Atmospheric CO_2 and climate from 65 to 30 ka B.P.

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[1]   Using new and existing ice core CO_2 data from $65 \sim 30$ ka a new chronology for CO_2 is established and synchronized with Greenland ice core records to study how high latitude climate change and the carbon cycle were linked during the last glacial period. Atmospheric CO_2 rose several thousand years before abrupt warming in Greenland associated with Dansgaard-Oeschger events, 8, 12, 14, 17, four large warm events that follow Heinrich events. The CO_2 rise terminated at the onset of Greenland warming for each of these events. Atmospheric CO_2 is strongly correlated with the Antarctic isotopic temperature proxy with an average time lag of 720 ± 370 yr (mean $\pm 1\sigma$) during the time interval studied. The new data and chronology should provide a better target for models attempting to explain CO_2 variability and abrupt climate change. **Citation:** Ahn, J., and E. J. Brook (2007), Atmospheric CO_2 and climate from 65 to 30 ka B.P., *Geophys. Res. Lett.*, *34*, L10703, doi:10.1029/2007GL029551.

1.   Introduction

[2]   Deciphering relationships between past atmospheric CO_2 variations and climate is important for understanding how climate change and the carbon cycle are linked. Prominent millennial scale climate changes during the last glacial period are now well known. Greenland ice cores show numerous abrupt warming events that are followed by gradual and then rapid cooling, known as Dansgaard-Oeschger (D-O) events (Figure 1a) [*Dansgaard et al.*, 1993; *Grootes et al.*, 1993]. Atmospheric CH_4 records from both Greenland and Antarctic ice cores show a very similar pattern (Figure 1d) [*Blunier and Brook*, 2001]. Recent studies show that the CH_4 variations are essentially synchronous with the abrupt warming of D-O events within a few decades during the time period covered by our data and for all other intervals where the relationship has been examined in detail [*Grachev and Severinghaus*, 2005; *Huber et al.*, 2006; *Landais et al.*, 2004; *Severinghaus et al.*, 1998; *Severinghaus and Brook*, 1999; *Severinghaus et al.*, 2003].

[3]   D-O events are believed to occur in groups [*Bond et al.*, 1993] separated by cold periods during which massive ice rafting events (Heinrich Events) occurred in the North Atlantic (blue vertical bars in Figure 1) [*Heinrich*, 1988; *Rashid et al.*, 2003; *Sarnthein et al.*, 2001]. Within each group, or Bond Cycle the first D-O event has the longest duration, and the amplitudes of the D-O events gradually decrease. There is evidence that D-O events reach beyond Greenland, to tropical and subtropical regions [*Broecker*

and Hemming, 2001]. In contrast to the abrupt climate changes in the northern hemisphere, in Antarctica gradual warming started 1 to 3 ka before the largest and longest D-O events, and ended when Greenland abruptly warmed (Figure 1b) [*Blunier and Brook*, 2001].

[4]   How atmospheric CO_2 varied during D-O and Heinrich events is an important question for understanding how the carbon cycle and climate change are linked. In order to answer to this question, we need common time scales for climate proxies and atmospheric CO_2 [*Stauffer et al.*, 1998]. Reliable CO_2 records come from Antarctic ice cores, but not from Greenland because Greenland ice has high levels of dust that alter the CO_2 content of the ice by the carbonate-acid reaction [*Delmas*, 1993; *Anklin et al.*, 1995; *Barnola et al.*, 1995; *Anklin et al.*, 1997; *Smith et al.*, 1997a; *Smith et al.*, 1997b] and oxidation of organic compounds [*Tschumi and Stauffer*, 2000]. Previous studies of the $17-47$ ka section of the Antarctic Byrd ice core showed that atmospheric CO_2 appeared to rise at about the same time as Heinrich events H4-H5 [*Stauffer et al.*, 1998] although the precision of these previous CO_2 data was not sufficient for precise comparison with Greenland ice core records (Figure 1c). High-quality CO_2 records from the Taylor Dome ice core show atmospheric CO_2 variation of ~ 20 ppm during the period from ~ 60 to 20 ka. However, the relative timing of the CO_2 variations from Taylor Dome and Greenland temperature is not well constrained [*Indermühle et al.*, 2000].

[5]   Here we provide atmospheric CO_2 records from ~ 65 to 30 ka B.P. (thousand years before 1950) on a chronology synchronized with Greenland ice core records, allowing direct comparison of CO_2 with Greenlandic [*Grootes et al.*, 1993] and Antarctic [*Johnsen et al.*, 1972] temperature proxies, Heinrich events [*Rashid et al.*, 2003; *Sarnthein et al.*, 2001] and atmospheric CH_4 [*Blunier and Brook*, 2001]. Our new data were obtained from the Byrd (Antarctica) ice core using a new dry extraction/analytical system (see methods section), with a mean 1σ (standard error) for replicate (n = 2 to 4) analysis of 1.6 ppm (total 86 samples from 34 different depths). This error is larger than we obtain for high quality late Holocene ice samples from the Taylor Dome (Antarctica) (± 0.9 ppm). This is presumably due to variable ice quality for Byrd (collected in 1968) but the value of the new data lies in the widely accepted chronology based on correlating methane variations with those in Greenland ice cores [*Blunier and Brook*, 2001].

