Ice core records of atmospheric carbon dioxide*

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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_2 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_2 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_2 can be measured at sufficient accuracy to quantify the sources and sinks of CO_2 over these same timescales. In combination, the concentration and isotope composition of CO_2 allow us to constrain both the past climate sensitivity (i.e., how climate responds to a change in CO_2) and carbon-climate feedbacks (i.e., how the carbon cycle responds to a change in climate).

Contents

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1 Introduction: What have ice core CO_2 data ever done for us?

In 1958, when modern measurements of the concentration of atmospheric CO_2 began, CO_2 was near 315 ppm (Keeling et al. 2001). In 2021, atmospheric CO_2 surpassed a significant milestone when it reached 415 ppm, thus marking a 100 ppm increase in just 63 years. CO_2 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_2, mostly in the form of proxies. The gold standard among these archives are ice core reconstructions which faithfully record the concentration of atmospheric CO_2 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_2 (along with CH_4 and N_2O: 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_2 ($\delta^{13}C\text{-}CO_2$) allows us to, in part, trace the sources and sinks of CO_2 over time and thus hone -in on the mechanisms that alter the natural carbon cycle and drive the observed changes in CO_2. Together, ice core CO_2 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_2**
- **The current levels of atmospheric CO_2 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_2 is similarly unprecedented.**
- **Ice core CO_2 records shows variability on timescales ranging from glacial-interglacial (60-90ppm), millennial (10-30ppm), and centennial (5-15ppm).**
- **The stable isotopes of CO_2 help fingerprint the sources and sinks responsible for this variability.**

2 Overview of ice core CO_2

Ice core CO_2 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 of ice), a small amount of air, but enough that the 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 CO_2 in ice cores is measured as the dry mole fraction of CO_2 in the total amount of air released during extraction (reported as part per million or ppm).

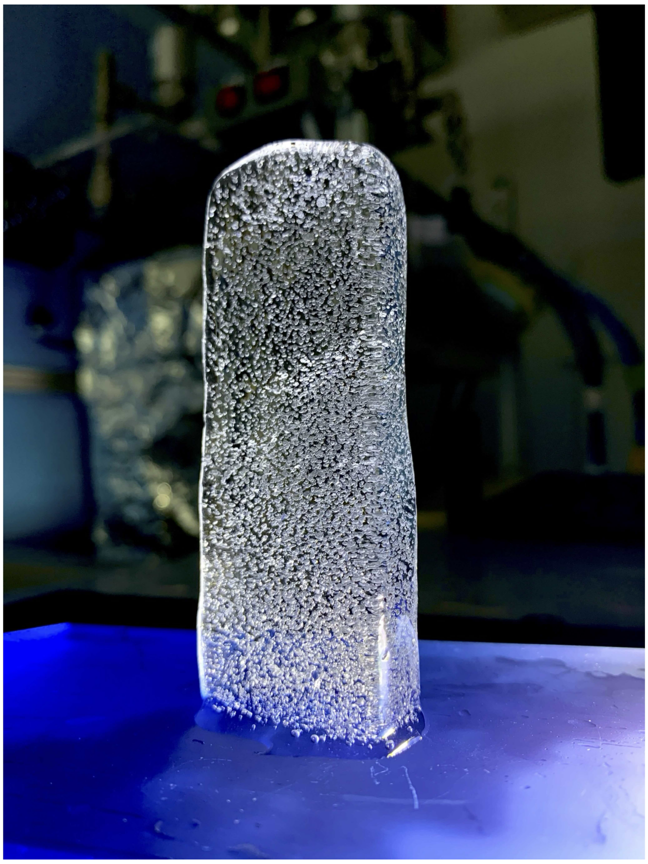

Figure 1: An ice core sample showing the bubbles that contain near prestine samples of ancient atmosphere

The stable isotopes of CO_2 can also be measured in similarly small amounts of air to a high-degree of precision (~0.05-0.1‰) (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 ($\delta^{13}C\text{-}CO_2$) or oxygen ($\delta^{18}O\text{-}CO_2$) 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 CO_2. Three major processes fractionate carbon isotopes: less ^{13}C is taken up by plant material during photosynthesis; more ^{13}C is taken up by the ocean during air-sea gas exchange; and on average, no more or no less ^{13}C is taken up by reefs, shells and other $CaCO_3$ material during the formation of $CaCO_3$ from seawater. The net effect is that the major reservoirs of carbon are measurably different in their $\delta^{13}C$ values (Figure2). The pre-Industrial atmosphere ranges between -6 and -7‰ (VPDB). Organic carbon stocks are lighter than the atmosphere including: C3 plant material (-20 to -35‰), C4 plant material (-12 to -18‰), 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‰) and marine plankton (-18 to -30‰). Inorganic stocks are heavier than the atmosphere with seawater ranging between 0 and +2‰, marine $CaCO_3$ covering a very similar range; and volcanic emissions, which reflect a combination of both $CaCO_3$-rich substrates (e.g., limestone) and organic-rich substrates (e.g., shales) typically range between -3 and -5‰.

