Measurement of CO_2 Concentrations Through Time Using Ice Core and Stomatal Proxy Data

CO2COALITION

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INTRODUCTION

CO_2 records from air bubbles in Antarctic ice cores are regarded as the gold standard for paleo-atmospheric global CO_2 concentrations during past interglacial and glacial periods over the last 800,000 years. Antarctic ice-core data are openly available from the National Centers for Environmental Information (NCEI) and have been studied extensively. The trapped gas in ice is the most direct measurement of CO_2 concentrations for past atmospheric records, providing a continuous global CO_2 baseline. CO_2 measurements are repeatable and have low analytical errors of 1-2 ppmv per sample. CO_2 measurements from ice cores show that CO_2 ranged from 180 ppmv during glacial periods to as much as 300 ppmv during interglacials.

CO_2 concentrations from plant stomata on the other hand are indirect proxy measurements consisting of discontinuous records over the Holocene and deglaciation period. The highly variable CO_2 concentrations have high uncertainties in measurements as well as calibration models. Plant stomata studies are mostly from the Northern Hemisphere where local conditions can strongly influence the resulting CO_2 proxy estimates. The uncertainties and shortcomings associated with plant stomata CO_2 reconstructions outweigh using this dataset as a valid quantitative indicator for paleo-atmospheric global CO_2 concentrations.

SCIENTIFIC DISCUSSION

ICE CORE DATA

Cores from Antarctic glacial ice provide past temperature proxies from oxygen isotopes as well as gas composition from small air bubbles trapped within the ice. As snow accumulates and compacts over time, it is transformed into firn, a granular intermediate stage between snow and ice. The firn eventually becomes dense enough that open pores begin to close, forming bubbles that trap atmospheric gases. Bender (1997) is a good overview of the firn to ice processes. This section examines how the CO_2 concentrations measured in ice bubbles have varied over the past and the effects of compaction on the temporal resolution of these data.

Figure 1 shows key Antarctic ice cores and global CO_2 concentrations over the past 800,000 years. In general, CO_2 concentrations rise to nearly 300 ppmv during warm interglacial periods and decrease to as low as 180 ppmv during the cold glacial periods. The interglacial periods are noted using the marine isotope stage (MIS). There are numerous ice cores that cover our current interglacial (MIS1) known as the Holocene and the preceding glacial period, with only a few that extend over the previous interglacial period referred to as MIS 5, and only one that extends the entire 800,000 years, the EPICA Dome C ice core.

Notable differences exist between ice cores taken in high accumulation/warmer temperature sites versus low accumulation/colder temperature sites. The deeper, older ice cores tend to occur in low-snow accumulation sites in Eastern Antarctica, and include EPICA Dome C, Vostok, and Dome Fuji. These cores tend to have a prolonged entrapment of gas within ice bubbles and more extensive gas mixing of CO_2 with the atmosphere, resulting in lower temporal resolution. The shallower ice cores are drilled in high-snow accumulation sites and in the peripheral areas of the ice field. High-accumulation sites such as Law Dome and WAIS have rapid burial, less gas diffusion within the firn, and better temporal resolution, but shorter records.

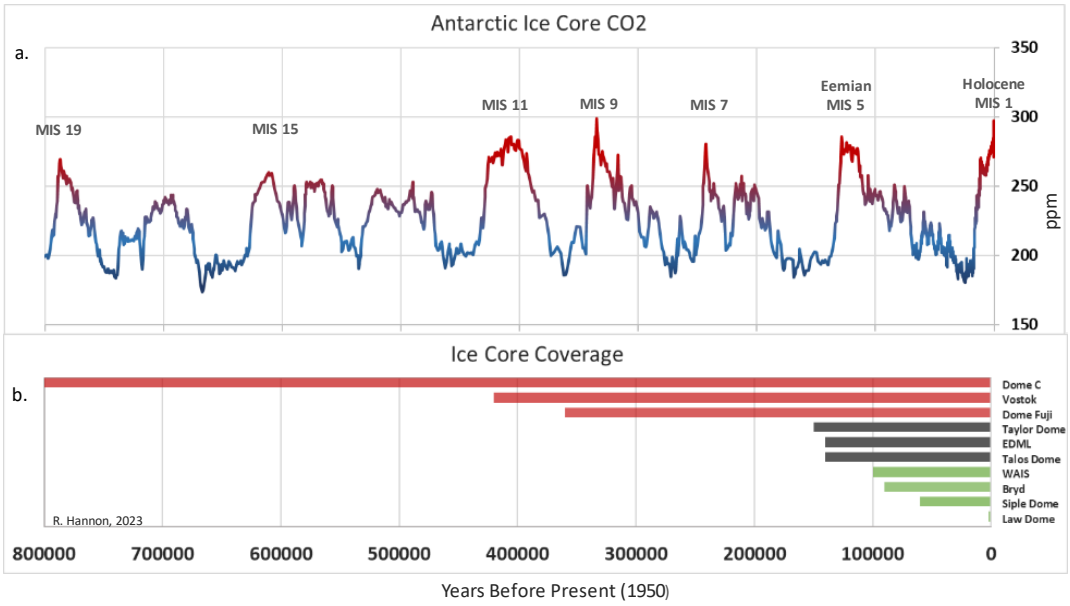

Figure 1: *a. Global CO_2 concentrations from ice cores after Bereiter, 2014, plotted over time. b. Key ice cores showing approximate cored interval length. Colors indicate CO_2 temporal resolution: red is low ($\geq$100 years), gray is intermediate (50-100 years), and green is high (10-50 years).*

Ice Age to Gas Age Time Shift

Two key adjustments occur to atmospheric gases during the firn transition to ice prior to being trapped in ice bubbles. First, atmospheric CO_2 concentrations are smoothed over time due to atmospheric mixing and gas diffusion within the firn. Second, the gas is believed to be younger than the age of the ice when it is eventually trapped within bubbles (Trudinger, 2002; Schwander, 1984). Once trapped within the bubbles, gas is assumed to age with the ice. This age difference is referred to as the ice-gas age delta. The delta ranges from 31 years in Law Dome to 835 years in the lower snow accumulation EDML ice core. Very low snow accumulation sites such as Dome C and Vostok have a delta of thousands of years. In addition, the ice-gas age delta varies between interglacial and glacial periods due to varying snow accumulation rates.

