

Atmospheric CO₂ over the last 1000 years: A high-resolution record from the West Antarctic Ice Sheet (WAIS) Divide ice core

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[1] We report a decadal resolved record of atmospheric CO₂ concentration for the last 1000 years, obtained from the West Antarctic Ice Sheet (WAIS) Divide shallow ice core. The most prominent feature of the pre-industrial period is a rapid ~ 7 ppm decrease of CO₂ in a span of ~ 20 – 50 years at ~ 1600 A.D. This observation confirms the timing of an abrupt atmospheric CO₂ decrease of ~ 10 ppm observed for that time period in the Law Dome ice core CO₂ records, but the true magnitude of the decrease remains unclear. Atmospheric CO₂ variations over the time period 1000–1800 A.D. are statistically correlated with northern hemispheric climate and tropical Indo-Pacific sea surface temperature. However, the exact relationship between CO₂ and climate remains elusive due to regional climate variations and/or uneven geographical data density of paleoclimate records. We observe small differences of $0 \sim 2\%$ ($0 \sim 6$ ppm) among the high-precision CO₂ records from the Law Dome, EPICA Dronning Maud Land and WAIS Divide Antarctic ice cores. However, those records share common trends of CO₂ change on centennial to multicentennial time scales, and clearly show that atmospheric CO₂ has been increasing above preindustrial levels since ~ 1850 A.D.

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1. Introduction

[2] The continual rise of atmospheric CO₂ from anthropogenic emissions is the main concern for modern climate and ecological changes [Solomon *et al.*, 2007]. Understanding the carbon cycle is thus very important for accurately predicting, managing and adapting to future climate. The relationship between climate and the carbon cycle remains incompletely understood, however. For example, the predicted magnitude of additional CO₂ rise by climate-carbon cycle feedbacks is model-dependent and ranges from 20 to 200 ppm by the end of 21st century [Friedlingstein *et al.*, 2006].

[3] In this context, construction of precise and continuous paleoatmospheric CO₂ records is essential to improving our understanding of the carbon cycle. However, since precise instrumental measurements of atmospheric CO₂ began only in the late 1950s (C. D. Keeling and T. P. Whorf, http://gcmd.nasa.gov/records/GCMD_CDIAC_CO2_SIO.html) direct records of the natural background levels of atmospheric CO₂ and how they changed in the past are limited. Ancient air trapped in Antarctic ice provides a unique archive that provides the best record of ancient atmospheric CO₂ concentrations and extends to the last 800 ka [Lüthi *et al.*, 2008; Petit *et al.*, 1999; Fischer *et al.*, 1999]. Atmospheric CO₂ records for the last millennium are of great importance because they include information about preindustrial (before 1800 A.D.) and early industrial carbon cycles. “Preindustrial” CO₂ was likely controlled mainly by natural processes [Goosse, 2010] but may have been influenced by human activities such as deforestation, farming and wars [Ruddiman, 2003, 2007].

[4] A precise, multidecadal resolution record of CO₂ spanning the last 1000 years was first obtained from Law Dome ice cores [Etheridge *et al.*, 1996]. Additional study of the same ice increased the resolution of the record and extended the record to the last 2000 years [MacFarling Meure *et al.*, 2006]. The sampling resolution is 20 years for $0 \sim 1500$ A.D. and ~ 10 years or better after ~ 1500 A.D. The Law Dome records show ~ 10 ppm variability of CO₂ on multidecadal to centennial time scales. The Law Dome

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Table 1. Glaciological Characteristics of the Antarctic Ice Cores Where High Resolution of CO₂ Was Studied

| Ice Core Name | Mean Temp. (°C) | Acc. Rate (cm we/yr) | Ice-Gas Age Diff. (yr) | Gas Age Distribution (yr) | Reference for Gas Age Distribution |
|----------------------|-----------------|----------------------|------------------------|---------------------------|------------------------------------|
| Dronning Maud Land | -44.6 | 6.4 | 835 | 59 ± 5 | <i>Siegenthaler et al.</i> [2005] |
| DE-08 (Law Dome) | -19 | 110 | 31 | 10 | <i>Trudinger</i> [2000] |
| DSS (Law Dome) | -22 | 60 | 58 | 14 | <i>Trudinger</i> [2000] |
| WDC05A (WAIS Divide) | -31 | 22 | 205 | ≥30? | this study |

records are unusual because the site has a very high snow accumulation rates of 60 ~ 110 cm we/yr (water equivalent per year) (Table 1) which minimize the smoothing of gas records, which occurs by diffusion in the firn, or unconsolidated snow layer, and gradual bubble close-off [Schwander *et al.*, 1988; Trudinger *et al.*, 2002a; Spahni *et al.*, 2003; Buizert *et al.*, 2011].

[5] Another high-resolution record spanning the last 1000 years has been obtained from EPICA Dronning Maud Land (EDML) [Siegenthaler *et al.*, 2005]. The ~15 year sampling resolution record generally shares centennial trends with Law Dome records but does not capture rapid changes in CO₂, such as a rapid decrease of CO₂ in ~A.D. 1600, that were clearly shown in the Law Dome core. Presumably the absence of rapid CO₂ change is due to more intensive smoothing of gas records at the low accumulation site [Siegenthaler *et al.*, 2005]. Thus, it is important to obtain high-resolution records from various Antarctic cores that formed in different glaciological conditions, particularly at sites with high accumulation rates. Antarctic records are the focus of CO₂ studies because Greenland ice cores are not believed to provide reliable atmospheric CO₂ levels because of in situ production of CO₂ via the carbonate-acid reaction [Delmas, 1993; Anklin *et al.*, 1995; Barnola *et al.*, 1995; Anklin *et al.*, 1997; Smith *et al.*, 1997a, 1997b; Wahlen *et al.*, 1991] and oxidation of organic compounds [Tschumi and Stauffer, 2000], both enhanced in Greenland ice due to high dust and organic carbon content.

