

Abrupt change in atmospheric CO₂ during the last ice age

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Received 6 July 2012; revised 21 August 2012; accepted 23 August 2012; published 28 September 2012.

[1] During the last glacial period atmospheric carbon dioxide and temperature in Antarctica varied in a similar fashion on millennial time scales, but previous work indicates that these changes were gradual. In a detailed analysis of one event we now find that approximately half of the CO₂ increase that occurred during the 1500-year cold period between Dansgaard-Oeschger (DO) events 8 and 9 happened rapidly, over less than two centuries. This rise in CO₂ was synchronous with, or slightly later than, a rapid increase of Antarctic temperature inferred from stable isotopes. **Citation:** Ahn, J., E. J. Brook, A. Schmittner, and K. Kreutz (2012), Abrupt change in atmospheric CO₂ during the last ice age, *Geophys. Res. Lett.*, 39, L18711, doi:10.1029/2012GL053018.

1. Introduction

[2] Ancient air preserved in ice cores provides important information about past variations in atmospheric CO₂, which can inform understanding of future climate-carbon cycle feedbacks [Friedlingstein *et al.*, 2006]. Previous ice core work for the last glacial period showed that CO₂ and Antarctic temperature rose during long, cold stadial periods in the northern hemisphere, and that Antarctic temperature cooled and CO₂ slowed or stopped rising when stadials ended with abrupt northern hemisphere warming [e.g., Ahn and Brook, 2008; Bereiter *et al.*, 2012]. Although these observations have been simulated in models forced by freshwater input in the North Atlantic [e.g., Schmittner and Galbraith, 2008], the governing mechanisms for the climate-carbon cycle interactions are not well understood, in part due to insufficient resolution, precision and/or chronology of previously published ice core records.

2. Methods

[3] Details of CO₂ analysis at Oregon State University (OSU) are described in Ahn *et al.* [2009]. We analyzed Siple Dome ice samples from 58 depths from 819–905 m depth (37.1–52.4 ka) and 105 Byrd ice samples from 40 depths from 1685.1–1814.5 m (36.8–42.9 ka). CO₂ concentrations are reported on the WMOX2007 CO₂ mole fraction scale. We utilized nitrogen isotope data from Brook *et al.* [2005],

Sowers *et al.* [1992] and Bender *et al.* [1995] for corrections of 0.8–0.9 and 1.0–1.5 ppm for gravitational fractionation in Siple Dome and Byrd ice, respectively.

[4] CH₄ analysis was performed at OSU using methods described by Mitchell *et al.* [2011]. We analyzed 62 new samples from 40 depths of the Siple Dome core, 87 samples from 48 depths of the Byrd core, 56 samples from 34 depths from the Taylor Dome core, and 88 samples from 44 depths of the GISP2 core. Data are reported on the NOAA04 methane concentration scale [Dlugokencky *et al.*, 2005].

3. Results

[5] Our Siple Dome and Byrd records cover the time period from 37–47 ka, during which Antarctica experienced two major warming events (A1 and A2) and several abrupt warming/cooling (DO) events occurred in Greenland (Figure 1 and Figure S1 in the auxiliary material).¹ To place the records on the same chronology we synchronized the age scales using existing and new methane data, assuming methane concentration variations in Greenland and Antarctica were synchronous [Blunier and Brook, 2001] (Figure 1, and Figure S1 and Table S1 in Text S1). Although measurements of CO₂ in Greenland ice cores might provide a more direct way to compare Greenland climate variations with carbon dioxide changes, reconstruction of the CO₂ history from Greenland ice cores is difficult due to high levels of impurities in ice [Stauffer, 2006].