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}C to the ocean from the atmosphere (and likewise preferential transfer of ^{12}C to the atmosphere from ocean) will decrease with increasing sea surface temperature. Thus, a warming of the ocean will drive more CO_2 out the ocean due to decreased solubility, but

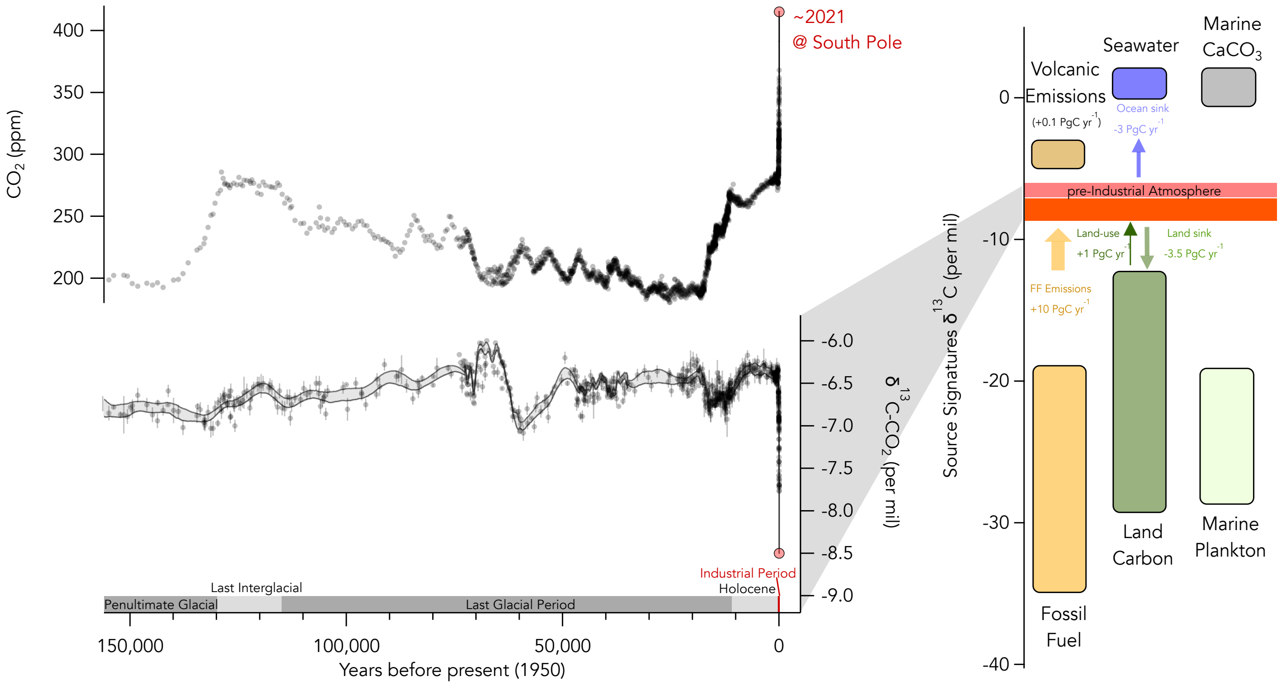

Figure 2: Left panel: The concentration and isotopic composition of atmospheric CO_2 from near the present day to the penultimate glacial period. The instrumental data is sourced from South Pole Station measured as part of the Scripps Institution of Oceanography atmospheric monitoring programme (Keeling 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_2 which can constrain some of the sources and sinks of CO_2 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_2. The arrows between the various reservoirs and atmosphere represent net fluxes of CO_2 from a simplified version of the recent carbon budget based on data from the Global Carbon Project Friedlingstein et al. 2023)

also "pull" the atmospheric $\delta^{13}C\text{-}CO_2$ (-6‰) closer to the mean surface ocean value (~0‰), thus increasing atmospheric $\delta^{13}C\text{-}CO_2$.The oxygen isotopes, on the other hand, reflect the exchange of oxygen between the CO_2 and the surrounding water ice and are thus set by a combination of $\delta^{18}O\text{-}H_2O$ 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 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}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 CO_2