2.   Methods

[6]   Ice samples from Byrd were stored and carefully cut with a band saw in a freezer at $-25°C$. The sample size is ~ 13 g after trimming ~ 1 cm from all surfaces.

[7]   The detailed gas extraction and gas chromatographic methods used will be reported elsewhere. Briefly, the

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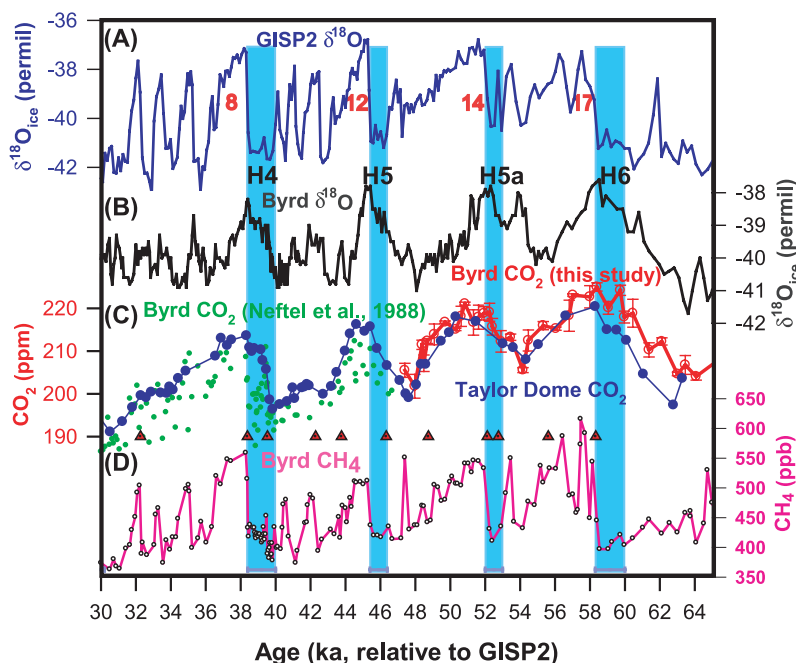[1]Department of Geosciences, Oregon State University, Corvallis, Oregon, USA.

Figure 1. (a) $\delta^{18}O_{ice}$ from Greenland Ice Core Project 2 [*Grootes et al.*, 1993], as a proxy of a surface temperature. Red numbers, Dansgaard-Oeschger events. (b) $\delta^{18}O_{ice}$ from Byrd station and Antarctic warm events A1 to A4 [*Blunier and Brook*, 2001]. (c) Atmospheric CO$_2$. Green circles are existing data from Byrd [*Neftel et al.*, 1988]; red circles connected by a line are new data from Byrd measured at Oregon State University; blue dots are data from Taylor Dome [*Indermühle et al.*, 2000] on newly constructed GISP2-based age scale in this study. Red triangles are control points for the synchronization of gas ages between Byrd and Taylor Dome records (Table 1). (d) CH$_4$ from Byrd ice core [*Blunier and Brook*, 2001]. Ages from *Blunier and Brook* [2001] are adjusted so that abrupt increase of CH$_4$ and Greenland temperature are synchronized (see method section). Blue shaded bars represent Heinrich events [*Sarnthein et al.*, 2001; *Rashid et al.*, 2003]. Data are available at http://www.ncdc.noaa.gov/paleo/icecore.html. The origin of the discrepancy between Byrd and Taylor Dome CO$_2$ records older than 58 ka is not clear, but may in part be due to poor age control in that time interval.

crushing chamber is a double-walled stainless steel vacuum chamber kept at $-35°C$ using cold ethanol. The chamber is flushed with ultrapure N$_2$ gas while loading ice samples. After pumping for ~15 minutes using a clean pumping system, sample were crushed with a stainless steel plate containing 91 steel pins, affixed to a pneumatically actuated bellows-based linear motion feedthrough. Air liberated from the ice is dried at $-85°C$ and trapped in 6.35 mm o.d. stainless steel sample tubes at $-262°C$.