[6] We obtained sub-centennial CO₂ data for the period from about 40 to 38 ka (Figure 1), corresponding to the Greenland stadial between Dansgaard-Oeschger [DO] events 8 and 9, and the time period of the A1 warming in Antarctica [Blunier and Brook, 2001] or AIM8 (Antarctic Isotope Maximum 8) [EPICA Community Members, 2006]. Heinrich event 4, an abrupt glacial discharge event in the North Atlantic occurred in the time interval and the stadial is referred to Heinrich stadial 4 [Skinner and Elderfield, 2007]. In general, CO₂ strongly covaries with the Antarctic stable isotope records on centennial time scales over this period. After the DO9 warming event in Greenland, both CO₂ and $\delta^{18}\text{O}_{\text{ice}}$ in the Byrd and Siple Dome records started to increase at ~40.0 ka. The initial CO₂ rise was somewhat gradual, but at 39.6 ka a 10 ppm jump occurred over ~150 years in both Siple and Byrd records. Following that jump CO₂ levels show two oscillations of smaller amplitude (5 ppm) before an additional abrupt increase at ~38.3 ka, synchronous with DO-8 warming in Greenland. After the abrupt DO8 warming in Greenland, CO₂ remained high for 700–800 years while Antarctica cooled as shown in both the Byrd and Siple Dome records, confirming the decoupling of CO₂ and Antarctic temperature proxies following Antarctic

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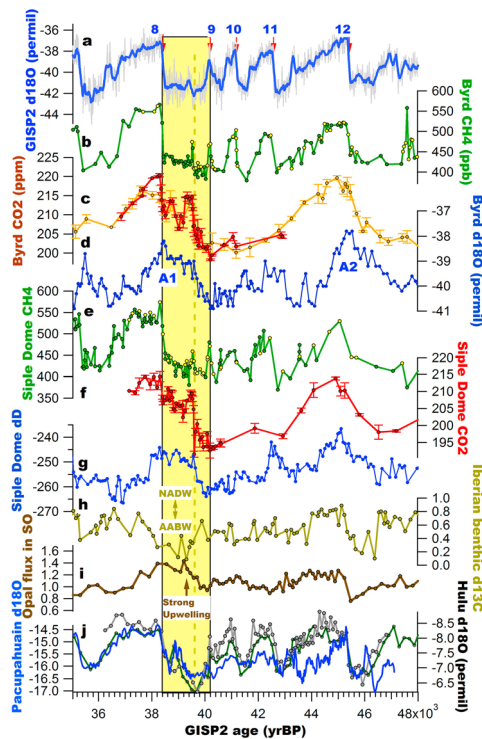


Figure 1. Synchronization of ice core records and comparison with marine sediment records. (a) Greenland isotopic temperature [Blunier and Brook, 2001]. Blue numbers indicate the timing of Dansgaard-Oeschger (DO) events. Red arrows are age tie points (see auxiliary material for details). (b) Byrd ice core CH₄ records [Blunier and Brook, 2001]. Yellow circles are new data for this study. (c) Byrd ice core CO₂ records [Ahn and Brook, 2008]. Red circles are new data for this study. (d) Byrd ice core $\delta^{18}\text{O}_{\text{ice}}$ temperature proxy [Blunier and Brook, 2001]. (e) Siple Dome ice core CH₄ records [Brook et al., 2005]. Yellow circles are new data for this study. (f) Siple Dome ice core CO₂ records for this study. (g) Siple Dome $\delta\text{D}_{\text{ice}}$ for a temperature proxy [Brook et al., 2005]. (h) Benthic foraminifera $\delta^{13}\text{C}$ from Iberian margin sediment core [Margari et al., 2010]. The $\delta^{13}\text{C}$ is used for proxies for deep water sources that are indicated with a dark yellow arrow, NADW, North Atlantic Deep Water. (i) Opal flux in the Southern Ocean as a proxy for upwelling [Anderson et al., 2009]. AABW, Antarctic Bottom Water. (j) Speleothem $\delta^{18}\text{O}$ records from Chinese Hulu (green and gray) [Wang et al., 2001] and Pacupahuain (blue) [Kanner et al., 2012] caves, proxy for precipitation. More negative $\delta^{18}\text{O}$ indicates increased rainout. Proxy ages are synchronized with GISP2 $\delta^{18}\text{O}$ at age tie points (red arrows, see auxiliary material for details). Ages between the tie points are linearly interpolated. Yellow box indicates the time interval between two abrupt DO 8 and 9 warming events, for which high-resolution CO₂ records were obtained. Dotted vertical line points timing of abrupt CO₂ changes.