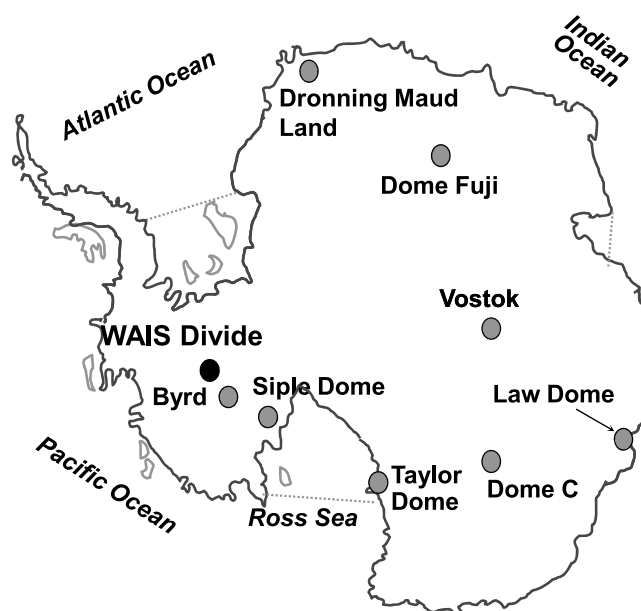
[6] Here we provide a record of atmospheric CO₂ at 10-year sampling resolution from the WAIS Divide Antarctic ice core. The record spans from 960 to 1940 A.D. We take advantage of a relatively small smoothing and high temporal resolution of gas records provided by the high accumulation rate at WAIS Divide [Schwander *et al.*, 1988; Trudinger *et al.*, 2002a; Spahni *et al.*, 2003] (Table 1).

2. Methods

[7] Samples come from the WAIS Divide shallow core (WDC-05A), drilled at 79°27.78'S, 112°7.51'W (Figure 1) in the 2005/2006 field season and analyzed from late 2007 to early 2010 at Oregon State University. The core length is 298.055 m. The ancient air trapped in the core exists in bubbles and did not experience clathrate formation, which can occur in deeper depths by unification of air with ice, during which mixing ratios of gas species fractionate between air in bubbles and in clathrate crystals [Ikeda-Fukazawa *et al.*, 2005]. The shallow core was specially drilled without drilling fluid. With deep coring, drilling fluid is required to keep the drilled hole from closing, but can also potentially contaminate gas records in ice cores. Our reconstruction of atmospheric CO₂ records is restricted to before

~1940 A.D. because the CFC-12 measurements in firn air and ice core samples showed that bubble close-off after coring had resulted in contamination of gas records in ice collected from depths shallower than 78.6 m (corresponding to ~1940 A.D.) [Aydin *et al.*, 2010]. In addition, our own ice core analysis at depths of 72.3 ~ 72.6 m showed CO₂ variation of ~60 ppm over short depth ranges, which was not expected in a 30-cm long ice core (corresponding to 1.5-year age interval). The CO₂ concentration from this depth was inversely correlated with total air content. Higher open porosity with lower air content may have facilitated post-coring air trapping of CO₂-enriched modern air during ice storage.

[8] The analytical methods for measurement of CO₂ are well established [Ahn and Brook, 2007, 2008] and details are described in Ahn *et al.* [2009]. Briefly, after shipment from Antarctica, ice samples were stored at the National Ice Core Laboratory (NICL) at -35°C and sub-samples of the ice were collected at NICL, shipped to Oregon State University (OSU), and stored in a walk-in freezer at -25°C. Using a clean band saw we trimmed ~0.5 cm from the outer surfaces of our samples. Final sample sizes ranged from 8 to 12 g. We routinely measured 5–6 ice samples each day, from 2 to 3 depth intervals. Air was extracted from the samples by crushing the samples with steel pins at -35°C and was trapped in stainless steel tubes at -262°C. The CO₂ mixing ratio in the extracted air was precisely determined using gas chromatography.

**Figure 1.** Location map of Antarctic ice cores.

[9] We routinely used a standard air of 291.13 ppm CO₂. The standard air was calibrated at National Oceanic and Atmospheric Administration (NOAA) in 2005 and 2009, and those two calibrations agreed within an analytical uncertainty of 0.03 ppm (1 σ). We also made a daily calibration for a range of air pressures in the sample loop of the gas chromatograph (GC). CO₂ peak area in the GC was proportional to air pressure in the sample loop. To do an additional check for the linearity of the GC, we made a calibration curve with the standard air of 291.13 ppm CO₂ and then analyzed standards with CO₂ mixing ratios of 197.54 and 386.82 ppm. The difference between measurement relative to the 291.13 ppm standard and the assigned concentration was 1 ppm or less. This supports our assumption of linearity in the range of 197 ~ 387 ppm when the 291.13 ppm tank is used as a standard.

[10] We made two kinds of corrections. First, air liberated from ice will experience alteration during analysis. The alteration might occur by CO₂ adsorption and/or desorption in the crusher, extraction line, sample tube and GC line. In order to estimate this offset we expanded standard air into the crushing chamber after air extraction from an ice sample. After the expansion of standard air into the crushing chamber we used the same procedures for gas extraction and GC analysis as would be used for an air sample liberated from ice. The tests using the standard gas were conducted once for every 1 or 2 gas extractions of ice samples. We usually observed a 1 ~ 2 ppm increase in CO₂ in these tests and all sample measurements were corrected for this enrichment on a daily basis. These tests do not provide a measure of contamination introduced by the crushing itself, for example by CO₂ production or degassing from the flexing of the metal bellows. To determine if crushing caused additional contamination we crushed air-free ice in the presence of standard air and analyzed that air as if it were a sample. We made air free ice by freezing degassed Milli-Q water in a cylindrical vacuum chamber as described in Mitchell *et al.* [2011]. We found that crushing air-free ice causes enrichment of CO₂ of 0 to ~1 ppm (measurements on 6 to 8 different days each year), depending on time intervals of the analyses, and we applied corrections derived from the measurements of the closest date.

[11] We also corrected our data for gravitational fractionation, a process that naturally occurs by diffusion in the uppermost layer of an ice sheet known as the firm [Craig *et al.*, 1988; Schwander, 1989]. We estimated gravitational fractionation using measurements of $\delta^{15}\text{N}$ from the main borehole (WDC06A) which reveal an enrichment of $0.303 \pm 0.006\%$ (J. Severinghaus, personal communication, 2010). The correction for gravitational fractionation can be calculated as follows:

$$\delta^{15}\text{N} \times (M_{\text{CO}_2} - M_{\text{air}}) \times [\text{CO}_2] = 0.303 \times 10^{-3} \\ \times (44.01 - 28.96) \times [\text{CO}_2]$$

where M_{CO_2} and M_{air} are molecular weight of CO₂ and mean air in a unit of g/mol, respectively, and $[\text{CO}_2]$ is the CO₂ concentration in ppm. The correction for gravitational fractionation lowered the blank corrected CO₂ concentration by 1.2 ~ 1.5 ppm.

[12] The chronology for the WDC05A ice core, denoted “WDC05A-2,” is described in detail in Mitchell *et al.* [2011].

