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Thomas Blunier, *et al.*
Science **291**, 109 (2001);
DOI: 10.1126/science.291.5501.109

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29. When a large excess of olefin is used, the equilibrium constant can be reduced to: $K_{\text{eq}} = (1 - x)/(xC_0)$, where $x = i_c/i_a$ for the 0/-1 couple from the CV, and C_0 is the concentration of the olefin.
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7 September 2000; accepted 21 November 2000

Timing of Millennial-Scale Climate Change in Antarctica and Greenland During the Last Glacial Period

Thomas Blunier^{1*} and Edward J. Brook²

A precise relative chronology for Greenland and West Antarctic paleotemperature is extended to 90,000 years ago, based on correlation of atmospheric methane records from the Greenland Ice Sheet Project 2 and Byrd ice cores. Over this period, the onset of seven major millennial-scale warmings in Antarctica preceded the onset of Greenland warmings by 1500 to 3000 years. In general, Antarctic temperatures increased gradually while Greenland temperatures were decreasing or constant, and the termination of Antarctic warming was apparently coincident with the onset of rapid warming in Greenland. This pattern provides further evidence for the operation of a "bipolar see-saw" in air temperatures and an oceanic teleconnection between the hemispheres on millennial time scales.

Ice core and marine sediment records from the North Atlantic region show that climate during the last glacial period oscillated rapidly between cold and warm states that lasted for several thousand years. Understanding the manifestation of these rapid changes in other parts of the world may help unravel the underlying climate dynamics and predict the likelihood of future rapid climate change. Developing this understanding requires precise relative chronologies of events recorded in paleoclimate records. Polar ice cores provide one way of developing such a chronology for high-latitude sites.

Because of the rapid mixing time of the atmosphere (~1 year between hemispheres),

large-scale changes in the concentration of long-lived atmospheric gases are essentially globally synchronous. This synchronicity provides a tool for correlating ice core chronologies and thereby comparing the timing of climate and other environmental change, recorded by various proxies in the ice, between the hemispheres. The correlation is complicated by the fact that air is trapped in bubbles 50 to 100 m below the surface, creating an age offset between the trapped air and the surrounding ice (1). This age offset (referred to as Δage) must be corrected for when comparing the timing of climate events recorded in the ice by stable isotopes or other proxies. Here we compare the timing of climate events in the Greenland Ice Sheet Project 2 (GISP2) ice core (Summit, Greenland) with the Byrd ice core (Byrd Station, Antarctica), using atmospheric methane as a correlation tool.

Blunier *et al.* (2) used methane records from the Greenland Ice Core Project (GRIP), Byrd, and Vostok to compare the timing of millennial-scale events between 10 and 45 thousand years ago (ka). They showed that

warming in Antarctica preceded, by several millennia, the onset of warming in Greenland for Dansgaard-Oeschger (D-O) events 8 and 12—interstadial events that occurred at 38 and 45 ka (GISP2 chronology). Previous work showed a similar relationship for the Antarctic cold reversal and the Younger Dryas, cold periods that punctuate the last deglaciation in Antarctica and Greenland (3), respectively. Here we extend the comparison to 90 ka using new methane data from the Byrd ice core and existing records from GRIP and GISP2. The study of Blunier *et al.* (2) was based on data from the GRIP ice core and the GRIP time scale. However, the GISP2 ice core provides the most detailed northern CH_4 record between 40 and 110 ka, and we base our study on those results (4) and the GISP2 time scale (5). We adopt the GISP2 ice age time scale of Meese *et al.* (6) and the Δage calculations of Schwander *et al.* (7). We estimate the uncertainty in Δage from the uncertainty of the input parameters as ± 100 years between 10 to 20 ka, increasing to ± 300 years during the glacial period.

As expected, the Byrd and GISP2 methane records show a high degree of similarity. For example, between 53 and 60 ka both cores faithfully record a sequence of four major methane oscillations lasting 1000 years (1 ky) or less. Differences in concentration between the records are due to the latitudinal distribution of methane sources and sinks [(8) and references therein].

To create a gas age time scale for Byrd, we synchronized the Byrd methane record with the Greenland methane records from GISP2 and GRIP (9). We used a Monte Carlo method to search for a maximal correlation between the CH_4 records (1). For the period from 10 to 50 ka, we transferred the results of Blunier *et al.* to the GISP2 ice age time scale by correlating the rapid variations in $\delta^{18}\text{O}_{\text{ice}}$, which are virtually identical between GRIP and GISP2. We then adopted the previous correlation of GRIP and Byrd methane (2) to put the Byrd methane record for this period on the GISP2 time scale. For the time period from 50 to 90 ka, we directly correlated the

¹Department of Geosciences, Guyot Hall, Princeton University, Princeton, NJ 08544, USA; Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. ²Department of Geology and Program in Environmental Science, Washington State University, 14204 Northeast Salmon Creek Avenue, Vancouver, WA 98686, USA.

