Abrupt changes in atmospheric methane at the MIS 5b–5a transition

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[1] New ice core analyses show that the prominent rise in atmospheric methane concentration at Dansgaard-Oeschger event 21 was interrupted by a century-long 20% decline, which was previously unrecognized. The reversal was found in a new ~100-year resolution study of methane in the GISP2 ice core, encompassing the beginning of D-O event 21, which also corresponds to the transition from MIS 5b to 5a. Although a corresponding reversal (within age uncertainty) is observed in climate proxies measured in GISP2 ice, including $\delta^{18}O_{ice}$, electrical conductivity, light scattering, and several ions, this feature has not been discussed previously. Abrupt changes in methane are paralleled by changes in $\delta^{15}N$ of trapped air, a quantity that reflects local temperature change at Greenland summit. The reversal described here supports the hypothesis that climate can be unstable during major transitions, as was previously described for the last deglaciation. **Citation:** Grachev, A. M., E. J. Brook, and J. P. Severinghaus (2007), Abrupt changes in atmospheric methane at the MIS 5b–5a transition, *Geophys. Res. Lett.*, *34*, L20703, doi:10.1029/2007GL029799.

1. Introduction

[2] Climate at high Northern latitudes was punctuated by abrupt changes associated with the so-called Dansgaard-Oeschger (D-O) events during the last glacial period [*Alley et al.*, 2003]. The D-O events are prominently recorded in Greenland ice cores and other climate archives [*North Greenland Ice Core Project Members (NGRIP Members)*, 2004]. The effects associated with these events are thought to have been hemispheric in extent [*Alley et al.*, 2003]. Atmospheric methane changed dramatically during D-O events and at deglaciation [*Chappellaz et al.*, 1993; *Blunier and Brook*, 2001]. Gas isotopes that trace abrupt temperature change show an increase that is synchronous with methane within a few decades at the onset of all abrupt D-O warmings studied so far [*Severinghaus et al.*, 1998; *Lang et al.*, 1999; *Severinghaus and Brook*, 1999; *Landais et al.*, 2004; *Huber et al.*, 2006].

[3] Methane emissions during glacial time are thought to come mostly from tropical wetlands, with boreal peatlands serving as an important secondary source. Increased temperature and moisture balance favor increased methane emissions from tropical and boreal regions. Because sink strength is unlikely to have varied by more than 25% [*Valdes et al.*, 2005], and the oceanic methane hydrate source appears to be stable, dramatic changes of climate over large land areas are implied for D-O events [*Flückiger et al.*, 2004; *Sowers*, 2006]. This view is strengthened by the speleothem records from China and subtropical Brazil, reflecting abrupt changes in local moisture balance at all or nearly all D-O events [*Wang et al.*, 2001; *Cruz et al.*, 2005; *Kelly et al.*, 2006a, 2006b]. Direct aerobic emission of methane by land plants [*Keppler et al.*, 2006] appears to be small according to new experimental results [*Dueck et al.*, 2007].

[4] Figure 1 shows a ~90,000-year ice core record of atmospheric methane from the GISP2 ice core, with the GISP2 $\delta^{18}O_{ice}$ record and the Northern hemisphere summer insolation shown for reference. The time interval encompassed by this study (82 to 87 ka) corresponds to the onset of D-O event 21, the longest in the Greenland record, which also corresponds to the transition from Marine Isotope Stage (MIS) 5b to MIS 5a. This event was characterized by Northern Hemisphere summer solar insolation reaching its peak value associated with MIS 5a at around 84 ka, conditions not reached again until last deglaciation. The overall methane concentration change at the onset of D-O event 21 was similar to the change at the last deglaciation (Figure 1) [*Brook et al.*, 1996], which was the largest change in the Greenland record.

[5] In this paper we present a highly resolved atmospheric methane record complemented by measurements of $\delta^{15}N$ of N_2 from the time encompassing the onset of D-O event 21. This record captures a transient reversal in the methane concentration increase. This abruptly switching sequence is analogous to the well-known Bølling-Allerod/Younger Dryas/pre-Boreal sequence of changes in methane during the last deglaciation [*Chappellaz et al.*, 1993; *Brook et al.*, 1996], but occurred on a centennial rather than a millennial timescale.