warming observed in previous Byrd ice core results [Ahn and Brook, 2008]. We note that the CO₂ in Byrd is uniformly 3–7 ppm higher than in Siple Dome for the studied age interval (Figure S2 in Text S1), which we believe is probably related to the long duration of storage for the Byrd

core (drilled in 1968), but the timing and patterns of CO₂ change are similar. High resolution Ca²⁺ and non-sea-salt Ca (nssCa²⁺) concentration records from the Siple Dome ice core [Mayewski et al., 2009] do not show any significant correlation with the abrupt CO₂ rise (Figure S3 in Text S1), indicating that the abrupt CO₂ rise is not likely produced by carbonate-acid reaction in the ice. Similar data are not available for Byrd. Although the abrupt changes in our data are defined by only a few data points, they are reproducible in the two ice cores, and we further note that each plotted point is the mean of several replicate samples. The replicate Byrd ice samples were generally analyzed on different days over 6 months.

4. Abrupt Rise of CO₂ During Heinrich Stadial 4

[7] We call attention to the abrupt change in CO₂ of ~10 ppm at ~39.6 ka. The Siple Dome record shows the rise interrupted by a rapid initial drop of ~9 ppm, but this is not confirmed in the Byrd ice core. If this event were real, we would expect both cores show the initial drop of CO₂. Thus we disregard this data point in the Siple Dome record for a conservative calculation of the rate of CO₂ increase (Figure 1 and Figures S1, S2, and S4 in Text S1). In Siple Dome 60% of the 10 ppm increase occurred over at most ~70 years (9 ppm/century). In Byrd, an ~8 ppm increase is observed over 50 years (~15 ppm/century). Considering the data resolution and the smoothing of the gas record by diffusion in the firm [Brook et al., 2005] and ice matrix [Ahn et al., 2008], the actual atmospheric CO₂ change could have been faster. The exact rate of the abrupt CO₂ change is difficult to estimate but it is likely that the entire change took place in less than two centuries.

[8] The 10 ppm increase is about half the amplitude of the multi-millennial variations associated with the major Antarctic warm events and indicates that atmospheric CO₂ can change more rapidly than suggested by previous lower-resolution ice core records for the last glacial period. Previous high-resolution, but highly scattered and lower precision Byrd CO₂ measurements from the University of Bern [Stauffer et al., 1998] also showed abrupt CO₂ change at the same depth as we observed (Figure S5b in Text S1). In addition, Taylor Dome ice core records [Indermühle et al., 2000] also show a rapid rise of CO₂ with a lower resolution at similar ages (on our improved chronology with better CH₄ correlation, Figure S5d in Text S1). EDML ice core records also show a similar two step abrupt rise in CO₂ at A1, with lower resolution [Lüthi et al., 2010].

[9] The abrupt rise of CO₂ at ~39.6 ka is synchronous with or slightly later than a rapid rise of temperature proxies ($\delta^{18}\text{O}$, δD) in the Byrd and Siple Dome records within the uncertainty of ice age–gas age difference of 150–200 years [Blunier and Brook, 2001; Brook et al., 2005]. The rapid warming occurred ~400 yrs after the start of A1 warming in both Siple Dome and Byrd ice cores (Figures 1 and 2). Rapid warming at a similar time interval is also observed in EDML [EPICA Community Members, 2006] and Dome C [Jouzel et al., 2007] ice core records (Figure 2 and Figures S6f–S6i in Text S1). Similar features may be present in Vostok [Petit et al., 1999] and Dome Fuji [Watanabe et al., 2003] records, but are difficult to interpret due to low time resolution and/or chronological uncertainty. The abrupt CO₂ rise is also