*To whom correspondence should be addressed. E-mail: blunier@princeton.edu

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GISP2 and Byrd methane records using the same Monte Carlo technique. The precision of the correlation, generally between 200 and 500 years, is limited by the sampling resolution of the two records [see Web table 1 (10) for uncertainties at the start of individual D-O events]. For the 11-ky period between D-O events 21 and 20, methane decreased gradually (Fig. 1), and uncertainty in the inter-polar methane gradient makes our correlation more subjective. The relatively small variations during D-O events 19 and 20 also make correlation more difficult. However, we regard the presented synchronization as the most likely one for two reasons. First, new and existing Vostok CH₄ measurements (11) for this period agree well with Byrd concentrations when plotted on a Vostok time scale synchronized with GISP2 using the $\delta^{18}\text{O}$ of O₂ (12), which varies significantly over this time period. Because there is no reason to expect methane to vary between Byrd and Vostok, this confirms that our synchronization for this period is accurate within the uncertainty of the $\delta^{18}\text{O}$ of O₂ synchronization (± 600 years). Second, $\delta^{15}\text{N}$ of N₂ measurements show that the small methane oscillation associated with D-O event 19 immediately followed the rapid warming that occurred at the beginning of this event, suggesting that the methane oscillation is not an analytical artifact (13).

To create an ice age time scale for Byrd, Δage was calculated using the Schwander *et al.* (1) model. We estimate that the uncertainty in Byrd Δage is ± 200 years (14). In Fig. 1, the isotopic records ($\delta^{18}\text{O}_{\text{ice}}$) from Byrd and GISP2 are plotted on the common time scale we created (15).

Millennial-scale variability in GISP2 and GRIP is characterized by abrupt temperature increases, followed by gradual decreases and abrupt returns to baseline glacial conditions. In contrast, at Byrd warming and cooling was gradual. Blunier *et al.* (2) showed that the onset of Antarctic warmings A1 and A2 preceded the onset of D-O events 8 and 12 by more than 1 ky. Our new results suggest that this is a persistent pattern. Seven warm events in our record, labeled A1 to A7 in Fig. 1, precede D-O events 8, 12, 14, 16/17, 19, 20, and 21 by 1.5 to 3 ky. In general, during the gradual warmings in the Byrd record, Greenland temperatures were cold or cooling. The Antarctic temperature rise for each of these events was apparently interrupted at or near the time when Greenland temperatures rose abruptly to interstadial states (16). Subsequently, temperatures decreased in both hemispheres to full glacial level, but cooling in the Byrd record was more rapid.

Our records are best constrained at the culmination of the main Antarctic warmings (A1 to A7 in Fig. 1), which are coincident

with onsets of long-lasting D-O events, because CH₄ increased rapidly at those times. It is unlikely that the Greenland/Antarctic temporal temperature offset we infer is an artifact of our Δage calculation. Systematic error in Δage is extremely unlikely to change the phasing of events. Independent constraints of the $\delta^{15}\text{N}$ of the N₂ thermal fractionation signal (17, 18) verify the Schwander *et al.* Δage model (1) to within ± 100 years for GISP2/GRIP. For Byrd, Δage would have to be reduced by 1500 years to bring the isotopic records into phase (19). As Δage is only on the order of 500 years, this would result in a negative Δage , which is impossible.

Our results illustrate that the large difference in timing of millennial-scale climate variability between West Antarctica and Greenland was a pervasive characteristic of the last glacial period. This temporal relation was maintained despite large changes in the background state of the climate system. Ice volume, sea level, and orbital geometry varied significantly (20, 21) between 90 and 10 ka (corresponding roughly to the period from marine isotope stage 5a to early marine isotope stage 2), while the Byrd/GISP relationship remained remarkably consistent.