To first order, the concentration of 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 (~decades) and is enriched in the heavier gases Craig, Horibe, and Sowers 1988; Etheridge et al. 1996). 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 CO_2, containing the stable isotope of carbon (^{13}C), is heavier than the major isotopologue by one neutron (~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 N_2 (the $^{15}N^{14}N$-to-$^{14}N^{14}Nr$ ratio) - a gas with a lifetime of $\sim 10^4$ years Mariotti 1983)and a mass difference of ~1 amu — the same mass difference as $^{13}C\text{-}CO_2$. 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 $\delta^{13}C\text{-}CO_2$ and between about 0.8 and 2.5 ppm artificially elevated values for CO_2 concentration.

The slow diffusion of gases within the firn (~a decade) and gradual trapping of bubbles (~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-scales 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 diffusive more rapidly than the heavier isotopes. This is only significant when the 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 $\delta^{13}C\text{-}CO_2$across the rise in CO_2 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 $\delta^{13}C\text{-}CO_2$ 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_2 dissolving into the melt. Upon (re)freezing within the snowpack, a substantial portion of the CO_2 will remain dissolved within the ice matrix. This dissolved CO_2 can then diffuse across the sharp concentration gradient surrounding the melt layer and into the otherwise pristine bubbles. The dissolved CO_2 can also be liberated during the extraction of the air. The net effect is artificially high CO_2 observed across melt layers. These melt layers are rare in most of the polar ice cores in which CO_2 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_2 in polar ice Ahn, Headly, et al. 2008).

After bubble closure, the concentration of CO_2 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_2 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_2, 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_2 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_2(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_2 starting around 1800 C.E. Accompanying the sharp rise in CO_2 is a similarly rapid decrease in $\delta^{13}C\text{-}CO_2$ Friedli, Lötscher, et al. 1986; Francey et al. 1999; Bauska, Joos, et al. 2015; Rubino, Etheridge, Thornton, et al. 2019). This shift to more ^{13}C-depleted values is consistent with the release of photosynthetically fixed carbon (i.e., organic carbon) as the main source of CO_2 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 ^{13}C and ^{14}C records provide some of the key evidence that the rise in atmospheric CO_2 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_2 rise comes from volcanic sources, which have very similar source signature (-3 to -5‰) to the pre-Industrial atmosphere and would not cause the $\delta^{13}C\text{-}CO_2$ 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 $\delta^{13}C\text{-}CO_2$ to increase rather than decrease.

To date, only the Law Dome ice core overlaps with the instrumental record of 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