To obtain the age of CO₂ we used the results from a 1-D firm air diffusion model as described in Mischler *et al.* [2009] and Mitchell *et al.* [2011]. The mean age of CO₂ at the Lock In Depth (LID, 65.5 m at WDC05A) is 9.9 years and the age of the ice at this depth is 215 years. Therefore the gas age-ice age difference (Δage) is 205.1 years and we have added this value to the age of the ice (in yrs CE) to obtain the age of the air at each of our sample depths. We have assumed that Δage has remained constant throughout the record which is supported by the strong correlation between the Law Dome and WDC05A methane records. The estimated uncertainty of this timescale is ± 10 years [Mitchell *et al.*, 2011].

3. Results

3.1. Data Quality

[13] We measured samples from 109 depth intervals of the WDC05A core (Figure 2). Each depth interval was usually less than 10 cm and 3 ~ 6 replicates (4 on average) were analyzed for each depth interval. The average standard deviation of replicates from the same depth interval was 1.6 ppm. This is larger than previously obtained in our laboratory for Siple Dome and Taylor Dome ice (0.8 ppm) [Ahn *et al.*, 2009]. However, the standard error of the mean of the replicates from a 10 cm depth interval was 0.8 ppm on average, comparable to data uncertainties obtained in other laboratories for EDML ice (1.0 ppm) [Siegenthaler *et al.*, 2005] and the Law Dome ice (1.2 ppm) [Etheridge *et al.*, 1996; MacFarling Meure *et al.*, 2006].

[14] To estimate spatial homogeneity of CO₂ in WDC05A we collected 2 ~ 3 replicates from 1 ~ 3 cm ranges at certain depths, and analyzed them on the same day. Replicates from 36 depth intervals were analyzed this way, mostly duplicate measurements (76 total measurements). The pooled standard deviation for these measurements was 1.5 ppm (1 σ). We also collected samples every 3 cm from two 30-cm long ice samples (corresponding to 1.5-year time intervals) from 80 m (1935 A.D.) and 221 m (1320 A.D.). The sample to sample CO₂ variability was 0.8 and 1.3 ppm (1 σ) at 80 m and 220 m, respectively, indicating that centimeter-scale CO₂ variability along the depth direction is similar to that of horizontal direction (1 σ = 1.5 ppm).

[15] We often observed one or two bubble-free layers with ~1 mm thickness within ~10 cm ice core segments. It is not known whether the layers are refrozen melt layers or snow crusts. However, we did not detect any statistically significant enrichment associated with the bubble-free layers. We also analyzed ~1 mm-thick bubble-free layers in the Law Dome DE08 ice core at depths of ~99 and ~216 m and observed no significant CO₂ elevation associated with those layers.

3.2. General Features

[16] Our 10-year sampling resolution record from the WDC05A core shows a CO₂ range of 8 ~ 9 ppm in the pre-industrial period (Figure 2). CO₂ increased slightly between 1000 and 1100 A.D. then decreased by ~5 ppm from 1100 to 1500 A.D. with small decreases at ~1200 and ~1420 A.D. CO₂ increased by ~3 ppm at ~1500 and remained high until 1570 A.D. then rapidly decreased by ~7 ppm in the following ~20–50 years. After that, CO₂ slowly decreased with a local minimum at 1650 ~ 1750 A.D. CO₂ began to rise at

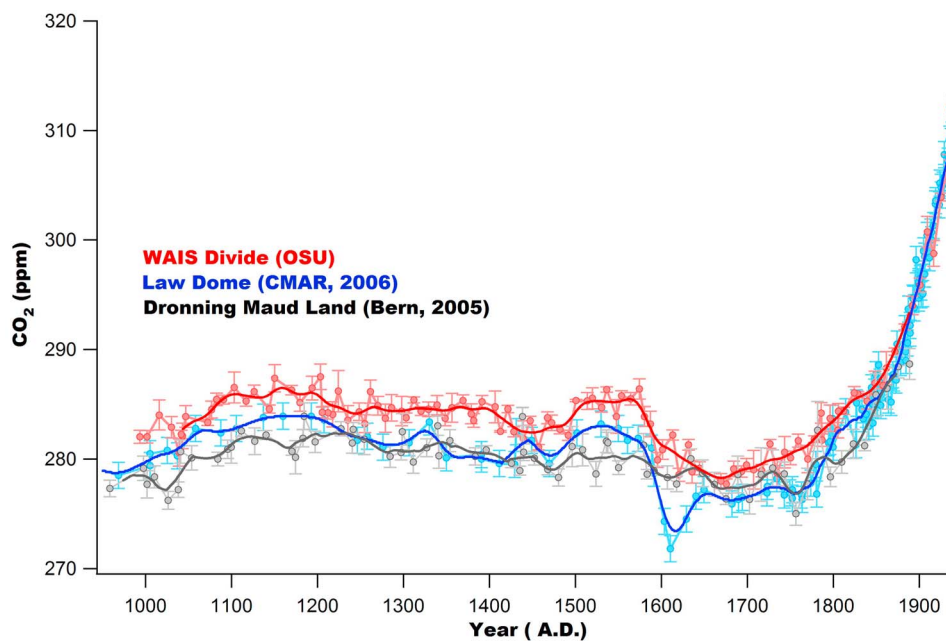


Figure 2. Atmospheric CO₂ for the last 1000 years. WAIS Divide data (red, this study) are compared with those from the Law Dome (blue) [Etheridge *et al.*, 1996; MacFarling Meure *et al.*, 2006] and EPICA Dronning Maud Land (black) [Siegenthaler *et al.*, 2005]. To facilitate comparison of CO₂ records, a Gaussian filter ($1\sigma = 10$ years) was applied to interpolated annual data sets (darker lines). OSU stands for Oregon State University and CMAR, CSIRO Marine and Atmospheric Research.

~1750 A.D., reached levels above the range of variability of the previous 850 years at ~1850 A.D., and has rapidly increased since.

[17] Our new data are compared with previously published high-resolution records from Law Dome [Etheridge *et al.*, 1996; MacFarling Meure *et al.*, 2006] and EDML ice cores [Siegenthaler *et al.*, 2005] in Figure 2. Although the three high-resolution records show differences of about 0 ~ 6 ppm (corresponding to 0 ~ 2%), they all show atmospheric CO₂ increasing until ~1150 A.D., gradually decreasing until ~1470 A.D., and continually rising since ~1750 A.D. They also clearly show that atmospheric CO₂ surpassed preindustrial levels around 1850 A.D.

[18] The offset between WAIS Divide and Law Dome ice cores seems relatively constant during the time intervals of 1100 ~ 1400 and 1680 ~ 1760 A.D., where CO₂ is stable, and an interlaboratory comparison described further below (Section 3.4) shows that the difference of 2 ~ 4 ppm is not likely due to interlaboratory differences. It is difficult to compare the two records for time periods younger than ~1800 A.D. because of the effect of small errors in chronology during times when CO₂ changes rapidly.