Inland Antarctic ice cores from Byrd, Dome C, Dome B, Dome F, and Vostok (3, 22, 23) and Southern Ocean sea surface temperature (SST) reconstructions (24, 25) show a basically similar pattern of millennial-scale variability, with relatively slow to moderate temperature changes in the glacial period, and a slow increase from glacial to interglacial with a cold reversal (the Antarctic Cold Reversal) at the end of the deglaciation. In the inland records, only Vostok has an objective chronology that can be compared to our results for Byrd. Bender *et al.* (12) synchronized the Vostok and GISP2 isotopic signal based on $\delta^{18}\text{O}$ of O₂ and concluded that Greenland and Antarctic interstadials were in phase within ± 1.3 ky. Although our results appear to contradict this conclusion, the two studies actually agree on the relative timing of Greenland and Antarctic events. Bender *et al.* determined that the peak warmings in the Greenland and Antarctic records are on average in phase, which is also true in our records. However, the start of warmings at Byrd (and also Vostok) occurred several thousand years before warmings at GISP2 (Fig. 1). The similarity of inner Antarctic ice core records and many Southern Ocean SST records suggests that the timing of millennial-scale climate variability that we infer for Byrd characterized a large area of the Antarctic continent and Southern Ocean and has importance for understanding millennial-scale climate variability. However, as summarized by Alley and Clark (26), some southern Indian Ocean marine records and the Taylor Dome Ice Core in coastal East

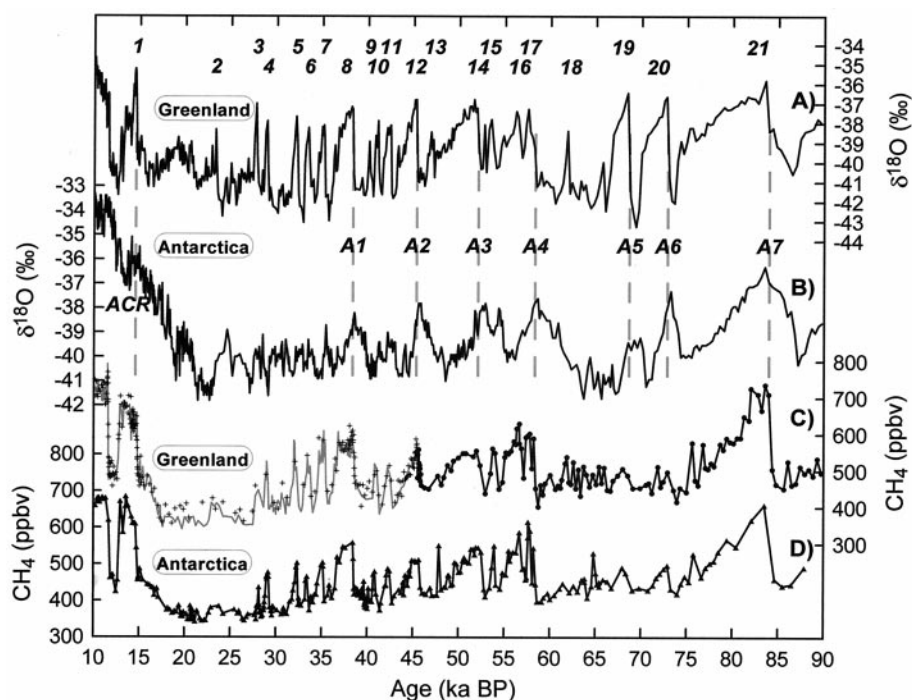


Fig. 1. Isotopic and CH₄ data from Greenland and Antarctica on the GISP2 time scale. Dashed lines indicate the onset of major D-O events. (A) $\delta^{18}\text{O}_{\text{ice}}$ from GISP2, Greenland (16). (B) $\delta^{18}\text{O}_{\text{ice}}$ from Byrd station, West Antarctica (23). (C) CH₄ data from GISP2 and GRIP. Crosses and dots are from GISP2 [(4) and new data]; the solid gray line is from GRIP (2, 8). The solid line runs through the data used for the synchronization: GISP2 (black line) up to 45.5 ka and GRIP data (gray line) from 45.5 ka to the Holocene. (D) CH₄ data from Byrd station [(2) and new data]. Data are available as supplemental information on Science Online (10) and at the NOAA Geophysical Data Center (5).

Antarctica show a pattern of deglacial warming more similar to GISP2 than Byrd. Although the Taylor Dome chronology has been questioned (27), these observations suggest the possibility of a more complex regional pattern of millennial-scale temperature variability in the high-latitude Southern Hemisphere than can be inferred from the Byrd core alone.