Figure 2 shows CO_2 concentrations versus the age of ice in which it is trapped for five ice cores in the Antarctic before adjustments. Atmospheric data from Cape Grim and firn data are included on the plot for comparison. Noted are the delta differences in years between the (younger) gas age and (older) ice age as well as the age of the ice at the boundary between firn and ice (which roughly corresponds to the base of the bubble trapping zone). This plot is a profile rarely found in published literature.

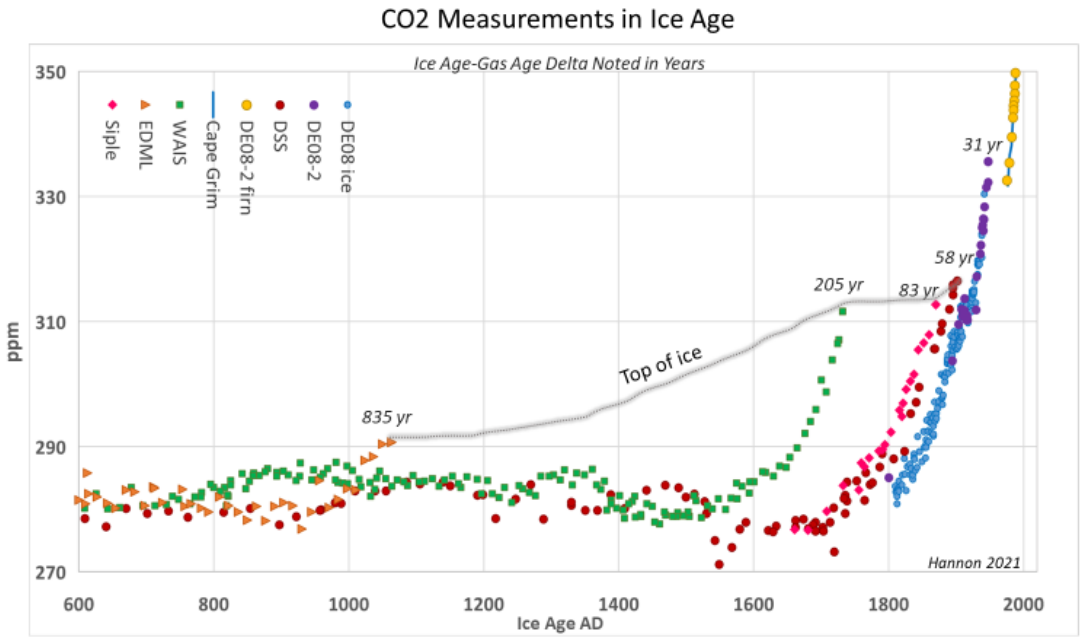

Figure 2: *CO_2 concentrations measured in ice age. The numbers show the average ice-gas age difference in years. The dashed line is the top of ice and approximate position of the base of the bubble zone. CO_2 data for Law Dome (DE08, DSS) is from Rubino 2019; WAIS is from Bauska 2015; Siple is from Neftel 1994; and EDML is from Siegenthaler, 2005.*

There are several methods to calculate the delta between ice age and gas age. Stratigraphic markers such as volcanic markers and distinct gas variations are used to determine the ice-gas age delta and for multi-core synchronization (Buizert, 2021). When gas measurements in ice or firn show the same dramatic increase as modern records, they are shifted to the age of instrumental data. For example, Law Dome DE08 ice gas data is uniformly shifted by 31 years to match instrumental atmospheric data. DSS and Siple are shifted 58 and 83 years, respectively, to match the DE08 data. Various other methods are used to estimate the delta and resulting shift. Firn models calculate the ice-gas age delta for ice cores using density and temperature data and are constrained by using nitrogen-15 data, a proxy for firn thickness (Buizert, 2021). Another approach uses ice depths in the core that are contemporaneous with ice cores where gas ages are well constrained (Bender, 1997). Ice-gas age deltas have uncertainties of 10-15%, especially

in low accumulation sites where the ice-gas age deltas are exceptionally large (Seigenthaler, 2005).

Gas age is the age of CO_2 which is reported in most public datasets and graphs. Different CO_2 datasets overlap quite nicely, with few exceptions, when corrected to the appropriate gas age (Figure 3). Within multiple ice cores, these gas shifts appear reasonable as distinct CO_2 highs, such as the CO_2 bulge, and lows, such as the Little Ice Age (LIA). Law Dome ice and firn CO_2 measurements also closely match the modern CO_2 rise measured in southern hemisphere monitoring stations.