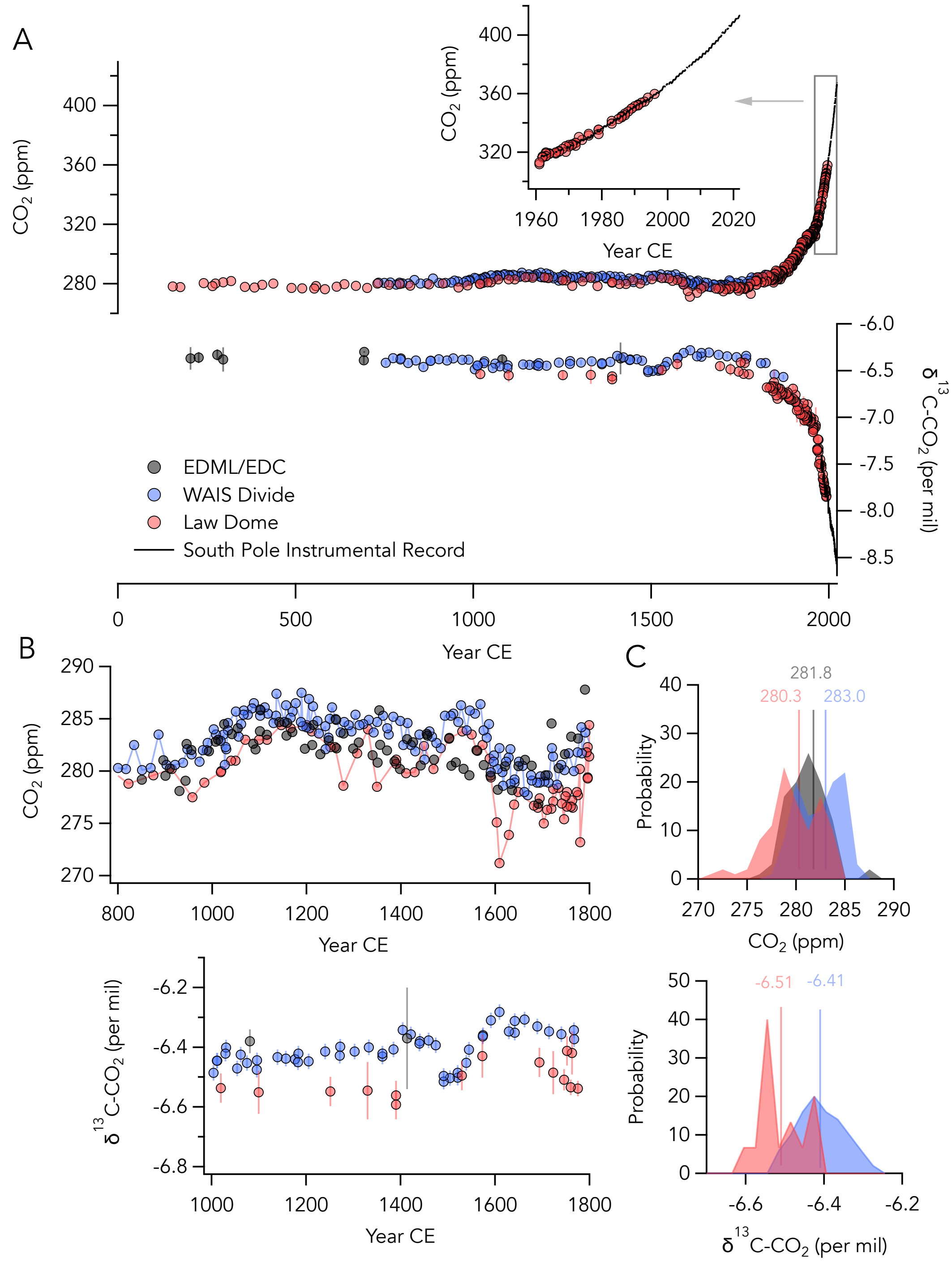

Figure 3: Panel (A): The concentration and isotopic composition of atmospheric CO_2 over the past two millennia. As in Figure 2, the instrumental data (black line) is sourced from South Pole Station measured as part of the Scripps Institution of Oceanography atmospheric monitoring program (Keeling et 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_2 and δ^{13}C-CO_2. Narrow bars indicate the mean and show the overall offsets between the various records.

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 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 CO_2 cannot be determined to within 3 ppm. Although a measurable error, within the context of current atmospheric levels (∼140 ppm higher than the pre-Industrial) and the major swings of the past (∼100 ppm lower than the pre-Industrial), the error represents at most a 3% uncertainty.For δ^{13}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 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 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 CO_2 around 1450 C.E., followed soon thereafter by the most dramatic change in CO_2 of the pre-Industrial with a rapid drop in 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 CO_2 are negatively correlated with changes in the δ^{13}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; Rubino, Etheridge, Trudinger, Allison, Battle, et al. 2013).

The mechanisms behind multi-decadal 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_2. The CO_2 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_2 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_2-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_2, 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_2 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 δ^{13}C-CO_2 have been ruled out as erroneous (Smith et al. 1999). Recent studies have also examined the CO_2 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 $CaCO_3$ deposition due to $CaCO_3$ 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; Riechelson et al. 2024).

The gradual drawdown of CO_2 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_2 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_2, and possibly increased volcanism that would have propped up CO_2 level in the early Holocene.

The exacts causes of the rise in CO_2 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_2 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_2 as coming from the land, has largely ruled out humans as the sole driver of the CO_2 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_2 as both forcing and feedback

5.1 Constraints from CO_2 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_2 (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_2 change but could not precisely define the timing. High-quality data from EDC demonstrated