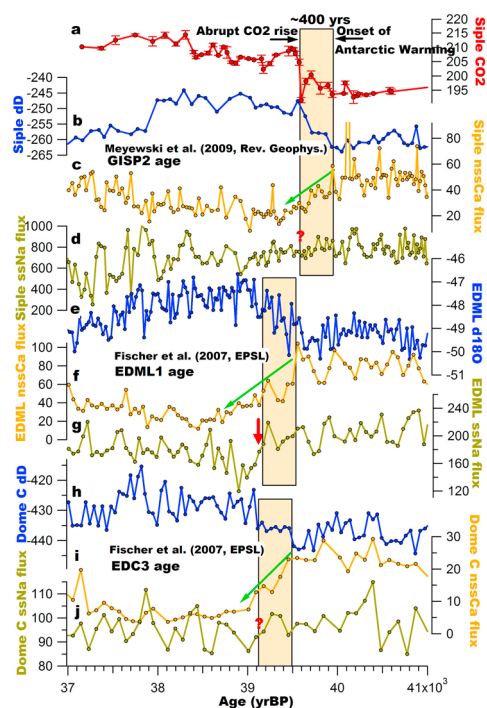


Figure 2. Comparison of abrupt atmospheric CO₂ change with non-sea-salt (nss) Ca flux and sea-salt (ss) Na flux in Antarctica. The abrupt CO₂ rise occurred ~400 years (widths of yellow boxes) after the onset of Antarctic warming event 1 and the nssCa flux (proxy for dust flux). The records from three different ice cores were plotted on the original timescales: GISP2 age for Siple Dome [Mayewski *et al.*, 2009], EDML 1 age for EDML [Fischer *et al.*, 2007], EDC3 age for Dome C core [Fischer *et al.*, 2007] records.

synchronous with a small step-like increase of CH₄ at ~39.6 ka in the high resolution Byrd and Siple Dome CH₄ records (Figure 1). The synchronicity of these events is firmly established because the CO₂ and CH₄ increases occurred at the same depth in the same ice cores, circumventing uncertainty in the ice age – gas age difference (Figures 1 and 2 and Figure S5 in Text S1). The Byrd and Siple Dome ice cores also show that the step-like increase of CH₄ starts with a short CH₄ peak.

[10] Our new high-precision data from GISP2 ice core also show a step in CH₄ during Heinrich stadial 4, synchronous with a small oscillation of $\delta^{18}\text{O}_{\text{ice}}$, within the relative age uncertainty between ice and gas ages (Figure S5 in Text S1), indicating that abrupt CO₂ rise at ~39.6 ka might have been synchronous with this small Greenland warming. However, we point out that the small rise of $\delta^{18}\text{O}$ in GISP2 records is not clearly apparent in other Greenland ice cores [Blunier and Brook, 2001; EPICA Community Members, 2006]. Nonetheless, the CH₄ change itself indicates that a climate event occurred during the abrupt CO₂ increase.

5. Possible Mechanisms and Discussion

[11] To explore possible governing mechanisms for the abrupt CO₂ changes, we first compared our CO₂ data with nssCa²⁺ and ssNa⁺ (sea-salt-Na⁺) flux records from Antarctic