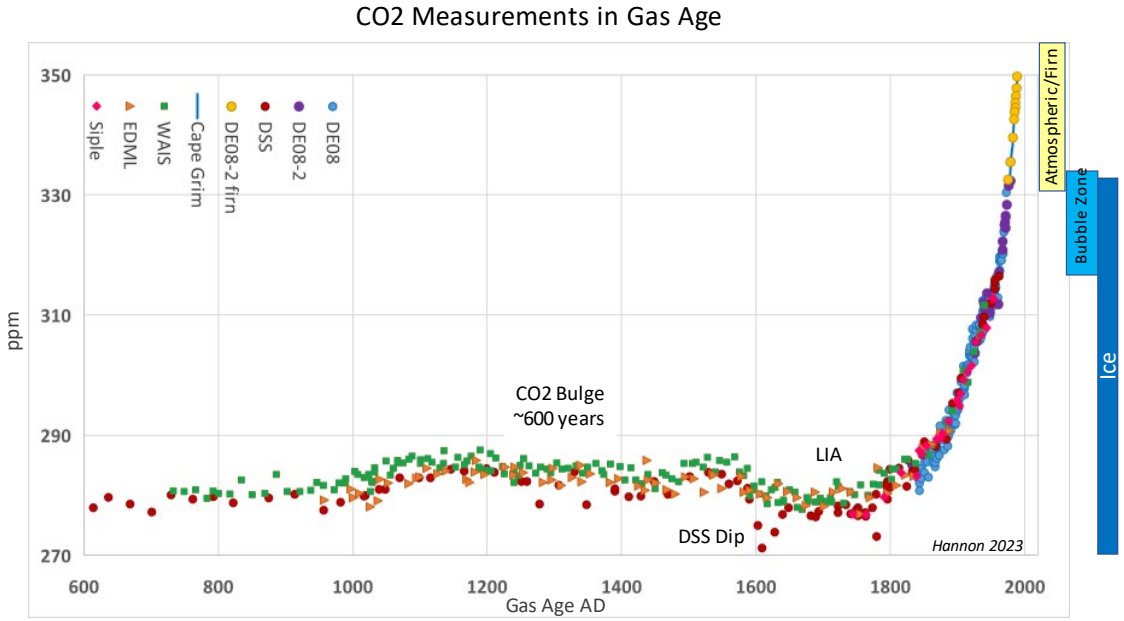

Figure 3: *CO_2 concentrations corrected to appropriate gas age. Boxes on the right side highlight different data medium and approximate location of the ice bubble zone. CO_2 data references noted in Figure 2.*

Ice Core CO_2 Resolution

Variations in atmospheric CO_2 concentrations are smoothed over time due to atmospheric mixing and gas diffusion within firn. The gas-age distribution is modeled and represents the time it takes for gas to be trapped in bubbles and the amount of gas mixing. Its temporal width is a representation of the resolution or smoothing of ice-core gas in years. High-snow accumulation sites at Law Dome have a CO_2-age distribution of only 10-14 years. Low-accumulation sites, such as Dome C and Vostok, contain gas that is mixed with the atmosphere over hundreds of years. According to Monnin 2001, Dome C is smoothed over 200 years in the Holocene interglacial and smoothing increases to 550 years during glacial periods. However, a

more recent publication shows Dome C resolves CO_2 fluctuations as brief as 100 years during the MIS 9 and 11 interglacials (Nehrbass-Ahles, 2020).

Figure 4 shows CO_2 concentrations over the past 1,000 years in high-resolution records from Law Dome and WAIS. As mentioned, Law Dome can identify CO_2 rises and dips as brief as 10 to 14 years. Law Dome shows modest CO_2 rises of 5 to 7 ppmv during the MWP beginning around A.D. 1050 and continuing to A.D. 1600. Rubino, 2019, discusses the CO_2 decrease of 10 ppmv around A.D. 1610 in the Law Dome record, which is not evident in lower resolution records, confirming the higher resolution of the Law Dome record.

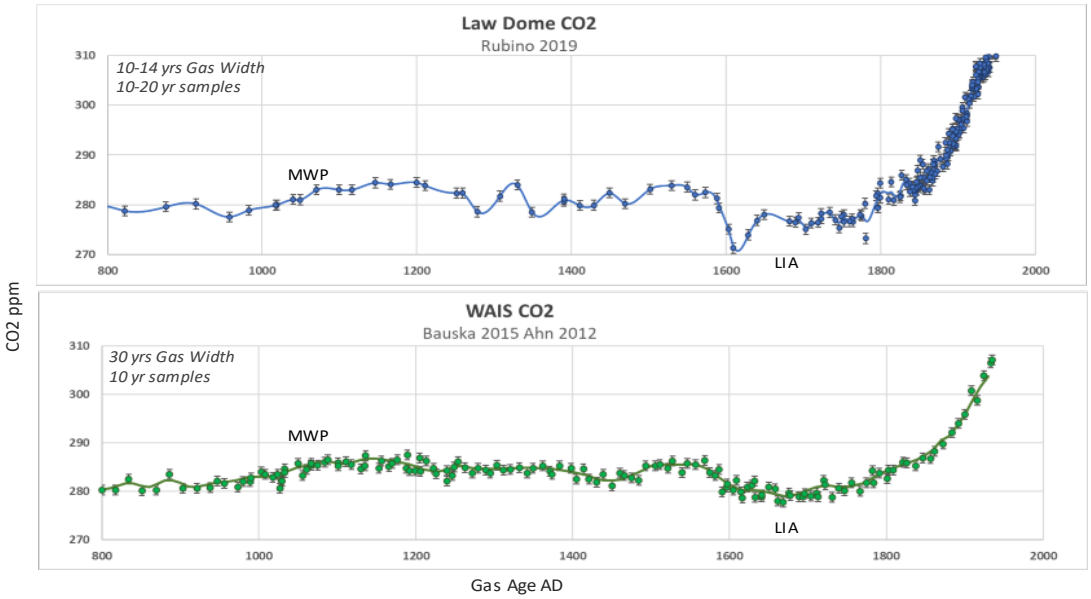

Figure 4: *High resolution Antarctic ice core CO_2 data during the past 1000 years. Data points are plotted with 20-year trend lines. Law Dome trend is the 20-year spline provided by Rubino, 2019. Gas width due to firn-ice transition and sample spacing resolution in years (yr) are noted in the text box. Data references are shown on the plots.*

Ahn et al, 2012, compiled CO_2 records from WAIS and compared them to other key datasets, such as DML and Law Dome. Their study recognizes and discusses elevated CO_2 during the Medieval Warm Period (MWP) at A.D. 1000, CO_2 decrease around A.D. 1600 during the Little Ice Age (LIA), and the subsequent rapid increase beginning around A.D. 1850. The increase of CO_2 during the MWP is similar to Law Dome, about 7 ppmv. Around A.D. 1610, WAIS does not show the Law Dome dip and is up to 10 ppmv higher than Law Dome due to lower resolution. Ahn, 2012, used the dip to estimate the amount of smoothing occurring in the WAIS CO_2 records. Using synthetic age distributions and modeling, they deduced that WAIS experiences about 30 years of smoothing due to gas diffusion within the firn.