[19] Low resolution records from South Pole showed CO₂ levels 2–3 ppm lower than EDML records [Siegenthaler *et al.*, 1988, 2005] (not shown in Figure 2). Other low resolution records from Taylor Dome [Indermühle *et al.*, 1999], EPICA Dome C [Flückiger *et al.*, 2002], D57 and D47 [Barnola *et al.*, 1995] cores also show similar CO₂ levels of 272–287 ppm during 1000–1850 A.D. as the high-resolution records, but direct comparisons are limited by lack of accurate chronology and/or imprecise experimental methods (not shown in Figure 2).

[20] Atmospheric CO₂ records during 1000–1500 A.D. reconstructed from leaf stomata are 20 ~ 23 ppm higher on average than those from the high-resolution Antarctic ice core CO₂ records [van Hoof *et al.*, 2008]. It is difficult to compare these reconstructions with the ice core record because of the very high variability (30 ppm) and high uncertainty (6 ppm (1σ)) for those records during preindustrial times [van Hoof *et al.*, 2008].

3.3. Abrupt CO₂ Decrease in ~1600 A.D.

[21] We draw attention to the rapid decrease of CO₂ and CH₄ concentrations at ~1600 A.D. (Figures 2 and 3). The WAIS Divide CO₂ record shows a drop of ~7 ppm between 1570 and 1600 AD, then a broader decline until ~1650 AD, while the Law Dome Record shows a sharper decrease that starts slightly later in the Law Dome chronology. The midpoint of the rapid CO₂ decrease occurred between 1580 to 1590 A.D. in the WAIS Divide record. The timing of the midpoint is slightly earlier than that of Law Dome by ~5–20 years, but the difference can be explained by age uncertainty of ~10 years [Mitchell *et al.*, 2011], local variation of CO₂ in ice and imprecise estimation of the experimental uncertainty. We note a small variation of 2–3 ppm during 1600–1650 A.D. after the initial drop of ~7 ppm in the WAIS Divide ice. However, it remains unclear if the variation is really a signal of atmospheric CO₂ change or experimental uncertainty and/or local variation of ice core quality. We also note that the apparent local minimum in the Law Dome CO₂ record at ~1600 A.D. is not clearly observed in our WAIS Divide record.

[22] The difference in magnitude of the CO₂ decrease between the two records may be due to more extensive smoothing of gas records at WAIS Divide ice than Law

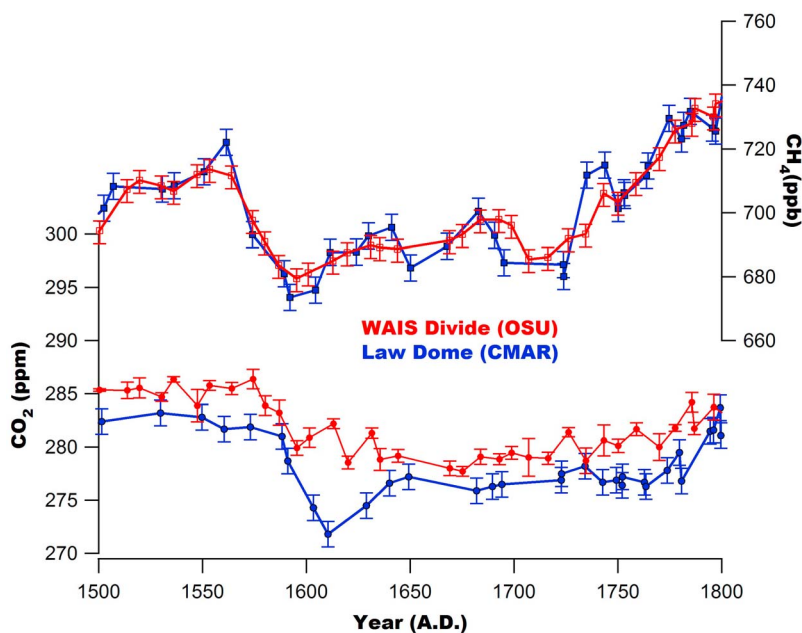


Figure 3. (bottom) Abrupt CO₂ decrease at ~1600 A.D. [MacFarling Meure *et al.*, 2006; this study] and (top) associated CH₄ change [Etheridge *et al.*, 1998; MacFarling Meure *et al.*, 2006; Mitchell *et al.*, 2011]. Red lines indicate WAIS Divide and blue lines Law Dome ice core records.

Dome, due to lower accumulation rate (Table 1). This hypothesis is supported by the apparently greater smoothing of the WAIS Divide CH₄ record relative to the Law Dome CH₄ record (Figure 3). We expect slightly more smoothing in CO₂ than in CH₄ because the diffusivity of CO₂ is smaller than that of CH₄ by factor of 1.3 [Fuller *et al.*, 1966]. In support of this idea, model results for Law Dome DE08 core show that CO₂ has a wider age distribution than that of CH₄ by ~17% (C. Trudinger, personal communication, 2010).

[23] To estimate potential smoothing of the CO₂ records, we created a synthetic CO₂ time series that is similar but has a larger CO₂ decrease than the Law Dome CO₂ records at ~1600 A.D., then smoothed the record to produce a similar CO₂ decrease as the Law Dome records (Figure 4). We then smoothed the same synthetic atmospheric history with a smoothing function based on conditions at the WAIS Divide site, and alternate functions that produce more smoothing (Figure 4). Smoothing functions used were age distributions for the closed porosity of the ice derived from the Oregon State University firm air model (see Buizert *et al.* [2011] for model description). Like most of the models in Buizert *et al.* [2011], our model differs from previous firm air models in that we include eddy diffusion in the lock-in zone. Increasing diffusivity in the lock-in zone (LIZ) fits the WAIS Divide firm air data [Battle *et al.*, 2011] as well or better than in model runs with a non-diffusive LIZ, making it impossible to rule out the presence of such a mixing mechanism at this site. We find that allowing eddy diffusivity in the LIZ does not significantly increase the gas age distribution at Law Dome because of the high snow accumulation rate, but it doubles the width of the age distribution at the WDC05A site from ~10 years (in excellent agreement with Battle *et al.* [2011]) to ~19 years. However, this is still not enough smoothing to explain the different CO₂ records across the 1600 AD decrease.

