *Nature* 303.5919, pp. 685–687. ISSN: 1476-4687. DOI: [10.1038/303685a0](https://doi.org/10.1038/303685a0). URL: <https://doi.org/10.1038/303685a0>.
- Martinerie, Patricia et al. (1992). “Physical and climatic parameters which influence the air content in polar ice”. In: *Earth and Planetary Science Letters* 112.1, pp. 1–13. ISSN: 0012-821X. DOI: [https://doi.org/10.1016/0012-821X\(92\)90002-D](https://doi.org/10.1016/0012-821X(92)90002-D). URL: <https://www.sciencedirect.com/science/article/pii/0012821X9290002D>.
- Menking, James A. et al. (Sept. 16, 2022). “Multiple carbon cycle mechanisms associated with the glaciation of Marine Isotope Stage 4”. In: *Nature Communications* 13.1, p. 5443. ISSN: 2041-1723. DOI: [10.1038/s41467-022-33166-3](https://doi.org/10.1038/s41467-022-33166-3). URL: <https://doi.org/10.1038/s41467-022-33166-3>.

- Menviel, L. et al. (June 27, 2018). “Southern Hemisphere westerlies as a driver of the early deglacial atmospheric CO<sub>2</sub> rise”. In: *Nature Communications* 9.1, p. 2503. ISSN: 2041-1723. DOI: [10.1038/s41467-018-04876-4](https://doi.org/10.1038/s41467-018-04876-4). URL: <https://doi.org/10.1038/s41467-018-04876-4>.
- Mitchell, Logan E. et al. (2015). “Observing and modeling the influence of layering on bubble trapping in polar firn”. In: *Journal of Geophysical Research: Atmospheres* 120.6. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2014JD022766>, pp. 2558–2574. DOI: <https://doi.org/10.1002/2014JD022766>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2014JD022766>.
- Monnin, Eric, Andreas Indermühle, et al. (2001). “Atmospheric CO<sub>2</sub> Concentrations over the Last Glacial Termination”. In: *Science* 291.5501. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.291.5501.112>, pp. 112–114. DOI: [10.1126/science.291.5501.112](https://doi.org/10.1126/science.291.5501.112). URL: <https://www.science.org/doi/abs/10.1126/science.291.5501.112>.
- Monnin, Eric, Eric J. Steig, et al. (2004). “Evidence for substantial accumulation rate variability in Antarctica during the Holocene, through synchronization of CO<sub>2</sub> in the Taylor Dome, Dome C and DML ice cores”. In: *Earth and Planetary Science Letters* 224.1, pp. 45–54. ISSN: 0012-821X. DOI: <https://doi.org/10.1016/j.epsl.2004.05.007>. URL: <https://www.sciencedirect.com/science/article/pii/S0012821X04003115>.
- Neftel, A., E. Moor, et al. (May 1, 1985). “Evidence from polar ice cores for the increase in atmospheric CO<sub>2</sub> in the past two centuries”. In: *Nature* 315.6014, pp. 45–47. ISSN: 1476-4687. DOI: [10.1038/315045a0](https://doi.org/10.1038/315045a0). URL: <https://doi.org/10.1038/315045a0>.
- Neftel, A., H. Oeschger, et al. (Jan. 1, 1982). “Ice core sample measurements give atmospheric CO<sub>2</sub> content during the past 40,000 yr”. In: *Nature* 295.5846, pp. 220–223. ISSN: 1476-4687. DOI: [10.1038/295220a0](https://doi.org/10.1038/295220a0). URL: <https://doi.org/10.1038/295220a0>.
- Nehrbass-Ahles, C. et al. (2020). “Abrupt CO<sub>2</sub> release to the atmosphere under glacial and early interglacial climate conditions”. In: *Science* 369.6506. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.aay8178>, pp. 1000–1005. DOI: [10.1126/science.aay8178](https://doi.org/10.1126/science.aay8178). URL: <https://www.science.org/doi/abs/10.1126/science.aay8178>.
- Osman, Matthew B. et al. (Nov. 1, 2021). “Globally resolved surface temperatures since the Last Glacial Maximum”. In: *Nature* 599.7884, pp. 239–244. ISSN: 1476-4687. DOI: [10.1038/s41586-021-03984-4](https://doi.org/10.1038/s41586-021-03984-4). URL: <https://doi.org/10.1038/s41586-021-03984-4>.
- Parrenin, F. et al. (2013). “Synchronous Change of Atmospheric CO<sub>2</sub> and Antarctic Temperature During the Last Deglacial Warming”. In: *Science* 339.6123. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.1226368>, pp. 1060–1063. DOI: [10.1126/science.1226368](https://doi.org/10.1126/science.1226368). URL: <https://www.science.org/doi/abs/10.1126/science.1226368>.