[8] The CO$_2$ mixing ratio was measured with an Agilent 6890N Gas Chromatograph (GC) with flame ionization detector, with nickel catalyst conversion of CO$_2$ to CH$_4$ prior to measurement. Sample air was inlet to an evacuated 5 cm^3 stainless steel sample loop and the pressure in the loop was measured with an MKS Baratron capacitance manometer (accuracy better than 0.015%). Daily calibration curves used several measurements of standard air (197.54 ppm CO$_2$, WMO scale). Reproducibility of standards averaged 0.22 ppm (1σ). Each air sample was measured two times. Correction for instrumental drift was made by measuring three or four standard airs every six sample runs. The linearity of the GC was tested by analyzing a second air standard with CO$_2$ mixing ratio of 291.15 ppm. The difference between measured and assigned values was ~0.2 ppm on average over 7 days. Daily corrections for the dry extraction and GC analysis were done using two identical

standard airs (197.54 ppm) that were introduced over the crushed ice and transported to sample tubes mimicking the procedure of the air samples from ice. From these measurements, we estimate a total analytical uncertainty for an individual sample of 0.8 ppm (1σ) during the measurement period.

[9] We adjusted the ages of abrupt methane shifts in the Byrd ice core record [*Blunier and Brook*, 2001] so that they are consistent with the synchroneity of CH$_4$ relative to abrupt warming at D-O events 8, 12, 14, 17 [*Severinghaus et al.*, 2003; *Huber et al.*, 2006]. This was necessary due to errors in the original GISP2 gas age scale resulting from uncertainties in modeling gas age – ice age differences. The new ages are younger than the old ages by 70 ~ 570 yr and the age differences among tie points were linearly interpolated. Byrd ice age was calculated from the resulting Byrd gas age scale by employing the ice age – gas age difference from the original chronology [*Blunier and Brook*, 2001].

[10] By comparing CO$_2$ and CH$_4$ data from the Byrd and the Taylor Dome ice cores, we established a new Taylor Dome gas age scale, which is synchronized with both the Byrd ice core and Greenland Ice Core Project 2 (GISP2) ages as shown in Figure 1c. For Byrd CO$_2$, we used both our new data and previous results [*Neftel et al.*, 1988]. Correlation using CH$_4$ from Taylor Dome utilized methane

Table 1. Depths and Corresponding GISP2 Ages for Control Points in Taylor Dome CO$_2$ Chronology

Taylor Dome Depth, m	GISP2 Age, ka	Gas Type Used
391.6	32.3	CH$_4$
411.5	38.4	CH$_4$
418.6	39.5	CO$_2$
433.5	42.3	CH$_4$
437.7	43.8	CO$_2$
444.1	46.3	CO$_2$
451.3	48.7	CO$_2$
456.1	52.1	CH$_4$
456.3	52.8	CO$_2$
460.7	55.6	CO$_2$
464.1	58.3	CH$_4$

data from *Brook et al.* [2000]. The tie points are listed in Table 1.

3. Results

[11] Our new data cover Antarctic warming events A3 and A4, using many of the same samples previously measured for methane [*Blunier and Brook*, 2001]. Comparison with previous Byrd and Taylor Dome CO$_2$ measurements [*Neftel et al.*, 1988; *Indermühle et al.*, 2000] and CH$_4$ [*Blunier and Brook*, 2001] on the new common time scale (Figure 1), reveals two important characteristics of CO$_2$ variability. First the maximum CO$_2$ level for each of the four A-events was reached at the onset of the associated abrupt CH$_4$ increase. As noted above, the abrupt CH$_4$ increase is synchronous with abrupt warming in Greenland within a few decades during the time period covered by our data [*Huber et al.*, 2006; *Severinghaus et al.*, 2003]. This allows us to use CH$_4$ in Antarctic ice cores as a marker of abrupt temperature change in Greenland, circumventing the uncertainties associated with gas age-ice age differences. Our data indicate that the onset of the CO$_2$ rise for each A-event predates those D-O events by 1.5, 2.5, 2.0 and 5.8 ka, respectively, and the H-events by 0 ∼ 3 ka, although the exact timing relative to H-events is uncertain due to uncertainties in marine-vs. ice core chronologies. Furthermore, atmospheric CO$_2$ began to decrease when Greenland abruptly warmed at D-O events 8, 12, 14, and 17, the long events that follow Heinrich events 4, 5, 5a and 6, respectively. Our results confirm previous results around D-O events 8 and 12 [*Stauffer et al.*, 1998] with better precision and age control, and reveal a similar pattern of variability associated with D-O events 14 and 17.