[24] To explore how much smoothing is necessary at WAIS Divide for both records to derive from our synthetic CO₂ time series, 3 synthetic age distributions were generated by varying the surface temperature input to the Herron and Langway firm density model [Herron and Langway, 1980], then employing that density profile in the OSU firm air model. This is somewhat arbitrary, but produces glaciologically reasonable age distributions. These distributions had full widths at half maximum (FWHM) of 30, 50, and 70 years. Smoothing the synthetic CO₂ record with these distributions reveals that a FWHM of greater than 30 years appears to produce an equivalent CO₂ decrease as observed in the WDC05A core (Figure 4). Estimates of the accumulation rate and temperature for this time are very similar to today, with differences in the diffusive column height as inferred from noble gas isotopes of up to 5 m (A. Orsi, personal communication, 2011). This results in a maximum modeled FWHM of ~24 years, somewhat closer to our synthetic smoothing with a FWHM of 30 years. However, it is important to note that exact curve fitting is not possible due to the under-constrained problem of tuning diffusivity for past firm density profiles, CO₂ data resolution and precision, and uncertainties in the mechanisms that influence mixing in the LIZ. Accurate and quantitative estimation for the gas age distribution in the WDC05A core at 1600 AD is beyond the scope of this paper.

[25] In summary, our WAIS Divide CO₂ records indicate that CO₂ probably experienced additional smoothing through processes that were not included in previous conventional models [e.g., Battle *et al.*, 2011], such as diffusivity in the lock-in zone. However, the nature of diffusion in the LIZ is not well understood, and thus cannot be used to precisely quantify the age distribution of the core in the past. With what we currently know about WAIS Divide, we cannot adequately explain the different magnitudes of CO₂ decrease

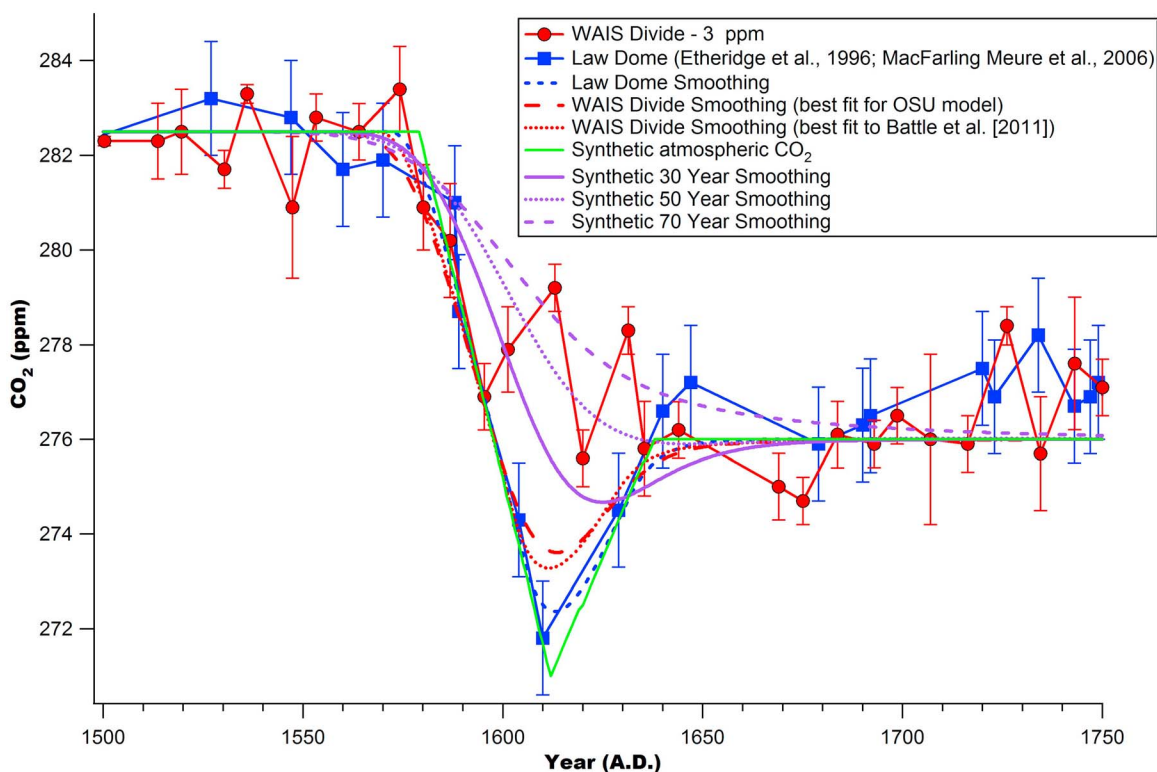


Figure 4. Smoothing an imaginary atmospheric CO₂ time series (green line). The synthetic atmospheric CO₂ time series has slightly larger decrease of CO₂ than Law Dome records at ~1600 A.D. To better compare magnitude of CO₂ decrease at ~1600 A.D., we subtracted 3 ppm of CO₂ concentration from WAIS Divide core record (blue line) and compared with three synthetic smoothing curves (purple lines).

at 1600 AD between the WAIS Divide and Law Dome cores. In addition, the local minimum in the Law Dome CO₂ records at ~1600 A.D. is not clearly confirmed by WAIS Divide records. Smoothing by diffusion through the ice matrix after bubble close-off should be negligible for the shallow Law Dome and WAIS Divide cores, as shown in a previous study with the Siple Dome ice core [Ahn *et al.*, 2008].

3.4. Interlaboratory Comparison

[26] We found that our WAIS Divide CO₂ data are mostly higher than those from Law Dome and EDML ice cores by 2 ~ 4 ppm on average during preindustrial times. Although the difference of ~1–2% is small, it is significant for studies on decadal to centennial timescales. In order to determine whether the offset between WAIS Divide and Law Dome records is due to real variability in ice cores or an analytical offset, we conducted an inter-laboratory calibration with CMAR (CSIRO Marine and Atmospheric Research), Aspendale, Australia.

[27] We analyzed Law Dome ice, which was previously analyzed at CMAR [Etheridge *et al.*, 1996; MacFarling Meure *et al.*, 2006] at OSU. Twenty-seven samples from two depth intervals were analyzed (Figure 5 and Table 2). At 215 ~ 216 m (~1855 A.D.) our results agree with the results from CMAR within analytical uncertainty, but at 98 ~ 99 m (~1959 A.D.) our results of 321.8 ± 2.8 (1σ) ppm ($n = 10$, two data were rejected because those were higher than the average of the others by more than 3σ) are higher than those

from CMAR by 4.9 ± 1.2 ppm, which is greater than the analytical uncertainty of ~1 ppm (Table 2).

[28] For additional comparison, we split five 18 cm-long WDC05-A ice samples so that each pair of samples shared the same depth interval, and OSU and CMAR analyzed ice from the same depth. Three of the five pairs at CMAR were lost due to power outage at CMAR, but the last 2 pairs were compared (Table 2). The results from both laboratories agree well within analytical uncertainties.

[29] In summary, we conclude that the difference of 2 ~ 4 ppm for the last 1000 years between Law Dome and WDC05A is unlikely due to laboratory offsets, but represent a real difference in the ice.