ice cores [Mayewski *et al.*, 2009; Fischer *et al.*, 2007]. Those records were used as proxies for Patagonian dust source strength and sea ice extent in the Southern Ocean, respectively, in previous studies for Dome C and EDML ice cores (Figure 2) [Fischer *et al.*, 2007]. Both have been suggested as potential controls on atmospheric CO₂ [Fischer *et al.*, 2007]. The Siple Dome, Dome C and EDML ice cores show that nssCa²⁺ flux is anti-correlated with the isotopic record (Figure 2), suggesting that Patagonian (or other continental) dust source strength (nssCa²⁺ flux) started to decrease ~400 years before the abrupt CO₂ rise at 39.6 ka. The gradual CO₂ rise starting at ~40.0 ka is inversely correlated with nssCa²⁺ and therefore presumably with reduced iron input in the Southern Ocean [Mayewski *et al.*, 2009; Fischer *et al.*, 2007], which could result in an increase in atmospheric CO₂ due to reduced iron-fertilization [Fischer *et al.*, 2007], but we do not observe an abrupt change in nssCa²⁺ at 39.6 ka. In contrast, ssNa⁺ flux records from the three Antarctic ice cores are not consistent (Figure 2). The EPICA EDML ice core shows a rapid drop of ssNa⁺ flux ~400 years after the onset of A1 warming, synchronous with the abrupt CO₂ rise we observed in the Siple and Byrd ice cores, indicating that the abrupt CO₂ rise might be related to increase of CO₂ outgassing from areas in the Southern Ocean, which had been blocked by sea ice [Stephens and Keeling, 2000]. However, the relationship between abrupt CO₂ change and ssNa⁺ flux is not clear in the Siple Dome and Dome C records. The differences in ssNa⁺ flux records among the three Antarctic ice cores could be due to difference in sea salt aerosol source regions (EDML from Atlantic sector, Dome C from Indian sector and Siple Dome from Pacific sector) and/or different sensitivity in the source areas and/or different degree of deposition and remobilization during transportation from the source regions [Fischer *et al.*, 2007].

[12] Oceanic meridional overturning circulation is another potential control on atmospheric CO₂ [Marchal *et al.*, 1998; Menviel *et al.*, 2008; Schmittner *et al.*, 2007]. To examine this we compared our data with Atlantic sediment records that indicate that Antarctic Bottom Water was strengthened and possibly Atlantic meridional overturning circulation (AMOC) was reduced during the Heinrich stadial 4 [Shackleton *et al.*, 2000] (Figure 1h). Similar changes are well simulated in carbon cycle models for millennial variations during the last glacial period. Such models start from weakening of the North Atlantic Deep Water (NADW) formation by fresh water forcing in the North Atlantic [Marchal *et al.*, 1998; Menviel *et al.*, 2008; Schmittner *et al.*, 2007] and predict that several different mechanisms for atmospheric CO₂ change are important, including increase in sea surface temperature in the Southern Ocean [Marchal *et al.*, 1998], reduced stratification in the Southern ocean [Schmittner *et al.*, 2007] and increased preformed nutrients in the global ocean [Schmittner and Galbraith, 2008]. Reduced AMOC due to freshwater forcing also affects terrestrial vegetation and carbon cycling in models, but the sign of CO₂ change is model dependent [Köhler *et al.*, 2005; Menviel *et al.*, 2008]. None of the models used to examine CO₂ variations in response to circulation shut down predict the abrupt features of CO₂ changes reported here. However, some marine proxies show sharp changes in the deep water off the Iberian Margin [Skinner and Elderfield, 2007; Margari *et al.*, 2010], sea surface temperature in the subtropical North Atlantic [Sachs and Lehman, 1999] and upwelling in the Southern Ocean [Anderson *et al.*, 2009] in

that time interval (Figures 1h and 1i), but the current degree of the data resolution and replication, and the exact timing relative to the abrupt CO₂ changes is not well constrained.