- Pearman, G. I. et al. (Mar. 1, 1986). “Evidence of changing concentrations of atmospheric CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>2</sub> from air bubbles in Antarctic ice”. In: *Nature* 320.6059, pp. 248–250. ISSN: 1476-4687. DOI: [10.1038/320248a0](https://doi.org/10.1038/320248a0). URL: <https://doi.org/10.1038/320248a0>.
- Petit, J. R. et al. (June 1, 1999). “Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica”. In: *Nature* 399.6735, pp. 429–436. ISSN: 1476-4687. DOI: [10.1038/20859](https://doi.org/10.1038/20859). URL: <https://doi.org/10.1038/20859>.
- Petrenko, Vasilii V. et al. (2016). “Measurements of <sup>14</sup>C in ancient ice from Taylor Glacier, Antarctica constrain in situ cosmogenic <sup>14</sup>CH<sub>4</sub> and <sup>14</sup>CO production rates”. In: *Geochimica et Cosmochimica Acta* 177, pp. 62–77. ISSN: 0016-7037. DOI:

- <https://doi.org/10.1016/j.gca.2016.01.004>. URL:  
<https://www.sciencedirect.com/science/article/pii/S0016703716000065>.
- Raynaud, D. and J. M. Barnola (May 1, 1985). “An Antarctic ice core reveals atmospheric CO<sub>2</sub> variations over the past few centuries”. In: *Nature* 315.6017, pp. 309–311. ISSN: 1476-4687. DOI: [10.1038/315309a0](https://doi.org/10.1038/315309a0). URL: <https://doi.org/10.1038/315309a0>.
- Rhodes, Rachael H. et al. (2015). “Enhanced tropical methane production in response to iceberg discharge in the North Atlantic”. In: *Science* 348.6238. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.1262005>, pp. 1016–1019. DOI: [10.1126/science.1262005](https://doi.org/10.1126/science.1262005). URL: <https://www.science.org/doi/abs/10.1126/science.1262005>.
- Riechelton, H. et al. (2024). “Southern Ocean Biological Pump Role in Driving Holocene Atmospheric CO<sub>2</sub>: Reappraisal”. In: *Geophysical Research Letters* 51.4. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2023GL105569>, e2023GL105569. DOI: <https://doi.org/10.1029/2023GL105569>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2023GL105569>.
- Rubino, M., D. M. Etheridge, D. P. Thornton, et al. (2019). “Revised records of atmospheric trace gases CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and  $\delta^{13}\text{C}$ -CO<sub>2</sub> over the last 2000 years from Law Dome, Antarctica”. In: *Earth System Science Data* 11.2, pp. 473–492. DOI: [10.5194/essd-11-473-2019](https://doi.org/10.5194/essd-11-473-2019). URL: <https://essd.copernicus.org/articles/11/473/2019/>.
- Rubino, M., D. M. Etheridge, C. M. Trudinger, C. E. Allison, M. O. Battle, et al. (2013). “A revised 1000 year atmospheric  $\delta^{13}\text{C}$ -CO<sub>2</sub> record from Law Dome and South Pole, Antarctica”. In: *Journal of Geophysical Research: Atmospheres* 118.15. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/jgrd.50668>, pp. 8482–8499. DOI: <https://doi.org/10.1002/jgrd.50668>. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/jgrd.50668>.
- Rubino, M., D. M. Etheridge, C. M. Trudinger, C. E. Allison, P. J. Rayner, et al. (Sept. 1, 2016). “Low atmospheric CO<sub>2</sub> levels during the Little Ice Age due to cooling-induced terrestrial uptake”. In: *Nature Geoscience* 9.9, pp. 691–694. ISSN: 1752-0908. DOI: [10.1038/ngeo2769](https://doi.org/10.1038/ngeo2769). URL: <https://doi.org/10.1038/ngeo2769>.
- Ruddiman, William F. (Dec. 1, 2003). “The Anthropogenic Greenhouse Era Began Thousands of Years Ago”. In: *Climatic Change* 61.3, pp. 261–293. ISSN: 1573-1480. DOI: [10.1023/B:CLIM.0000004577.17928.fa](https://doi.org/10.1023/B:CLIM.0000004577.17928.fa). URL: <https://doi.org/10.1023/B:CLIM.0000004577.17928.fa>.