The temporally offset pattern of warming and cooling at Byrd and Summit Greenland, as well as evidence from marine cores (24), suggest a teleconnection between the northern and southern high latitudes. Such a connection could be due to either oceanic or atmospheric processes. Changes in the Atlantic thermohaline circulation are believed to be the direct cause of millennial-scale temperature changes in central Greenland during the glacial period. These temperature changes were closely preceded by ice rafting and associated meltwater events in the North Atlantic region (28). It is thought that the associated injection of fresh water reduces the deep water formation and initiates cooling in the North Atlantic region. Cooling then reduces melt rate and reestablishes North Atlantic Deep Water (NADW) formation, causing rapid warming in northern high latitudes. The temperature increase then leads again to a freshwater input into the North Atlantic and to gradual shutdown of NADW formation (29). Model simulations demonstrate the sensitivity of NADW formation to freshwater input and indicate that the resumption of the conveyor belt circulation after a shutdown is a rapid process [(30) and references therein]. D-O events are preceded by ice-rafted debris (IRD) events, and particularly strong IRD events (Heinrich events) originating in the Hudson Bay generally precede long D-O events (28).

Ocean models suggest that an increase in North Atlantic thermohaline circulation cools at least parts of the Southern Hemisphere and warms the high-latitude Northern Hemisphere (30); this phenomenon has been called the “bipolar see-saw” (31). The same pattern, which Blunier *et al.* described as “asynchrony” (32), appears in our data. D-O events 21, 20, 19, 17, 15, 12, and 8 were preceded by Antarctic events A7 to A1 (Fig. 1). The timing of the Antarctic cold reversal and of D-O event 1 is similar (2). Support for this mechanism comes from SST data from the Atlantic showing a lead of the Southern Ocean warming relative to northern warming after Heinrich events 5 and 4 (25).

We can convincingly demonstrate asynchrony for the events indicated above. Close inspection of Fig. 1 suggests a similar pattern for smaller D-O events (such as D-O events 3 to 7, 10, or 11). The analogous Antarctic events are more obvious in the Vostok data, and it has been suggested that each small

peak actually corresponds to a D-O event (12). However, the nature and spatial extent of these small temperature excursions are uncertain, precluding a definitive conclusion about their meaning.

Previous work suggested that only strong D-O events, potentially following a major shutdown of NADW associated with Heinrich events, resulted in the large-scale expression of the inter-polar see-saw (2, 30). This is consistent with our results for events A1 to A7. It is also consistent with small CO₂ variations during major Antarctic warmings in the glacial period (33). However, if the speculation that the smaller variations in Antarctic temperature are also related to D-O events is correct, the see-saw mechanism would have been active throughout the glacial period, independent of the magnitude of the D-O events.

The ultimate forcing of millennial-scale climate change remains elusive. Our results are consistent with the idea of a forcing arising in the Northern Hemisphere. However, they do not prove that the ice sheets or some other Northern Hemisphere process triggered millennial-scale climate change. Other mechanisms, including rapid changes in tropical climate and teleconnections to northern high latitudes (34, 35) or an as yet unidentified process with a 1.5-ky period (36) [but see Wunsch (37) for an alternate view] are possible alternatives. Our results suggest that the bipolar see-saw was a persistent feature of glacial climate. However, it may be more accurate to view NADW changes and associated climate changes as part of a continuous interrelated system.

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- borehole temperature measurements for the glacial-interglacial transition, are inputs to the model. The $\delta^{18}\text{O}_{\text{ice}}$ -temperature ($\delta^{18}\text{O}_{\text{ice}}-T$) relation corresponds roughly to a linear dependence, with a slope of 0.33 per mil (‰) per °C, which is in contrast to today's relation with a slope of 0.67‰ per °C [see (7) for details and original references]. The $\delta^{18}\text{O}_{\text{ice}}-T$ relation calibrated by the borehole temperature profile is confirmed by independent measurements of Δ age based on thermal fractionation of nitrogen isotopes at the last termination and the termination of the Younger Dryas (17, 18).
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15. The chronology after 45 ka is based on the previous synchronization (2). The Byrd record for this period has been transferred from the GRIP to the GISP2 time scale, based on a synchronization of the $\delta^{18}\text{O}_{\text{ice}}$ signals of the two cores. The time period from 25 to 17 ka (corresponding to 27.5 to 18 ka on the GISP2 time scale) was excluded from the analysis in (2). Therefore, the small CH₄ peak around 25 ka in the Byrd record, which probably corresponds to a peak associated with D-O event 2 in the GRIP record, did not appear to be coincident with the D-O event 2 CH₄ peak in GRIP. In the chronology described here, we included the period around D-O event 2 in the synchronization. This brings the Byrd and GRIP CH₄ peaks into agreement and shifts the Byrd $\delta^{18}\text{O}$ by about 1000 years later for this period but does not affect the rest of the record.
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16 August 2000; accepted 29 November 2000