[30] The cause of the higher difference between OSU and CMAR measurements for the Law Dome ice at 98–99 m is not fully understood. However, we suspect trapping of modern air after coring of the shallow Law Dome ice like as Aydin *et al.* [2010] observed at the shallow WAIS Divide core. Longer storage and greater surface to volume ratio of the analyzed samples at OSU might have increased the alteration.

4. Discussion

4.1. Mechanisms for Preindustrial CO₂ Variations

[31] To gain a better understanding of the carbon cycle we first examine the relationship between preindustrial atmospheric CO₂ and climate records (Figure 6). The relationship

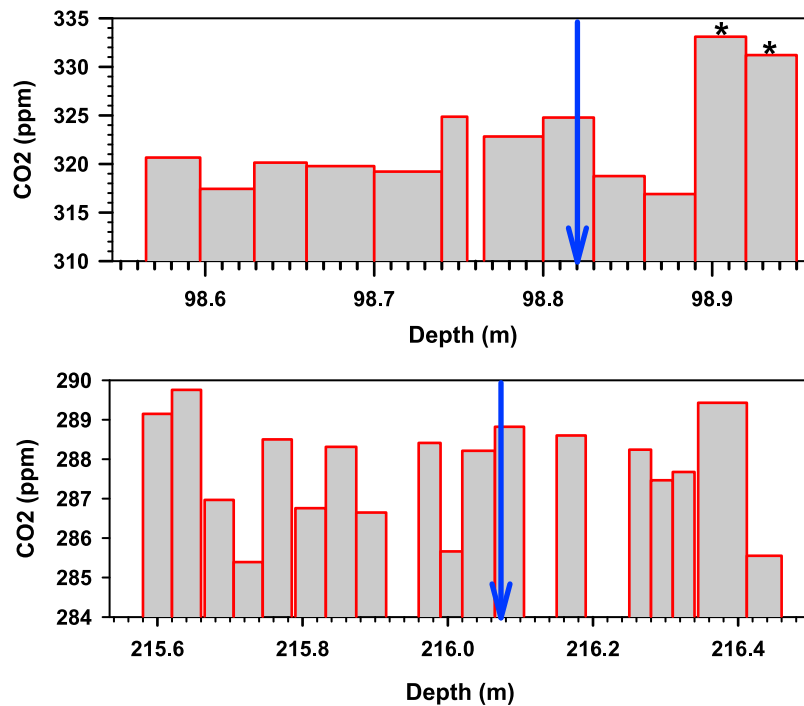


Figure 5. Analysis of Law Dome DE08 core at Oregon State University. Vertical arrows indicate depths where ~ 1 mm thick bubble-free layers locate. Asterisk represents a data point rejected. The experimental error of individual ice samples is ~ 1 ppm.

between CO₂ and average temperatures has been widely discussed and is important given the anthropogenic perturbation to atmospheric CO₂ levels. First we compared the WAIS CO₂ record with surface temperature change in the northern hemisphere (NH). Although a global temperature reconstruction would be preferable, most of the paleoclimate proxy records used for temperature reconstructions come from the NH global reconstructions are not as accurate. We chose published composite data that cover a wide spatial area. In most cases we found a statistically significant ($p < 0.01$) correlation between our CO₂ record and hemispheric temperature reconstructions that have been low-pass filtered (period = 20 years) and subsampled to the temporal spacing of CO₂ samples for the time period of 1000 \sim 1800 A.D., including northern hemisphere (NH) EIV (error-in-variables) temperature [Mann *et al.*, 2008] ($r = 0.50$), NH CPS (composite plus scale) temperature [Mann *et al.*, 2008] ($r = 0.30$), NH temperature [Hegerl *et al.*, 2007] ($r = 0.39$), and NH temperature [Moberg *et al.*, 2005] ($r = 0.42$).

Although, we did not obtain a significant correlation ($r = 0.08$, $p = 0.45$) with the extratropical NH temperature reconstruction from tree ring records [Esper *et al.*, 2002], we see rapid drops of temperature contemporaneous with rapid CO₂ decreases around 1200 and 1600 A.D. (Figure 5). Our findings with respect to NH temperature are consistent with a comparison of CO₂ variations with global temperature change [Frank *et al.*, 2010]. However, the composite data for a global change should be cautiously interpreted due to geographical data density differences. To further investigate correlations with temperature, we utilize a reconstruction of Indo-Pacific Warm Pool (IPWP) sea surface temperature (SST) because the IPWP is the largest warm water reservoir and closely linked to global average surface temperature [Oppo *et al.*, 2009]. We obtained a high correlation coefficient of 0.66 ($p = 1.4 \times 10^{-12}$) between WAIS Divide CO₂ record and IPWP SST [Oppo *et al.*, 2009] (Figure 6).

Table 2. Interlaboratory Comparison Between Oregon State University (OSU) and CMAR (CSIRO Marine and Atmospheric Research, Australia)

| Core Name | OSU | | | | CMAR | | | | OSU-CMAR | |
|----------------------|-----------------|------------------------------------|------------|--------------------------------|-----------|------------------------------------|------------|--------------------------------|---|--------------------------------|
| | Depth (m) | CO ₂ ^a (ppm) | Subsamples | Uncertainty ^b (ppm) | Depth (m) | CO ₂ ^a (ppm) | Subsamples | Uncertainty ^b (ppm) | Δ CO ₂ ^a (ppm) | Uncertainty ^b (ppm) |
| DE08 (Law Dome) | 98.565–98.950 | 321.8 ^c | 10 | 0.9 | 98–99 | 317.6 | 2 | 0.8 | 4.9 | 1.2 |
| DE08 (Law Dome) | 215.58–216.46 | 288.8 | 15 | 0.3 | 215–216 | 288.4 | 2 | 0.8 | 0.4 | 0.9 |
| WDC05A (WAIS Divide) | 182.252–182.395 | 283.9 | 6 | 0.7 | 182.29 | 284.9 | 1 | 1.2 | –1.0 | 1.4 |
| WDC05A (WAIS Divide) | 275.095–275.275 | 286.9 | 4 | 0.4 | 275.18 | 286.8 | 1 | 1.2 | 0.1 | 1.3 |

^aAll CO₂ data are not corrected for gravitational fractionation. Both OSU and CMAR used WMOX2007 scale for CO₂ analysis.

^bStandard error of the mean (standard deviation divided by square root of the number of subsamples).

^cWe rejected 2 data out of 12 (see Figure 5).