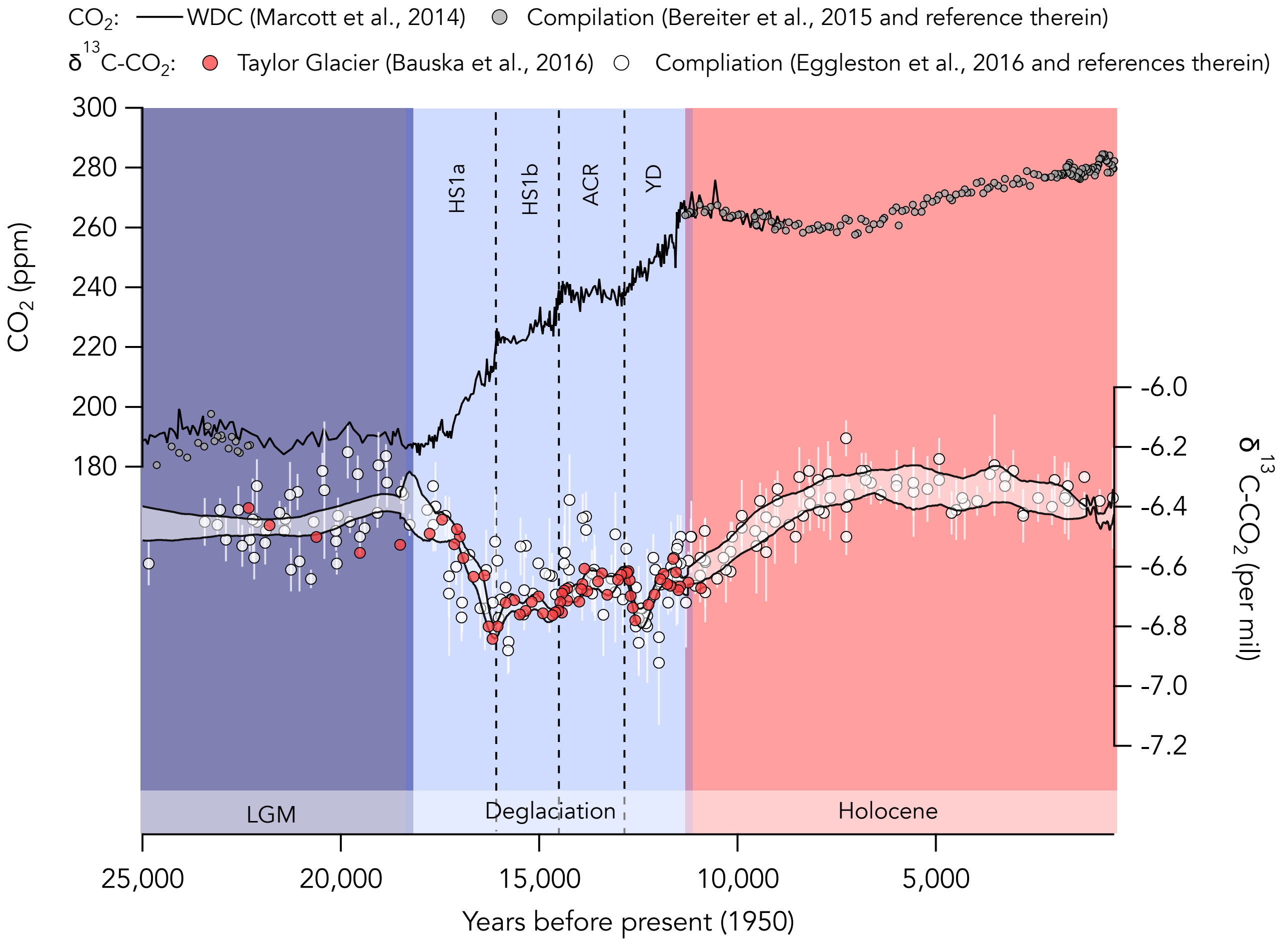

Figure 4: The concentration and isotopic composition of atmospheric CO_2 spanning the Last Glacial Maximum (LGM), Last Deglaciation and Holocene (prior the Industrial period). CO_2 data in grey come from a compilation of data primarily from (Monnin, Steig, et al. 2004; Ahn and Brook 2008; Bereiter, Eggleston, et al. 2015); CO_2 data in black come solely from the WAIS Divide Ice Core Marcott et al. 2014; Bauska, Marcott, and Brook 2021). $\delta^{13}C$-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).