[12] Second, atmospheric CO$_2$ varies together with the Byrd δ^{18}O$_{ice}$ temperature proxy, but with a time lag of CO$_2$ vs. Byrd δ^{18}O$_{ice}$ (Figures 1b and 1c). To compare the phasing of CO$_2$ and surface temperature from Byrd we interpolated the CO$_2$ [*Neftel et al.*, 1988; this study] and δ^{18}O$_{ice}$ [*Johnsen et al.*, 1972] data from Byrd on a 10-year spacing and determined the time lag providing maximum correlation. We used a Monte Carlo method to estimate uncertainty, producing 3000 versions of the CO$_2$ record, assuming analytical error is normally distributed. To obtain the final uncertainty in the time lag we incorporated a conservative uncertainty in Δage (ice age − gas age) of 25%. Using the lagged correlation analysis we find a lag of 720 ± 370 yr (mean ± 1σ) between 65 and 30 ka. Previous work suggested a similar CO$_2$ lag, but with larger uncer-

tainty [*Indermühle et al.*, 2000]. It is important to note that the time lag is a mean value during the studied interval and does not characterize all specific time intervals. For example, maxima in CO$_2$ concentration appear synchronous with maxima in the Atlantic temperature proxy but CO$_2$ decreased very slowly during the following 1 ∼ 2 kyr, while δ^{18}O$_{ice}$ decreased from its maximum levels. Because CO$_2$ does not lead temperature, CO$_2$ variations were not a direct trigger for the climate changes during the last glacial period.

[13] Our new age scale for atmospheric CO$_2$ variations during the last glacial period is provided for both the Byrd and Taylor Dome records (Figure 1c and Table 1). It provides a target for models of CO$_2$ variability with respect to abrupt climate change, previously hampered by uncertainty in the Taylor Dome age scale. Qualitatively, our results support the idea that atmospheric CO$_2$ is controlled by physical processes that control Antarctic or Southern Ocean and surface air temperatures, but with a link to abrupt change in the high latitude northern hemisphere [e.g., *Stocker and Marchal*, 2000; A. Schmittner et al., preprint, 2007]. The synchronous maxima of Antarctic temperature and atmospheric CO$_2$ associated with the large and long abrupt warming events in Greenland following Heinrich events imply a global mechanism that can simultaneously affect atmospheric CO$_2$ and temperature in both hemispheres. Important processes may include changes in CO$_2$ outgassing from the Southern Ocean due to variations in sea ice cover [*Stephens and Keeling*, 2000], changes of the position of midlatitude westerly winds (and overturning of southern deep water) [*Toggweiler et al.*, 2006], changes in southern ocean stratification (A. Schmittner et al., preprint, 2007), and changes in sea surface [*Marchal et al.*, 1999] or deep ocean [*Martin et al.*, 2005] temperature. Numerous models of the interhemispheric linkage of abrupt climate change during the last glacial period are based on changes in the Atlantic thermohaline circulation, commonly forced by freshwater input at the surface [e.g., *Ganopolski and Rahmstorf*, 2001], which might influence the above processes [*Marchal et al.*, 1999; *Martin et al.*, 2005; *Keeling and Stephens*, 2001; *Keeling and Visbeck*, 2005]. Recently, A. Schmittner et al. (preprint, 2007) specifically model the impact of changes in deep water formation in the North Atlantic on atmospheric CO$_2$ and Antarctic temperature, using a coupled climate-carbon cycle model. They produce CO$_2$ and temperature patterns similar to those observed here, and suggest that changes in the buoyancy driven ocean circulation in the North Atlantic impact southern ocean stratification and ultimately atmospheric CO$_2$.

[14] A further question of interest, which we cannot answer with the existing data, concerns the precise phase relationship between peak Antarctic temperatures, abrupt warming in Greenland, and changes in CO$_2$. The new U.S. WAIS Divide ice coring program in Antarctica will provide a higher resolution record which may be used to address this question.

4. Conclusions

[15] We provide a new chronology for atmospheric CO$_2$ from Antarctic ice cores covering 65 to 30 ka on GISP2-based ice core time scale, allowing direct comparison of CO$_2$ with atmospheric CH$_4$, Greenland and Antarctic tem-

perature proxies and Heinrich events. There are two main findings. First, atmospheric CO_2 rose several thousand years before abrupt warming in Greenland associated with Dansgaard-Oeschger events, 8, 12, 14, 17, four large warm events that follow Heinrich events. The CO_2 rise terminated at the onset of Greenland warming for each of these events. The CO_2 rise apparently predates Heinrich events associated with these D-O events. Second, CO_2 is strongly correlated with the Antarctic isotopic temperature proxy with an average time lag of 720 ± 370 yr (mean $\pm 1\sigma$). The lag does not appear to be constant within the 65-30 ka period, and the maxima of atmospheric CO_2 and the Antarctic temperature proxy appear synchronous within the resolution of the data. Our new data and chronology for atmospheric CO_2 during the last glacial period should provide a better understanding of the timing of changes in climate and the carbon cycle during the last ice age and a target for models attempting to explain CO_2 variability and abrupt climate change.

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