Ice Core CO_2 Repeatability

At least six ice cores with high resolution cover the Holocene or MIS 1 and preceding deglaciation shown in Figures 5 and 1b. These data provide the opportunity to understand CO_2 fluctuations as well as a comparison to lower resolution ice core data. All CO_2 values were measured with the dry extraction technique to minimize ice-core melt and potential chemical reactions. The precision of the individual measurements or analytical uncertainty is estimated to be 1.5 ppmv (Rubino, 2019). Data points are rejected due to obvious contamination, fractures or presence of melt layers.

All records show that CO_2 reached a high of about 280 ppmv at the end of the deglaciation about 11,700 years B.P. (Before Present). During the mid-Holocene, CO_2 concentrations decreased to a minimum of 260 ppmv around 8,000 years B.P. CO_2 concentrations gradually increased to 285 ppmv in the late Holocene, up to the time of Medieval Warm Period (MWP) about 1,000 years B.P. A distinct drop in CO_2 values to about 270 ppmv occurred during the Little Ice Age (LIA), followed by the modern increase in CO_2 (past 400 ppmv, and continuing to rise).

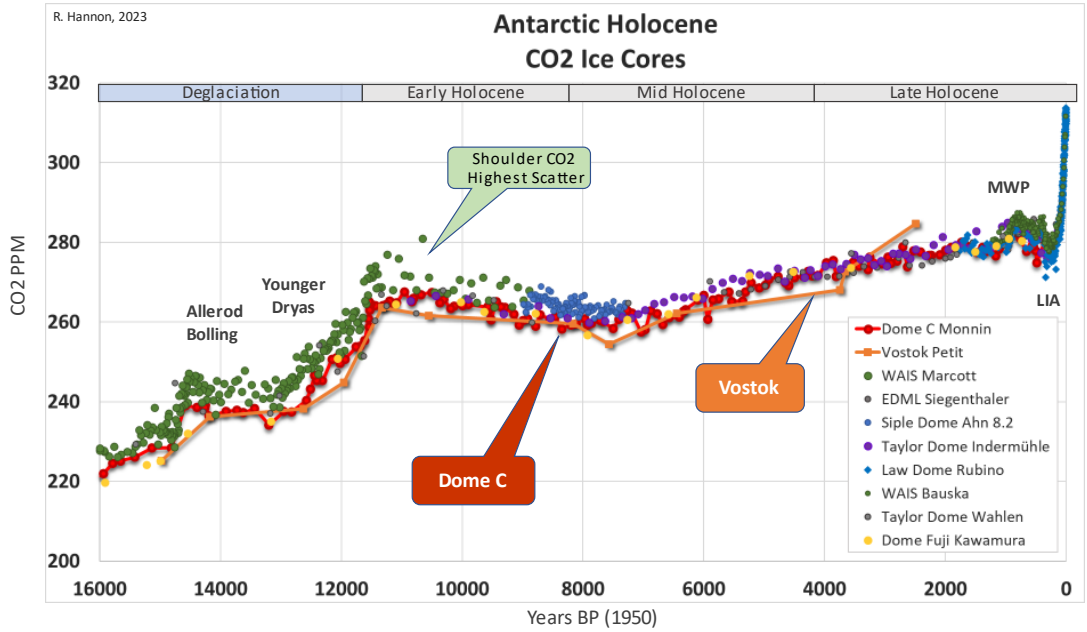

Figure 5: *Antarctic ice core CO_2 datasets compiled over the Holocene. High accumulation sites with higher resolution are shown in green and blues. Data references are shown on the graph.*

The repeatability and agreement between the ice core CO_2 records is quite impressive. There is less than 4 ppmv difference over most of the Holocene, consisting of over 1,000 data points. Standard deviations of the samples average 1.5 ppmv. Records from the higher resolution ice cores such as WAIS and Siple tend to show CO_2 measurements from 1 to 4 ppmv higher than

lower resolution records such as Dome C and Vostok. Ahn, 2012 and Rubino, 2019 have documented the 4-ppmv discrepancy in the WAIS records. This offset occurs with both CO_2 and its carbon isotopes but not with CH_4 (methane). The reason for the offset is not well understood.
The largest amount of discrepancy appears at the end of deglaciation and on the shoulder of the Early Holocene interglacial from 10,500 to 11,500 years B.P. The WAIS data shows CO_2 records of 10-15 ppmv higher than lower resolution Dome C and Vostok records. This may suggest that WAIS recognizes short-term higher variability during a period of climate transition at the end of deglaciation. WAIS also shows inflections around 14,500 years B.P. during the Allerod Bolling interstadial which are 7 ppmv higher than Dome C. Dome C does see a small CO_2 fluctuation during this time, barely visible in the Vostok ice core.

Clathrates

Bubbles begin to transition into solid clathrates or small crystals between 500-1,200 meters or about 20,000 to 85,000 years B.P. (Stauffer and Tschumi, 2000). This transition zone consists of both bubbles and clathrates. Below the transition zone, there are no more bubbles, and the ice is pure clathrates. The clathrate hydrates are now enriched with the CO_2, and the bubbles are depleted.