[13] Change in atmospheric circulation could also be involved in abrupt changes in CO₂. Changes in westerly wind stress strength and position in the Southern Ocean, perhaps driven by cooling in the high latitude northern hemisphere, might affect upwelling of CO₂-rich deep water, therefore CO₂ outgassing, as suggested for glacial-interglacial [Toggweiler *et al.*, 2006] and millennial [Anderson *et al.*, 2009; Lee *et al.*, 2011] CO₂ variations. Speleothem $\delta^{18}\text{O}$ records from Hulu cave in China [Wang *et al.*, 2001] and Pacupahuain Cave in the central Peruvian Andes [Kanner *et al.*, 2012] show increase in East Asian Summer Monsoon (EASM) and decrease in South American Summer Monsoon (SASM) strength, respectively, which are synchronous with Greenland DO events (Figure 1j). During Heinrich stadial 4, the speleothem $\delta^{18}\text{O}$ records show a peak (depletion in Hulu cave $\delta^{18}\text{O}$ and enrichment in Pacupahuain cave $\delta^{18}\text{O}$), which indicates enhanced (reduced) EASM (SASM) activity and shares the trend of CO₂ variation at the same time interval. The speleothem $\delta^{18}\text{O}$ change appears to occur slightly later than that of CO₂ in our age scales for Siple Dome and Byrd (Figure 1j). However, given uncertainties in the ice core and speleothem chronology it seems likely that the speleothem $\delta^{18}\text{O}$ peak is actually synchronous with the small CH₄ peak after DO 9 and therefore also the abrupt CO₂ increase at 39.6 ka and the small warming in the GISP2 record at this time (Figures 1b and 1e and Figures S1b, S1d, and S5a–S5c in Text S1). Perhaps climate changes associated with an enhanced (reduced) precipitation in northern (southern) hemisphere affected terrestrial carbon and atmospheric CO₂. The speleothem $\delta^{18}\text{O}$ reversal after the peak indicates a reduced EASM and enhanced SASM activity and southward shift of ITCZ (Intertropical Convergence Zone). If those events are associated with the abrupt glacial discharge in the North Atlantic during Heinrich event 4 (H4) [Kanner *et al.*, 2012], it is unlikely that H4 predates the abrupt CO₂ rise (Figure 1).

[14] Although the ocean is often called on to explain past changes in CO₂, some model studies suggest that abrupt CO₂ changes could be due to changes in the terrestrial carbon cycle [Gerber *et al.*, 2003; Köhler *et al.*, 2010]. To demonstrate that the terrestrial carbon cycle could change CO₂ quickly we use the UVic (University of Victoria) coupled climate-carbon cycle model (version 2.8) with a glacial background climate [Schmittner and Galbraith, 2008] (see Figures S7–S9 in Text S1). We force the model to undergo a rapid warming by changing global albedo (this is arbitrary, intended simply to cause a rapid climate change). This forcing induced a rapid global temperature rise of about 1 K within 50 years, and caused atmospheric CO₂ to rise by 10 ppm within 20–30 years, due to reduced soil carbon storage owing to accelerated respiration in warmer soils. Our model results are similar to previous work, but we take advantage of using more realistic paleoclimatic conditions during the Heinrich stadial 4.

[15] In summary, while the exact mechanism governing the abrupt changes in CO₂ is not yet clear, changes in terrestrial carbon storage, or changes in the ocean carbon cycle driven by changes in atmospheric circulation seem the likely candidates. Our results suggest that the standard model of the bi-polar seesaw and its impact on the carbon cycle,

where freshwater input in to the North Atlantic [Stocker and Johnsen, 2003] changes heat transport and ocean ventilation, resulting in cooling in the north and gradual warming in the south, and gradual CO₂ release from the deep ocean [Schmittner *et al.*, 2007] does not capture all of the processes involved in millennial scale CO₂ variations, providing a new challenge for carbon cycle-climate modeling.

[16] **Acknowledgments.** We thank Michael Kalk and James Lee for analytical assistance and the staff of the National Ice Core Lab for ice sampling and curation. We also thank Luke Skinner and Paul Mayewski for helpful discussions. Financial support was provided by the Gary Comer Science and Education Foundation, National Science Foundation grants OPP 0337891, 0944764 and ATM 0602395, and Korea Meteorological Administration Research and Development Program under grant CATER 2012-7030.

[17] The Editor thanks the two anonymous reviewers for assisting in the evaluation of this paper.

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