- Schmitt, J., R. Schneider, and H. Fischer (2011). “A sublimation technique for high-precision measurements of  $\delta^{13}\text{C}$ -CO<sub>2</sub> and mixing ratios of CO<sub>2</sub> and NO from air trapped in ice cores”. In: *Atmospheric Measurement Techniques* 4.7, pp. 1445–1461. DOI: [10.5194/amt-4-1445-2011](https://doi.org/10.5194/amt-4-1445-2011). URL: <https://amt.copernicus.org/articles/4/1445/2011/>.
- Schmitt, Jochen, Robert Schneider, Joachim Elsig, et al. (2012). “Carbon Isotope Constraints on the Deglacial CO<sub>2</sub> Rise from Ice Cores”. In: *Science* 336.6082. \_eprint: <https://www.science.org/doi/pdf/10.1126/science.1217161>, pp. 711–714. DOI: [10.1126/science.1217161](https://doi.org/10.1126/science.1217161). URL: <https://www.science.org/doi/abs/10.1126/science.1217161>.
- Schneider, R. et al. (2013). “A reconstruction of atmospheric carbon dioxide and its stable carbon isotopic composition from the penultimate glacial maximum to the last glacial inception”. In: *Climate of the Past* 9.6, pp. 2507–2523. DOI: [10.5194/cp-9-2507-2013](https://doi.org/10.5194/cp-9-2507-2013). URL: <https://cp.copernicus.org/articles/9/2507/2013/>.
- Schwander, J. et al. (1993). “The age of the air in the firn and the ice at Summit, Greenland”. In: *Journal of Geophysical Research: Atmospheres* 98 (D2). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/92JD02383>, pp. 2831–2838.

- DOI: <https://doi.org/10.1029/92JD02383>. URL:  
<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/92JD02383>.
- Severinghaus, Jeffrey P. et al. (Jan. 1, 1998). “Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice”. In: *Nature* 391.6663, pp. 141–146. ISSN: 1476-4687. DOI: [10.1038/34346](https://doi.org/10.1038/34346). URL:  
<https://doi.org/10.1038/34346>.
- Shakun, Jeremy D. et al. (Apr. 1, 2012). “Global warming preceded by increasing carbon dioxide concentrations during the last deglaciation”. In: *Nature* 484.7392, pp. 49–54. ISSN: 1476-4687. DOI: [10.1038/nature10915](https://doi.org/10.1038/nature10915). URL:  
<https://doi.org/10.1038/nature10915>.
- Shin, J., J. Ahn, et al. (2022). “Millennial variations in atmospheric CO<sub>2</sub> during the early Holocene (11.7–7.4 ka)”. In: *Climate of the Past* 18.9, pp. 2063–2075. DOI: [10.5194/cp-18-2063-2022](https://cp.copernicus.org/articles/18/2063/2022/). URL:  
<https://cp.copernicus.org/articles/18/2063/2022/>.
- Shin, J., C. Nehrbass-Ahles, et al. (2020). “Millennial-scale atmospheric CO<sub>2</sub> variations during the Marine Isotope Stage 6 period (190–135 ka)”. In: *Climate of the Past* 16.6, pp. 2203–2219. DOI: [10.5194/cp-16-2203-2020](https://cp.copernicus.org/articles/16/2203/2020/). URL:  
<https://cp.copernicus.org/articles/16/2203/2020/>.
- Siegenthaler, U., H. Friedli, et al. (1988). “Stable-Isotope Ratios and Concentration of CO<sub>2</sub> in Air from Polar Ice Cores”. In: *Annals of Glaciology* 10, pp. 151–156. DOI: [10.3189/S0260305500004341](https://doi.org/10.3189/S0260305500004341).
- Siegenthaler, Urs, Eric Monnin, et al. (2005). “Supporting evidence from the EPICA Dronning Maud Land ice core for atmospheric CO<sub>2</sub> changes during the past millennium”. In: *Tellus B: Chemical and Physical Meteorology* 57.1. Publisher: Taylor & Francis. eprint: <https://doi.org/10.3402/tellusb.v57i1.16774>, pp. 51–57. DOI: [10.3402/tellusb.v57i1.16774](https://doi.org/10.3402/tellusb.v57i1.16774). URL:  
<https://doi.org/10.3402/tellusb.v57i1.16774>.
- Siegenthaler, Urs, Thomas F. Stocker, et al. (2005). “Stable Carbon Cycle Climate Relationship During the Late Pleistocene”. In: *Science* 310.5752. eprint: <https://www.science.org/doi/pdf/10.1126/science.1120130>, pp. 1313–1317. DOI: [10.1126/science.1120130](https://www.science.org/doi/abs/10.1126/science.1120130). URL:  
<https://www.science.org/doi/abs/10.1126/science.1120130>.