that the deglacial CO_2 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_2 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_2 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_2 (Chowdhry Beeman et al. 2019). On a global scale, the opposite is the case. Global temperatures clearly lag the changes in CO_2 and thus solidifies the role of CO_2 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_2 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 Siple Dome ice core hinted that faster rates of change were possible, but generally scattered CO_2 data obscured some of the critical variability (Ahn, Wahlen, et al. 2004). The WAIS Divide ice core provided both a well-dated CO_2 (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_2 jumps at the onset of the B/A (12 ± 1 ppm within 200 ± 30 years) and pre-Boreal (13 ± 1 ppm within 100 ± 40 years) were confirmed and determined to be precisely in-phase with rises in CH_4. Additionally, a second mode of centennial-scale variability was observed at 16.3 ka (12 ± 1 ppm within 100 ± 20 years). This jump also demarcates the previously identified switch to a much slower rate of CO_2 rise (Monnin, Indermühle, et al. 2001), which in WAIS Divide is even more dramatic with a small plateau in CO_2 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_2 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_2 rise (18-16 ka) was associated with a 0.3‰ drop in $\delta^{13}C$-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_2 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_2 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_2 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) $CaCO_3$ compensation as a feedback from the transfer of CO_2 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 ten 10 or more mechanisms can be grouped into five categories that can be partially delineated using paired measurements of CO_2 and $\delta^{13}C$-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_2 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_2 is rising quickly, ends with an abrupt release of CO_2 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_2 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_2 jumps during the warming at B/A and the end of the YD. The second ramp up in CO_2 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 $CaCO_3$ 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_2 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_2 rise given that the carbon isotopes indicate a minimal role for changes in solubility? Precisely to what degree did $CaCO_3$ 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_2 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_2closely 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 cyclicity 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_2 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.

As opposed to the deglaciation, where we have radiocarbon dated proxy records, defining the lead-lag between temperature and CO_2 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_2. This apparent lag may be due to a gradual release of terrestrial carbon and lingering effects of the penultimate deglaciation via $CaCO_3$ compensation that maintain CO_2 at interglacial levels despite the nascent glacial conditions (Schneider et al. 2013). Additionally, the processes that drawdown CO_2 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_2 and $\delta^{13}C\text{-}CO_2$ 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 variably 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_2 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_2 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_2 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_4), CO_2 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_2 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

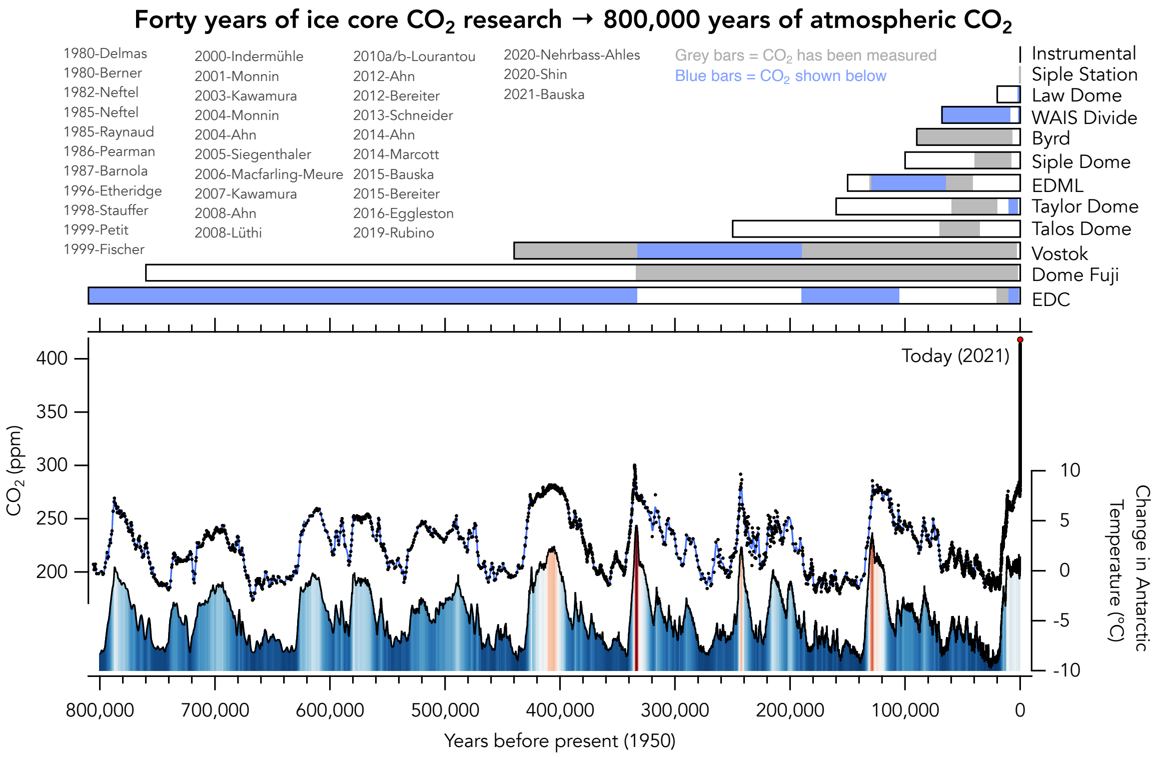

Figure 5: The complete record of atmospheric CO_2 from the present day to the oldest ice ever recovered from a deep, continuous ice core (black markers with blue smoothing spline). The bars on the top extending back in time indicate the span of ages of ice recovered in a given ice core with the grey bars indicating zones where CO_2 has been measured, but not shown in this compilation due to superior data from other cores, and the blue bars indicating zones where CO_2 has also been measured and displayed below. Alongside the CO_2 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_2 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)