2. Experimental Methods

[6] A melt-refreeze air-extraction technique was employed for methane measurements, modified from previous methods [*Brook et al.*, 2000] to improve precision. Ice samples (~62 gram) were cut in a −25°C walk-in freezer and transferred to a −25°C lab freezer. Each ice sample was placed inside a glass sample flask that was prechilled in a cold ethanol bath (−64°C). The glass flasks had a total volume of ~125 cm^3 and terminated in a glass-stainless steel transition which was welded to a 2 ¾″ stainless steel Conflat flange. Eight flasks were attached to the vacuum line with copper gaskets, while remaining submerged in the −64°C cold bath. Flasks containing ice were evacuated for 1 hour after which the system was tested for leaks. The ice was then melted with warm water (~20 min), and refrozen in the cold bath for a minimum of 40 min. The released air was analyzed four times by direct expansion into a ~10 cm^3 stainless steel sample loop of the gas chromatograph. An Agilent 6890 N gas chromatograph with flame ionization

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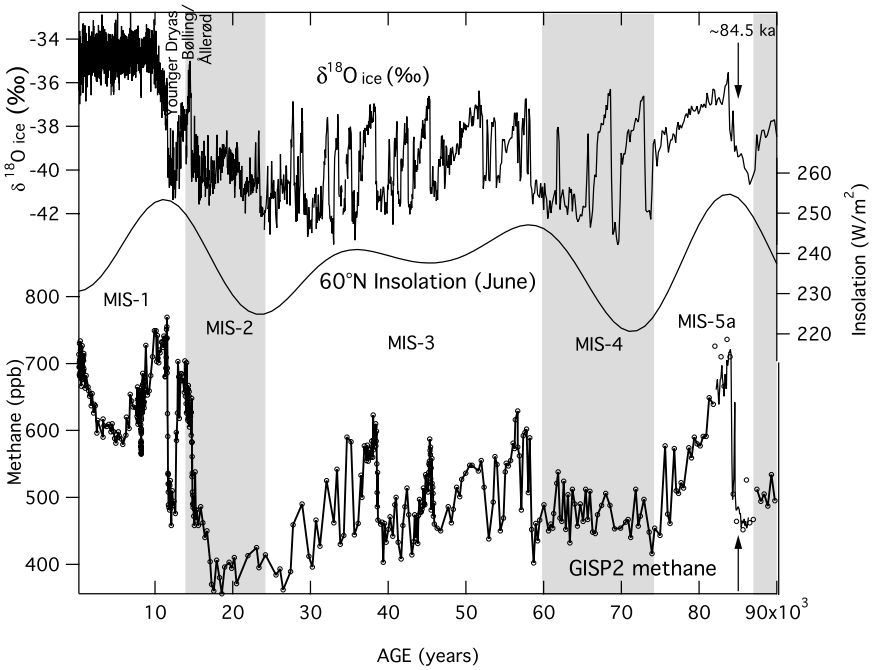

Figure 1. Atmospheric methane records from the GISP2 ice core covering the time interval between ~200 and ~90,000 years before present [*Blunier and Brook*, 2001; *Kobashi et al.*, 2007; *Brook et al.*, 1996, 2000, manuscript in preparation, 2007]. The portion of the old record in the range 82 to 87 ka is shown with individual circles, and the thin black line runs through the average values obtained in this study. Record for GISP2 $\delta^{18}O_{ice}$ (1-meter average [*Grootes and Stuiver*, 1997]) and 60°N June insolation [*Berger and Loutre*, 1991] are shown for reference. The abrupt feature in the $\delta^{18}O_{ice}$ record at MIS 5b–5a transition is shown with an arrow and illustrated in more detail in Figure 2.

detector was employed in this study. It was equipped with a 6-port two position gas sampling valve and utilized 99.9999%-pure nitrogen as a carrier gas, and a 6-foot 1/8″ Hayesep-D packed column. The sample loop was normally under vacuum and the amount of sample or standard air admitted was measured by a capacitance manometer. Calibration runs were performed daily covering the range of pressure yields observed for typical samples. A standard air tank containing 380.2 ppb of methane on the new NOAA04 calibration scale [*Dlugokencky et al.*, 2005] was employed as a reference.