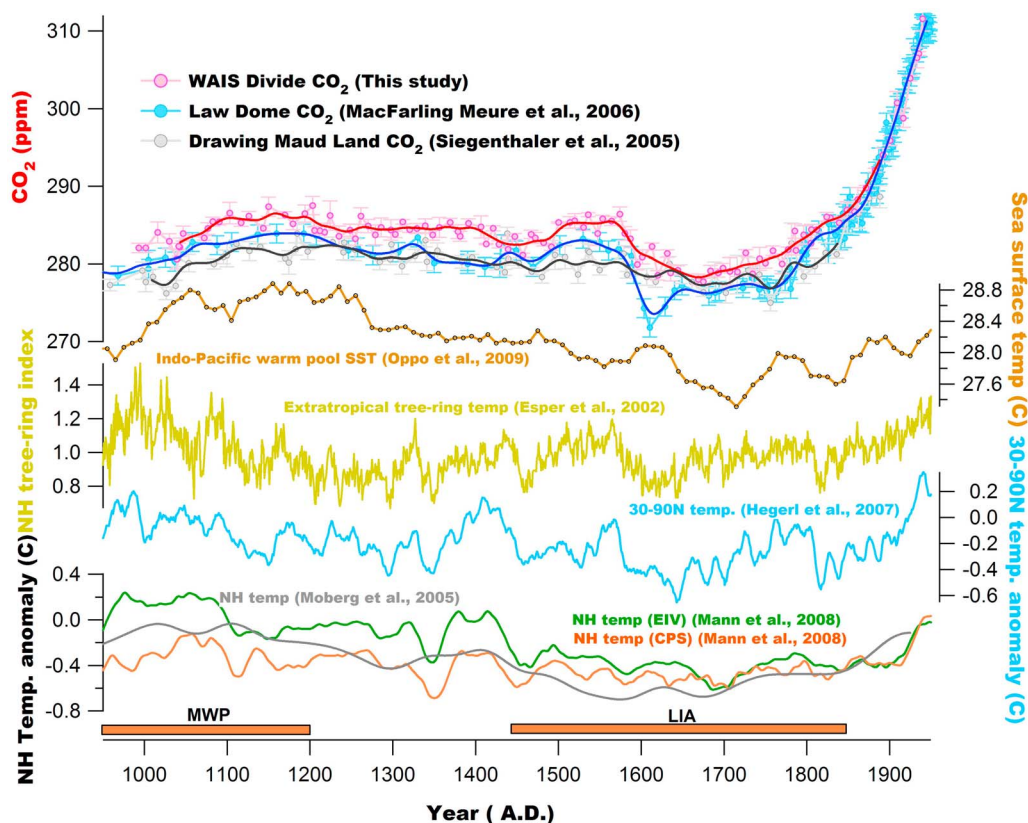


Figure 6. (top) Atmospheric CO₂ and (middle and bottom) climate proxies for the last 1000 years. WAIS Divide data (red) are compared with those from the Law Dome (blue) and EPICA Dronning Maud Land (black). To facilitate comparison of temperature and CO₂ records, a Gaussian filter ($1\sigma = 10$ years) was applied to interpolated annual data sets (darker lines).

[32] In general, the higher levels of CO₂ in the 1100 ~ 1200 A.D. period and lower levels in 1600 ~ 1800 A.D. that drive these correlations occurred during the Medieval Warming Period (MWP) and the Little Ice Age (LIA), respectively (Figure 6). The MWP is a warming event that occurred during 900–1250 A.D. [Grove and Switsur, 1994] and the LIA a cooling event during 1400–1900 A.D. [Bradley and Jones, 1993] in the northern hemisphere. Although often described as northern hemisphere phenomena, recent studies show that these events may have had wider influence [e.g., Mosley-Thompson, 1992; Oppo et al., 2009; Bertler et al., 2011]. The terrestrial biosphere and ocean may have played source or sink roles for atmospheric CO₂ at these times. It has been suggested that reduced soil respiration during the LIA decreased atmospheric CO₂ [MacFarling Meure et al., 2006; Trudinger et al., 1999, 2002b]. Model simulations have shown that global warming could change the terrestrial carbon balance (especially soil respiration) and can increase atmospheric CO₂ by 12 ppm/°C in the NH [Gerber et al., 2003]. Using this ratio, a CO₂ decrease of ~7 ppm from MWP to LIA corresponds to ~0.7°C cooling in the NH. This estimate appears to be similar or slightly greater than those from the NH temperature proxy data of 0.4–0.7°C [Esper et al., 2002; Moberg et al., 2005; Mann et al., 2008].

[33] Another climate-related mechanism that controls atmospheric CO₂ is solubility in the seawater. With $(dpCO_2/dT)/pCO_2 = 4.23\%/^{\circ}C$ in the ocean [Takahashi et al., 1993], we estimate that a 7 ppm CO₂ change from 1100 to 1750 A.D. can occur by a SST change of 0.6°C. This estimated SST change is comparable to the reconstructed SST change in the Indo-Pacific Warm Pool (IPWP) [Oppo et al., 2009] although we cannot accurately date and estimate global SST change yet.

[34] The two mechanisms above may be constrained with atmospheric $\delta^{13}C$ of CO₂ records because an oceanic source or sink is relatively in equilibrium with atmospheric $\delta^{13}C$ (−6.5‰ for the preindustrial), but the terrestrial biosphere has a depleted $\delta^{13}C$ of ~−25‰ [Trudinger et al., 2002b]. Sparse $\delta^{13}C$ records from Law Dome ice core show 0.1 ~ 0.15‰ increase from 1100 to 1760 A.D. [Francey et al., 1999], which is inconsistent with the estimated decrease of 0.06 ~ 0.11 ‰ by SST cooling of 0.5 ~ 1.0°C [Zhang et al., 1995]. By contrast, the increase in $\delta^{13}C$ support the idea that CO₂ has decreased by reduced soil respiration, which is a source of $\delta^{13}C$ -depleted CO₂ to the atmosphere [MacFarling Meure et al., 2006; Trudinger et al., 1999, 2002b].

[35] Other plausible natural mechanisms may include changes in carbonate chemistry in the ocean via changes in biological pump and mixing between deep and shallow seawater [Takahashi et al., 1993; Sarmiento et al., 1998].

However, the history of these variations is poorly constrained on this time scale.

[36] Preindustrial anthropogenic perturbation to the carbon cycle has been proposed as a possible explanation for late Holocene atmospheric CO₂ variability [Ruddiman, 2003, 2007]. According to this hypothesis, pandemic diseases caused a rapid reduction in population and widespread abandonment of farms which allowed rapid reforestation that sequestered atmospheric CO₂ [Ruddiman, 2003, 2007]. The rapid CO₂ decrease in ~1600 A.D. coincides with a pandemic among North American populations as a result of diseases introduced by Europeans. However, a modeling study does not support the idea and shows that the sequestration was not enough to decrease atmospheric CO₂ [Pongratz et al., 2009]; although the model methods were not accepted by Ruddiman and Ellis [2009].