It is frequently challenged that the dry-extraction method is inefficient for analyzing CO_2 concentration in ice samples containing both bubbles and clathrate hydrates. Air extracted from the transition zone using mechanical destruction preferentially extracts air from the bubbles which are depleted in CO_2 resulting in lower CO_2 concentrations (Bereiter, 2014). Ice recovered from the clathrate zone is allowed to relax during storage at ambient pressures. Clathrate hydrates gradually return to bubbles during storage of the ice core in about a year or so. Dry extraction is typically conducted after this long storage period and/or sublimation is conducted instead of mechanical crushing.

Kawamura, 2003, conducted a wet extraction technique on Dome Fuji. The wet extraction technique helps ensure that the extracted gas is free from the clathrate hydrate effect. A disadvantage of the wet extraction technique is acid-carbonate reactions or oxidation of organic components in the ice may result in higher CO_2 readings. However, Antarctic ice cores have low concentrations of impurities or dust, so differences between the wet and dry extraction can be attributed mostly to the clathrate hydrate effect.

Figure 6 shows the CO_2 concentrations from the Dome Fuji wet extraction compared to the dry extraction CO2 values from Dome C and Vostok ice cores. In general, high CO_2 values occur during the interglacial periods and low values in the glacial periods, paralleling dry extraction values from other Antarctic ice cores. The wet extraction values range from 190 ppmv to 300

ppmv over the past 350,000 years. Standard deviations on the wet extraction were on average 0.7 ppmv.

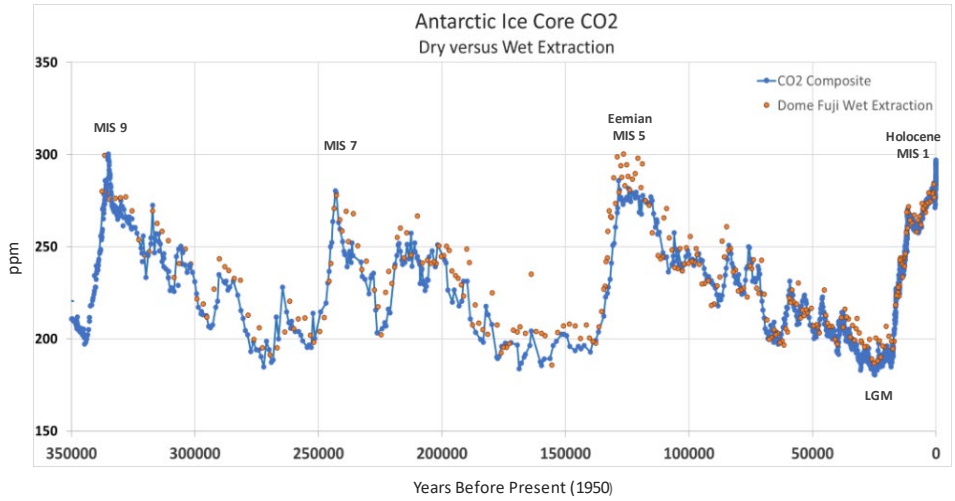

Figure 6: *Comparison of CO_2 measurements from wet and dry extraction techniques. Wet data is from Dome Fuji after Kawamura, 2003, and dry data is from a composite of various cores from Bereiter, 2014. LGM is Last Glacial Maximum.*

There are a few notable differences between the wet and dry extraction from the various ice cores. The wet CO_2 values in the Last Glacial Maximum (LGM) and the glacial period preceding MIS 5 are systematically higher by 10-20 ppmv than the records from dry extraction. The higher values could be due to more complete extraction efficiency in the clathrate transition zone.

There is also a notable increase of wet CO_2 values during the Eemian or MIS5 interglacial by 10-20 ppmv. In the Eemian interglacial, calcium (Ca^{2+}) is not significantly different between Antarctic ice cores, challenging the chemical reaction theory of elevated CO_2 values for wet extraction. Additionally, Ca^{2+} is significantly lower during interglacial periods than during glacial maximums by an order of magnitude. Therefore, Kawamura believes that the wet CO_2 values may be higher mostly due to incomplete extraction during the dry technique.

Kawamura states the wet extraction should be regarded as an upper limit estimation of atmospheric CO_2 in the past. Note that even though the wet extraction yields higher CO_2 values than dry extraction values, the wet CO_2 values rarely exceed 300 ppmv over the past 800,000 years.

Ice Core CO_2 Observations

Antarctic ice cores present high-quality records of atmospheric CO_2 that span paleo-timescales over the past 800,000 years. The trapped gas in ice is the most direct measurement of CO_2

concentrations for past atmospheric records, providing a continuous global CO_2 baseline. CO_2 measurements are accurate and repeatable with analytical errors of 1-2 ppmv per sample and standard deviations less than 4 ppmv. Ice core CO_2 records from high-resolution ice cores correspond well with modern CO_2 measurements representing well-mixed atmospheric global CO_2 trends.

CO_2 measurements from ice cores using various extraction techniques show that CO_2 over the past 800,000 years ranged from 180 ppmv during glacial periods to as much as 300 ppmv during interglacials. CO_2 measurements in the past do not exceed 300 ppmv, even using wet extraction techniques, which ensure that CO_2 is released from both bubbles and existing clathrates.

More than nine ice cores cover the Holocene and demonstrate remarkable agreement of CO_2 measurements, indicating excellent reproducibility. High-resolution ice cores, such as Law Dome and WAIS, have minimal gas diffusion in the firn, resulting in minor smoothing of CO_2 over 14 years and 30 years, respectively. Most of the Holocene interglacial CO_2 measurements are within 4 ppmv, with the highest departure of 10 to 15 ppmv for a brief period during the early Holocene.