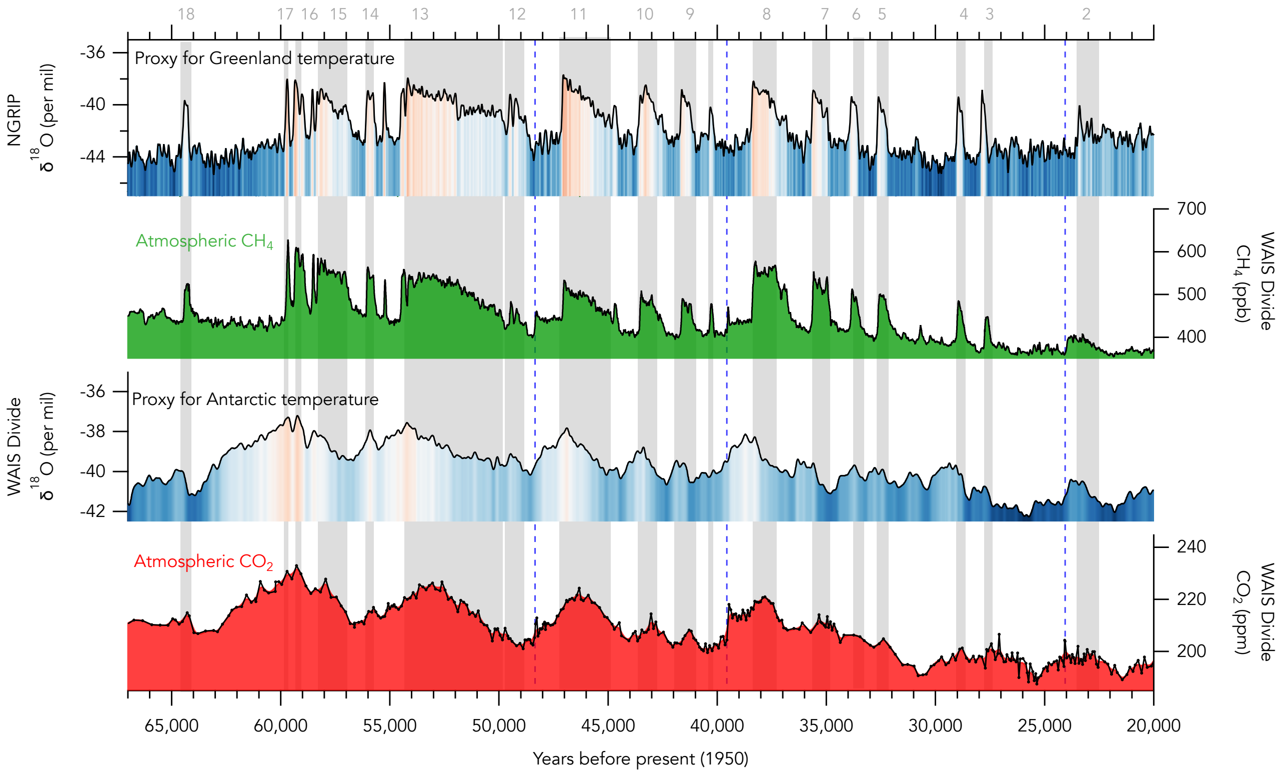

Figure 6: A simple synthesis of climate and carbon cycle variability during a portion (67-20 ka) of the Last Glacial Period. The four time-series are as follows: (1) a proxy for Greenland temperature based on NGRIP oxygen isotopes (Andersen et al. 2004) with the age model adjusted by 1.0063 as per (Buizert, Cuffey, et al. 2015) with a red (warm)-to-blue (cold) color ramp as fill; (2) the continuous CH_4 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_2 (Bauska, Marcott, and Brook 2021) with a red fill. Grey bars show interstadial periods; blue bars shows some of the major Heinrich Events.

yet to be fingerprinted.

Secondly, the most rapid natural increase in CO_2 occurs within a stadial (cold phase) in Greenland and is always associate 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_4 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_2 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_2 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_2 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 ^{40}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_2 from organic carbon as indicated by implausibly negative $\delta^{13}C$-CO_2 values and have subsequently been excluded.