Atmospheric CO₂ Concentrations over the Last Glacial Termination

Eric Monnin,^{1*} Andreas Indermühle,¹ André Dällenbach,¹ Jacqueline Flückiger,¹ Bernhard Stauffer,¹ Thomas F. Stocker,¹ Dominique Raynaud,² Jean-Marc Barnola²

A record of atmospheric carbon dioxide (CO₂) concentration during the transition from the Last Glacial Maximum to the Holocene, obtained from the Dome Concordia, Antarctica, ice core, reveals that an increase of 76 parts per million by volume occurred over a period of 6000 years in four clearly distinguishable intervals. The close correlation between CO₂ concentration and Antarctic temperature indicates that the Southern Ocean played an important role in causing the CO₂ increase. However, the similarity of changes in CO₂ concentration and variations of atmospheric methane concentration suggests that processes in the tropics and in the Northern Hemisphere, where the main sources for methane are located, also had substantial effects on atmospheric CO₂ concentrations.

The concentration of atmospheric CO₂ has been increasing steadily since the beginning of industrialization, from ~280 parts per million by volume (ppmv) to its present value of ~368 ppmv (1–4). By investigating earlier, natural CO₂ variations, we expect to obtain information about feedbacks between the carbon cycle and climate and also the possible impact of the anthropogenic CO₂ on the climate system. The transition from the Last Glacial Maximum (LGM) to the Holocene, during which CO₂ increased by ~40%, is a key period for such investigations.

The ice core record from Vostok, Antarctica, covering the past 420,000 years, shows increases of the CO₂ concentration between

80 and 100 ppmv for each of the past four glacial terminations (5). The increase during the last termination is well established on the basis of various polar ice cores from both hemispheres (6–10). However, not all ice cores are well suited to investigate the details of such an increase. Some CO₂ records, especially those from Greenland ice cores, are compromised by the production of CO₂ by chemical reactions between impurities in the ice (11–13). Ice cores from Antarctica are less affected, but a small amount of in situ CO₂ production by chemical reactions cannot be excluded for all Antarctic ice cores and all climatic periods (14, 15). CO₂ records from Vostok and Taylor Dome are thought to be the most accurate (5, 10, 16). However, the time resolution of these two records is too low to provide a history of CO₂ changes that shows the detailed evolution of atmospheric CO₂ over the last glacial termination.

Here, we present a record from the Dome

Concordia (Dome C), Antarctica (75°06'S, 123°24'E), ice core drilled in the frame of the European Project for Ice Coring in Antarctica (EPICA) during the field season 1998–99. We measured CO₂ in a total of 432 samples from 72 different depth intervals, between depths of 350 and 580 m, covering the period from 22 to 9 ky B.P. (ky B.P. is thousand years before present, where present is chosen as A.D. 1950). For each depth level, six samples were measured on a 60- to 100-mm length interval. On the same core, 74 methane measurements were performed. The analytical methods are described in (17).

The age scale for the ice, as well as for the enclosed air (which is younger than the surrounding ice because it is enclosed at the bottom of the firn layer), is based on the time scale by Schwander *et al.* (18). The uncertainty of the absolute time scale for the ice is estimated to ± 200 years back to 10 ky B.P. and up to ± 2000 years back to 41 ky B.P. The gas-ice age difference (Δ age) is calculated with a firn densification model. The value of Δ age is ~2000 years in the Holocene, increasing to ~5500 years during the LGM, and has an estimated uncertainty of ~10%.

The main feature of the CO₂ record (Fig. 1) is an increase from a mean value of 189 ppmv between 18.1 and 17.0 ky B.P. (19) to a mean value of 265 ppmv between 11.1 and 10.5 ky B.P. (beginning of the Holocene). The increase of 76 ± 1 ppmv occurs in four distinct intervals. From 17.0 to 15.4 ky B.P. (interval I), CO₂ increases from 189 to 219 ppmv at a mean rate of 20 ppmv/ky. From 15.4 to 13.8 ky B.P. (interval II), CO₂ rises from 219 to 231 ppmv at a rather constant rate of 8 ppmv/ky before a rapid increase of ~8 ppmv within three centuries at 13.8 ky B.P. Between 13.8 and 12.3 ky B.P. (interval III), a small decrease from 239 to 237 ppmv occurs at a rate of

¹Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. ²CNRS Laboratoire de Glaciologie et de Géophysique de l'Environnement, BP 96, 38402 St. Martin d'Hères Cedex, Grenoble, France.

*To whom correspondence should be addressed. E-mail: monnin@climate.unibe.ch