4.2. Potential Mechanisms for CO₂ Difference Between WAIS Divide and Law Dome Ice Cores

[37] In order to further explore the offset between the WAIS Divide and Law Dome records, we examined aerosol data to look for patterns in chemical species that might influence the CO₂ concentration.

[38] Both physical and chemical mechanisms could cause elevated CO₂ concentrations. Chemical processes include (1) reaction of carbonate dust with acid [Delmas, 1993; Anklin et al., 1995; Barnola et al., 1995; Anklin et al., 1997; Smith et al., 1997a], and (2) oxidation of organic compounds [Tschumi and Stauffer, 2000; Campen et al., 2003].

[39] Acid-carbonate reactions were suggested to explain elevated Greenland ice core CO₂ records [Delmas, 1993; Barnola et al., 1995; Anklin et al., 1995; Smith et al., 1997a, 1997b]. Neftel et al. [1988] suggested that the most likely mechanism is the chemical reaction between CaCO₃ and H⁺ (CaCO₃ + 2H⁺ → Ca²⁺ + CO₂ + H₂O), which can occur only when the ice is sufficiently acidic to drive decarbonation, and some CaCO₃ remains in the ice after bubble formation [Smith et al., 1997a]. To investigate this possibility we examined the non-sea-salt Ca (nssCa) record. nssCa may be transported as a dissolved form or produced by the acid-carbonate reaction. Previous ICPMS measurements of shallow (~100 m) cores show that >90% of the Ca at WAIS Divide is from sea salt and >96% at Law Dome. Using measurements of total Ca content from top 70 m of WAIS Divide core and 700 m of Law Dome core [Souney et al., 2002], we estimated nssCa of 0.12 and 0.14 ng/g for WAIS Divide and Law Dome cores, respectively, corresponding to CO₂ production of 0.69 and 0.76 ppm, respectively. The potential production values are upper limits of the estimates because part of nssCa might have been transported as a dissolved form, and not produced in ice after deposition at the coring site. Thus, the carbonate and acid reaction is unlikely to be the main cause of the difference between WAIS Divide and Law Dome CO₂ records.

[40] Oxidation of organic compounds could occur biologically [Campen et al., 2003] or abiologically [Tschumi and Stauffer, 2000] occur in ice. Data for organic compounds in the WAIS Divide and Law Dome cores are not available although preliminary measurements of dissolved organic carbon in Antarctic and Greenland ice cores indicate that concentrations of organic compounds typically are an order of magnitude lower in Antarctica than in Greenland

(J. McConnell, personal communication, 2011). Hydrogen peroxide (H₂O₂) is one of the important oxidants of organic compounds in ice. Measurements spanning the past 250 years in multiple WAIS Divide ice cores including WDC-05A show H₂O₂ concentrations of 34 ± 13 (1 σ) ppb [Lamarque et al., 2011]. While this H₂O₂ concentration is higher than that reported for the Byrd ice core [Neftel et al., 1983], concentrations at WAIS Divide are very comparable to those recently measured in Law Dome cores (J. McConnell, personal communication, 2011). Organic compounds may exist as various chemical species such as HCHO, CH₃COO⁻ and HCOO²⁻ [Tschumi and Stauffer, 2000], but no data for the concentrations of these compounds are available in the WAIS Divide and Law Dome ice cores.

[41] Physical processes for CO₂ elevation in ice cores include (1) snowmelting [Neftel et al., 1983; Stauffer et al., 1985] and may also include (2) fractionation during storage due to gas diffusion [Stauffer, 2006].

[42] CO₂ can be considerably elevated in snowmelt due to the high solubility of CO₂ gas in water. If the melt freezes in the coring sites, dissolved gas may be captured in small bubbles and may increase CO₂ mixing ratio in ice cores [Neftel et al., 1983; Ahn et al., 2008]. For example, at Dye 3, Greenland, the melt layers showed a mean CO₂ concentration of 1500 ppm [Stauffer et al., 1985]. In order to produce 3 ppm of excess CO₂, only 0.08% by volume of refrozen melt in the ice is required. However, samples measured in WAIS Divide core do not include any visible melt layers and the modern surface temperature at WAIS Divide is lower than at Law Dome (-31 versus -22°C). Thus it is unlikely that partial melting is the major factor that affects the difference in CO₂ records.

[43] Increase of CO₂ mixing ratio in the air bubbles during ice core storage is not fully understood due to lack of understanding nature of the gas diffusion [Ahn et al., 2008]. However, a computational approach showed the effect was negligible [Bereiter et al., 2009].

[44] In summary, the cause of the offset in CO₂ records between WAIS Divide and Law Dome remains elusive. Further study should include more extensive interlaboratory comparison for the Law Dome and WAIS Divide ice cores. $\delta^{13}\text{C}_{\text{CO}_2}$ analysis may help because atmospheric $\delta^{13}\text{C}_{\text{CO}_2}$ ($(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard(VPDB)}} - 1) \times 1000\text{‰}$) has a characteristic preindustrial value of $\delta^{13}\text{C}_{\text{CO}_2}$, approximately -6.5‰, compared to natural organic acids (about -25‰) and CaCO₃ (0 ~ +4‰). Thus, $\delta^{13}\text{C}_{\text{CO}_2}$ analysis may be used to examine the potential in situ production of CO₂.

5. Conclusions

[45] We provide a record of atmospheric CO₂ at 10-year sampling resolution for the last 1000 years with a newly drilled WAIS Divide ice core. Our results for the preindustrial period show CO₂ variability of 8 ~ 9 ppm. CO₂ decreased by ~5 ppm during 1100–1500 A.D., slightly increased by ~3 ppm during 1500–1570 A.D. and then decreased by ~9 ppm until ~1670 A.D. The most prominent feature of the entire pre-industrial portion of the record is a rapid decrease of ~7 ppm in ~20–50 years at ~1600 A.D. Our results support the timing of the abrupt atmospheric CO₂ decrease of ~10 ppm observed for that time period in

Law Dome records although the difference in magnitude cannot be clearly resolved. We observe that elevated CO₂ levels occurred during the Medieval Warm Period and lower levels during the Little Ice Age, implying a multicentennial link between climate and carbon cycles although the exact relationship is not clearly defined due to uneven geographical data of paleoclimate records, and the limited lengths of high-resolution CO₂ records. There are 0 ~ 6 ppm CO₂ differences (0 ~ 2%) among high-resolution records from Law Dome, EDML and WAIS Divide ice cores, but those records share centennial to multicentennial CO₂ trend.

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