Information gleaned from the covariation of the atmospheric CO_2 data with other gas records (notably CH_4) 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_2 data with concentrations that fall on the lower end of the glacial-interglacial spectrum. These suggests that the transition from the 40 k to 100 k world was accompanied by a shift towards lower glacial CO_2 concentration but potentially invariant interglacial CO_2 concentrations. Numerous international efforts are currently underway to recover continuous records of CO_2 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_2 have revealed multiple modes of natural variability in the carbon cycle that, first and foremost, clearly distinguish the rise in CO_2 since Industrial Revolution as unprecedented. The data have also demonstrated the tight coupling between CO_2 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. The root causes of much of the CO_2 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_2), improvements

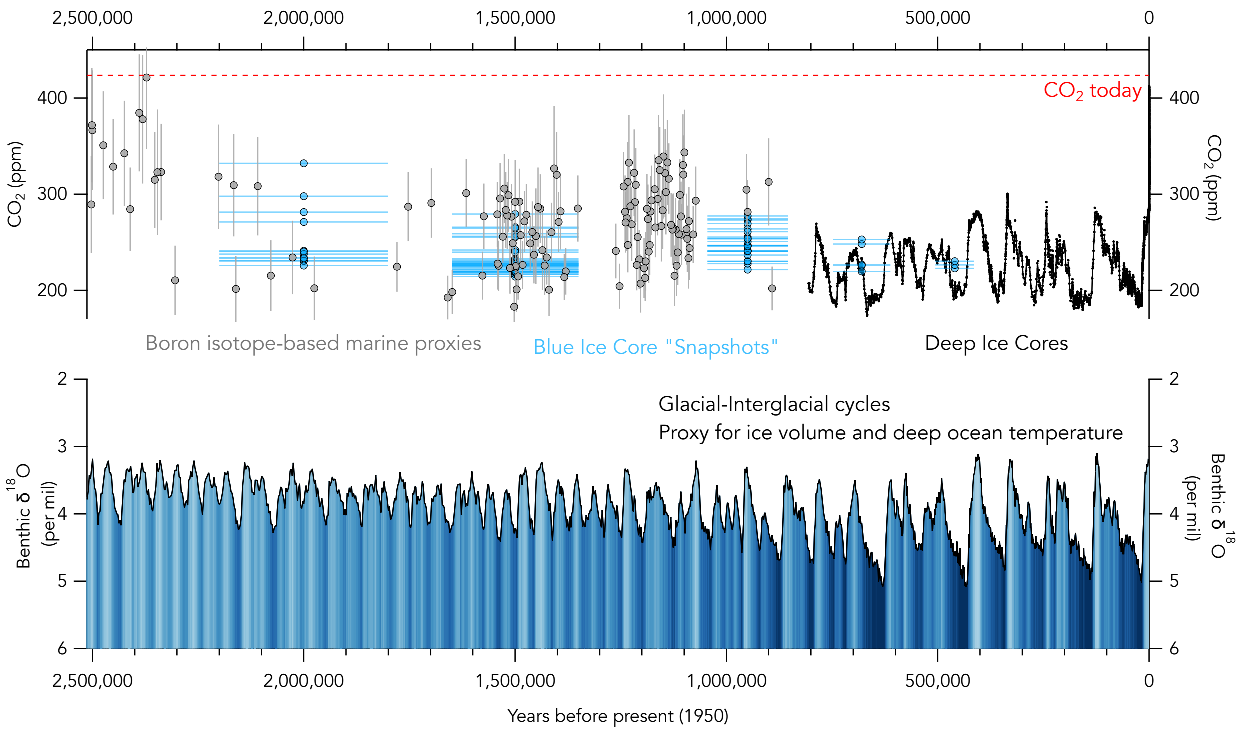

Figure 7: The complete record of atmospheric CO_2 from the present day to the oldest ice ever recovered as in Fig. 4 but with the additional of data from blue ice sites (Higgins et al. 2015; Yan et al. 2019) (light blue markers) along with boron isotope-based proxies for CO_2 (Chalk et al. 2017; Dyez, 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).

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_2 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_2 observed during glacial conditions?
3. What role did humans play, if any, in driving the gradual increase in CO_2 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_2 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 ^{12}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}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 (δ) notation.. 18

Carbon-14 ^{14}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 δ^{13}C-CO_2 in the case of "single deconvolution" or both CO_2 and δ^{13}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 CO2. 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

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