PLANT STOMATA CO_2 RECONSTRUCTIONS OVER THE HOLOCENE

This section provides a general overview of CO_2 proxy data from plant stomata with emphasis on the past Holocene. Stomata from leaves are used as indirect measurements for paleo-atmospheric CO_2 reconstructions (Jessen, 2005; Wagner, 2004). Basically, CO_2 enters through a plant leaf's stomata or pores. When CO_2 in the atmosphere increases, plants have fewer stomata. When atmospheric CO_2 decreases, stomata in plants increase to compensate for low CO_2 levels. Therefore, an inverse relationship exists between stomata frequency and atmospheric CO_2 concentration. Scientists count the number of stomata on different plant species, known as the stomata density (number of stomata per area). A more accurate measure is the stomata index (number of stomata proportional to the sum of stomata and epidermal cells) used to minimize the influence of local environmental variables. The stomatal index (SI) is calibrated with modern training sets to calculate the sensitivity to atmospheric CO_2 levels.

Plant Stomata CO_2 Reconstructions

Atmospheric CO_2 reconstructions from seven different plant stomata studies have been compiled over the Holocene interglacial and preceding deglaciation shown in Figure 7. Many of the CO_2 reconstructions are not readily available in digital format, and therefore are estimated from graphs in the publications. Individual stomata studies cover continuous time intervals ranging from only 500 years to almost 2,000 years. Stomata CO_2 reconstructions show a range

of 250 to 345 ppmv over the Holocene interglacial. In contrast during the deglaciation, stomata CO_2 reconstructions are very erratic and show ranges from 175 ppmv to almost 400 ppmv.

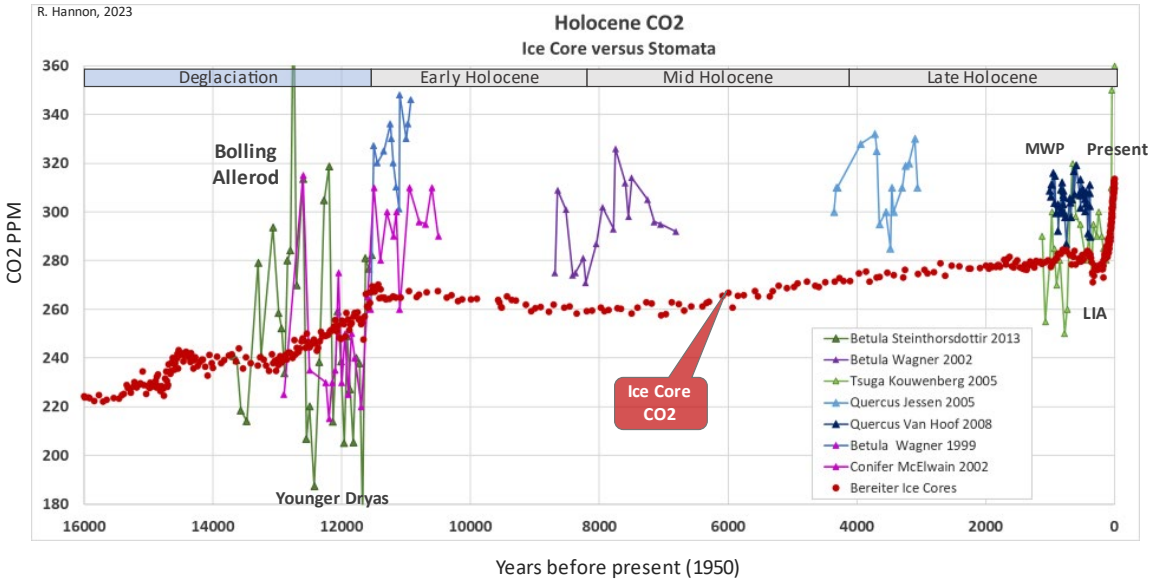

Figure 7: *CO_2 proxy reconstructions from plant stomata compared to CO2 concentrations from ice cores (red dots). References are shown on the graph.*

Different stomata CO_2 reconstructions during similar time periods do not overlie. Van Hoof's *Quercus* and Kouwenberg's *Tsuga* stomata CO_2 reconstructions during the late Holocene seem to be offset by almost 25 ppmv. McElwain's conifer and Wagner's *Betula* CO_2 reconstructions during the early Holocene are also offset by about 25 ppmv.

During the Holocene, almost all stomata CO_2 reconstructions are on average 30 to 40 ppmv higher than ice core CO2 concentrations, with higher amplitude variability. It is widely recognized that the average of stomata CO_2 reconstructions are consistently higher than Antarctic ice-core CO_2 values (Jesson 2006, Wagner 1999, Indermuhle, 1999). In contrast, during the deglaciation stomata, CO_2 values are both lower and higher than those from ice cores, with significant amplitude variability. McElwain states that CO_2 reconstructions from stomatal frequency data appear to consistently underestimate CO_2 levels during the stadials (ice advances) and overestimate them during interstadials (ice retreats), when compared to ice core direct measurements.

Normalized Plant Stomata CO_2 Reconstructions

Since stomata studies over the Holocene cover short age ranges, it is nearly impossible to establish a longer-term baseline trend in CO_2. A simple solution is to use the continuous ice core CO_2 records as the CO_2 baseline and normalize the stomata records to this baseline. Wagner,

2004, adopted a similar approach, where he normalized different stomata records on the long-term average of each record for comparison. This normalization approach is also utilized when evaluating and establishing a database for vastly different proxy temperature records (Kaufman, 2020). Figure 8 shows stomata CO_2 reconstructions normalized to the ice core CO_2 baseline. This allows for the comparison of amplitude trends and temporal synchroneity of the records.