- Smith, H. Jesse et al. (July 1, 1999). “Dual modes of the carbon cycle since the Last Glacial Maximum”. In: *Nature* 400.6741, pp. 248–250. ISSN: 1476-4687. DOI: [10.1038/22291](https://doi.org/10.1038/22291). URL: <https://doi.org/10.1038/22291>.
- Stauffer, B. et al. (Mar. 1, 1998). “Atmospheric CO<sub>2</sub> concentration and millennial-scale climate change during the last glacial period”. In: *Nature* 392.6671, pp. 59–62. ISSN: 1476-4687. DOI: [10.1038/32133](https://doi.org/10.1038/32133). URL: <https://doi.org/10.1038/32133>.
- Stocker, Benjamin David et al. (2017). “Holocene peatland and ice-core data constraints on the timing and magnitude of CO<sub>2</sub> emissions from past land use”. In: *Proceedings of the National Academy of Sciences* 114.7. eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.1613889114>, pp. 1492–1497. DOI: [10.1073/pnas.1613889114](https://www.pnas.org/doi/abs/10.1073/pnas.1613889114). URL:  
<https://www.pnas.org/doi/abs/10.1073/pnas.1613889114>.
- Studer, Anja S. et al. (Oct. 1, 2018). “Increased nutrient supply to the Southern Ocean during the Holocene and its implications for the pre-industrial atmospheric CO<sub>2</sub> rise”. In: *Nature Geoscience* 11.10, pp. 756–760. ISSN: 1752-0908. DOI: [10.1038/s41561-018-0191-8](https://doi.org/10.1038/s41561-018-0191-8). URL:  
<https://doi.org/10.1038/s41561-018-0191-8>.
- Stuiver, M. and P. D. Quay (1981). “Atmospheric 14C changes resulting from fossil fuel CO<sub>2</sub> release and cosmic ray flux variability”. In: *Earth and Planetary Science Letters* 53.3, pp. 349–362. ISSN: 0012-821X. DOI:

- [https://doi.org/10.1016/0012-821X\(81\)90040-6](https://doi.org/10.1016/0012-821X(81)90040-6). URL:  
<https://www.sciencedirect.com/science/article/pii/0012821X81900406>.
- Trudinger, C. M., I. G. Enting, D. M. Etheridge, et al. (1997). “Modeling air movement and bubble trapping in firn”. In: *Journal of Geophysical Research: Atmospheres* 102 (D6). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/96JD03382>, pp. 6747–6763. DOI: <https://doi.org/10.1029/96JD03382>. URL:  
<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/96JD03382>.
- Trudinger, C. M., I. G. Enting, P. J. Rayner, et al. (2002). “Kalman filter analysis of ice core data 2. Double deconvolution of CO<sub>2</sub> and δ<sup>13</sup>C measurements”. In: *Journal of Geophysical Research: Atmospheres* 107 (D20). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2001JD001112>, ACH 5–1–ACH 5–24. DOI: <https://doi.org/10.1029/2001JD001112>. URL:  
<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2001JD001112>.
- Trudinger, C. M., D. M. Etheridge, et al. (2002). “Reconstructing atmospheric histories from measurements of air composition in firn”. In: *Journal of Geophysical Research: Atmospheres* 107 (D24). \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2002JD002545>, ACH 15–1–ACH 15–13. DOI: <https://doi.org/10.1029/2002JD002545>. URL:  
<https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2002JD002545>.
- Wendt, Kathleen A. et al. (2024). “Southern Ocean drives multidecadal atmospheric CO<sub>2</sub> rise during Heinrich Stadials”. In: *Proceedings of the National Academy of Sciences* 121.21. \_eprint: <https://www.pnas.org/doi/pdf/10.1073/pnas.2319652121>, e2319652121. DOI: [10.1073/pnas.2319652121](https://doi.org/10.1073/pnas.2319652121). URL:  
<https://www.pnas.org/doi/abs/10.1073/pnas.2319652121>.
- Yan, Yuzhen et al. (Oct. 1, 2019). “Two-million-year-old snapshots of atmospheric gases from Antarctic ice”. In: *Nature* 574.7780, pp. 663–666. ISSN: 1476-4687. DOI: [10.1038/s41586-019-1692-3](https://doi.org/10.1038/s41586-019-1692-3). URL:  
<https://doi.org/10.1038/s41586-019-1692-3>.
- Yu, Zicheng et al. (2014). “Holocene peatland carbon dynamics in the circum-Arctic region: An introduction”. In: *The Holocene* 24.9. \_eprint: <https://doi.org/10.1177/0959683614540730>, pp. 1021–1027. DOI: [10.1177/0959683614540730](https://doi.org/10.1177/0959683614540730). URL: <https://doi.org/10.1177/0959683614540730>.