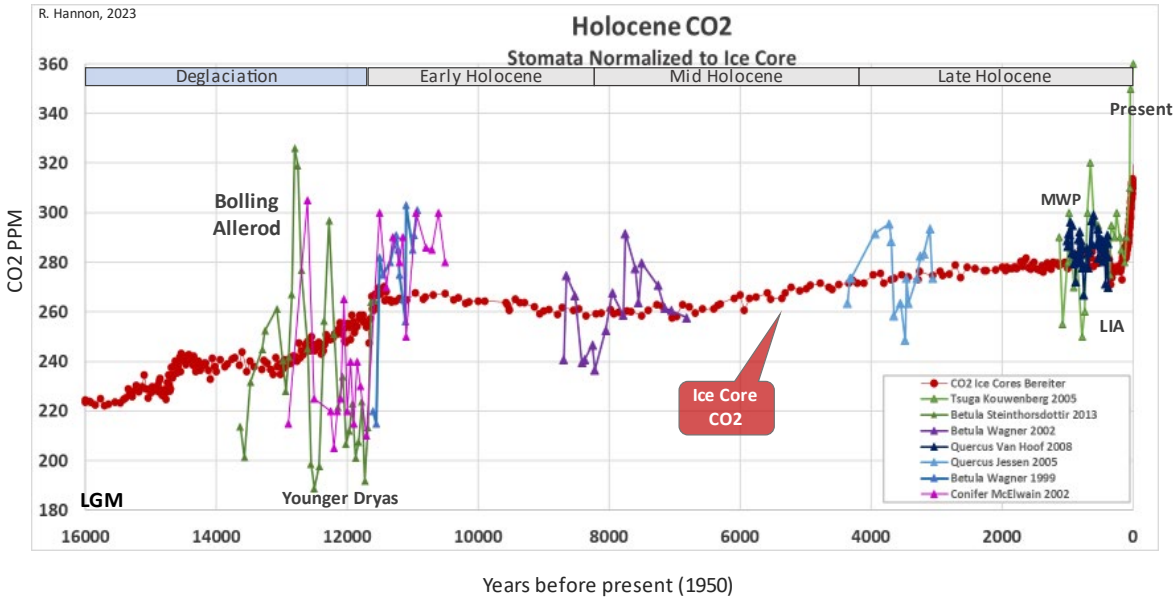

Figure 8: *CO_2 proxy data from plant stomata, with the mean normalized to CO_2 baseline from ice cores (red dots). A three-point average was applied to the Steinthorsdottir data.*

Once they are normalized to the ice-core records, one can examine stomata CO_2 amplitudes compared to ice-core CO_2 amplitudes. Over the Holocene, normalized stomata values show amplitudes approximately ±20 ppmv higher or lower than ice-core CO_2 values which show smaller increase and decreases of ±5 ppmv. Stomata CO_2 reconstructions during deglaciation suggest much more instability and higher fluctuations. Also, note that normalized stomata CO_2 rarely exceeds 300 ppmv.

Plant Stomata CO_2 Repeatability and Variability

Both Wagner, 2004, and Steinthorsdottir, 2013, compared various stomata CO_2 reconstructions over the Holocene and deglaciation. Stomata CO_2 reconstructions do, in fact, show general qualitative trends; however, direct comparisons prove to be difficult.

Holocene Reconstructions

Wagner, 2004, conducted a comparison study from three northern hemisphere regions over various Holocene timeframes: the early Holocene, the 300-year-long cooling that occurred

8,200 years ago, and the late Holocene (see Wagner's figure 8). As mentioned earlier, Wagner normalized the datasets to their long-term average to compensate for the offset between different stomata studies.

For the late Holocene, van Hoof and Kouwenberg stomata studies both show two CO_2 cycles with similar minima around A.D. 1050 and A.D. 1150. Kouwenberg utilizes a three-point average for his reconstruction due to considerable scatter in the CO_2 values. The *Quercus* oak leaves from the Netherlands show amplitudes of 15 to 20 ppmv, and the *Tsuga* pine needles from Washington State show much larger amplitudes of about 30 ppmv. Wagner suggests the larger amplitudes may be due to the lower accuracy of the modern training set for *Tsuga*. CO_2 mixing ratio uncertainties for the SI standard deviation ranged between 0.03 and 17.94 ppmv, with an average of 6 ppmv.

Two stomata records recognize the cooling 8,200 years ago, where CO_2 values generally decreased by about 25 ppmv over a century. The CO_2 reconstruction by Wagner, 2002, on *Betula* species from lake deposits in Denmark is shown in Figure 7. However, the mean sampling resolution of about 110 years and mean uncertainty of ±10 ppmv for CO_2 estimates suggest this record should be cautiously interpreted (van Hoof, 2005).

Jesson, 2005, evaluated *Quercus* and *Betula* in Sweden over 3050 B.P. to 4400 B.P. A three-point running average was used due to large error margins and is shown only for *Quercus*. Error bars with 95% confidence for CO_2 ranged from 50 ppmv to 100 ppmv. Differences exist between *Quercus* and *Betula* (not shown) due to global CO_2 seasonal variations. *Quercus* tend to have a later bud burst than *Betula*. Jesson used the longer *Quercus* data for his analyses but warned that the inconsistencies with *Betula* suggest this data is tenuous at best.

Early Holocene and Deglaciation

Steinthorsdottir's comparison focused on the early Holocene and deglaciation. This time is covered with five stomata CO_2 reconstructions, of which three are shown in Figure 7 (Steinthorsdottir, 2013, McElwain, 2002 and Wagnor, 1999). Steinthorsdotti, 2013, evaluated *Betula* dwarf birch leaves from southeastern Sweden. It was the first time a single species leaf dataset was used over this period. McElwain, 2002, evaluated three conifer species from Pine Ridge and Splan Ponds in Atlantic Canada. Wagner, 1999, evaluated *Betula* fossil birch leaves from northeastern Netherlands. Standard error bars range from 2 up to 75 ppmv. Time resolution is about 50 years.

There are general qualitative trends. The early Holocene is characterized by lower amplitude variations, about 15 to 20 ppmv. There is an interesting distinct low at 11,100 years B.P. seen in

several stomata records (Figure 8). All three stomata studies show an abrupt decrease in CO_2 values of 60-70 ppmv at the onset of the Younger Dryas stadial, around 11,500 years B.P. The stomata show moderate amplitude fluctuations during the Younger Dryas of ±40 ppmv. However, very few of the amplitudes overlie each other even after normalization. Steinthorsdottir states that it is impossible to correlate these records due to low sampling resolution and/or chronological uncertainties, as well as differences in calibration methods used.

Plant Stomata Limitations

Many authors of stomata studies discuss the smoothing effects of gas diffusion within the firn and attribute this to the absence of the CO_2 fluctuations seen in stomata. However, the WAIS and Law Dome ice cores are from high snow accumulation sites that experience lower gas diffusion rates and have high temporal resolution. WAIS has a resolution of 30 years and is sampled at 10-20 years intervals over the past 1,000 years. Law Dome has a resolution of about 14 years and is sampled at 10-year intervals. Since these high-resolution ice cores do not record the high CO_2 variations seen in stomata over the same period, the temporal resolution difference is a questionable hypothesis.

There are several shortcomings associated with stomata CO_2 reconstructions, including improper calibration, plant evolution, and local or seasonal bias. Plant stomata CO_2 reconstructions are derived from an empirically derived relationship between the stomatal index and CO_2 concentration. A general model covering multiple genera is difficult due to highly individual reactions of the various genera (Wagner, 2004). Different model regressions are developed for broad-leaved trees versus conifers. The SI-CO_2 model developed for *Betula* by Wagner has a strong correlation coefficient R^2 of 0.78. However, van Hoof's calibration for *Quercus* had an R^2 of only 0.52 with an RMSE of 10.2 ppmv. Additionally, fossil and herbarium leaves grown during the industrial CO_2 rise do not cover CO_2 levels below 280 ppmv (Rungden, 1999).

Rapid CO_2 fluctuations seen in plant stomata may be the result of improper assembling and calibration of the modern training sets (Wagner, 2004). Assuming that the physiological response of a modern modeled species is transferable to a fossil species is also problematic, according to Reichgelt, 2019. Typically, the nearest living relative is used, and plants tend to evolve. Reichgelt states that CO_2 proxies that use modern species assimilation rates based on phylogenetic relatedness to the fossil species results in CO_2 estimates that are biased by a factor greater than 2. In addition to phylogenetic errors, Royer, 2019, states that published uncertainties associated with the stomatal density proxies are probably too small. They only reflect uncertainty in either the calibration or in the measured values of fossil stomatal density,

but not both; when both sources are considered, errors often exceed ±30 % at 95 % confidence.

Plant stomata may retain local signatures of conditions that may not be truly global in nature. There are a wide variety of plant species and habitat conditions, but most represent Northern Hemisphere atmospheric conditions. Rungden, 1991, states that CO_2 concentrations recorded by *Salix* herbacea leaves during bud burst in spring may be 3-5 ppmv higher than ice cores due to the pronounced seasonal CO_2 variation in the northern hemisphere.

Arborescent tree species and herbaceous species experience different CO_2 environments. Herbaceous species grow near the forest floor where soil respiration can significantly raise the CO_2 concentration. If a species grows near a CO_2 source rather than a secluded forest, it will have a higher CO_2 reading. Significant differences can occur between the stomatal frequency in sun and shade leaves of *Quercus*, and therefore, Van Hoof restricted his analysis to sun morphotypes.

PAST CO_2 ICE CORE AND STOMATA CONCLUSIONS

CO_2 concentrations from bubbles in ice cores are considered the key paleo-atmospheric global CO_2 dataset, and rightfully so. The data consists of continuous records over 800,000 years, instrumental measurement error is low at around 1 ppmv, and the repeatability of multiple ice core datasets show CO_2 concentrations within 4 ppmv of each other. Additionally, the location of ice cores in Antarctica reduces potential local CO_2 modification due to seasonal fluctuations, which can range up to 25 ppmv in the Northern hemisphere.

CO_2 concentrations from plant stomata on the other hand are indirect proxy measurements consisting of discontinuous records over the Holocene and deglaciation period. The highly variable CO_2 concentrations have high uncertainties in both stomata density measurements as well as the CO_2-SI models. Plant stomata studies are mostly from the Northern Hemisphere where local conditions can strongly influence the resulting CO_2 proxy estimates. The uncertainties and shortcomings associated with plant stomata CO_2 reconstructions outweigh the use of this dataset as a valid quantitative indicator for paleo-atmospheric global CO_2 concentrations. The main value of such studies is to test and calibrate methodologies for application to earlier time periods for which ice core data is unavailable.

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About the Author

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About the CO_2 Coalition

The CO_2 Coalition was established in 2015 as a non-partisan educational foundation operating under Section 501(c)(3) of the IRS code for the purpose of educating thought leaders, policy makers and the public about the important contribution made by carbon dioxide to our lives and the economy. The Coalition seeks to engage in an informed and dispassionate discussion of climate change, humans' role in the climate system, the limitations of climate models and the consequences of mandated reductions in CO_2 emissions. In carrying out our mission, we seek to strengthen the understanding of the role of science and the scientific process in addressing complex public policy issues like climate change. Science produces empirical, measurable, objective facts and provides a means for testing hypotheses that can be replicated and potentially disproven. Approaches to policy that do not adhere to the scientific process risk grave damage to the economy and to science.

The Coalition is comprised of more than 160 of the top experts in the world who are skeptical of a theoretical link between increasing CO_2 and a pending climate crisis while embracing the positive aspects of modest warming and increasing CO_2. They include physicists, chemists, engineers, geologists, economists and more. More than 70% of the members hold doctorates or commensurate degrees and include three members of the National Academy of Sciences.

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