[7] Blank experiments were performed wherein standard gas was admitted over ~62-gram samples freshly-cut from an artificially-made ice-block. The latter was prepared by freezing deionized water in a sealed vacuum-tight flask. The water had been previously boiled in that same flask for 1 hour to remove air. Blank ice samples were melted and refrozen, after which measurements were performed as for actual samples. These experiments typically yielded values elevated by ~4 ppb, which is possibly due to contamination or small leakage in the line, or an artifact resulting from room air trapped in fractures in the ice created as the ice-block was removed from the container. An effort should be made in the future to look for ways to prevent formation of cracks or to make larger ice blocks that would allow having enough unaffected ice.

[8] Blank corrections were not applied to the data. Additional details on experimental procedure for methane measurements will be reported in a forthcoming paper.

[9] The procedure for measuring $\delta^{15}N$ of trapped air was based on the original approach of *Sowers et al.* [1989] with further refinement described by *Petrenko et al.* [2006]. Starting ice blocks for cutting samples for $\delta^{15}N$ analyses were obtained separately from depths close to the ones used for methane analyses and also had a vertical dimension of 10 cm.

3. Results and Discussion

[10] The new methane data reported here come from the section of the GISP2 ice core covering the time period from 82 to 87 ka. This represents the depth interval from 2668 to 2690 meters, sampled at resolution ranging between ~10 and ~100 cm, averaging ~60 cm. In this new data set we identify an unexpected reversal in methane concentration trend at the onset of D-O 21 (Figure 2). At this time, the ice core methane concentration rose by ~160 ppb in 150 years at around 84.5 ka, then fell by ~140 ppb in 300 years, and then finally rose again by ~220 ppb in 200 years at the onset of the warm phase of D-O 21. About 80% of the first abrupt rise was completed in ~50 years whereas 80% of the fall occurred over ~130 years. Because atmospheric changes are smoothed by diffusion in the firn layer, the ice core record only provides an upper bound on the duration of actual atmospheric changes and a lower bound on their magnitude.

[11] Amplitudes of changes in the new methane record are constrained with a high level of confidence because air from each ice sample has been analyzed 4 times with the uncertainty of the mean value of ~2 ppb. Two ice samples generally represent each depth, with the standard deviation

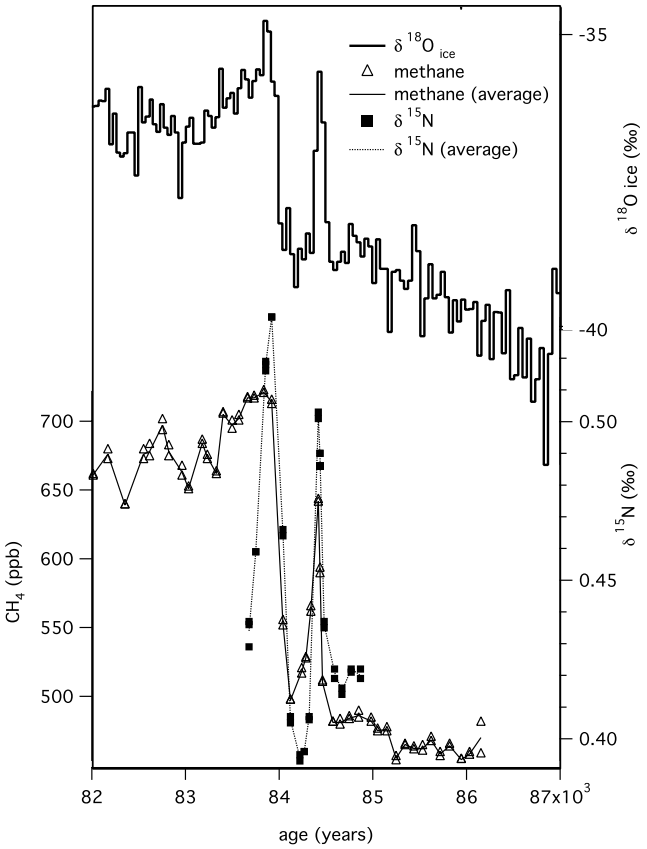

Figure 2. Abrupt climate change sequence at ~84.5 ka during the MIS 5b–5a transition. Methane and δ^{15}N are plotted on a gas age scale after *Brook et al.* [1996] adjusted by a constant value of −180 years, which is within the uncertainty of the gas age-ice age difference, in order to match the records. Each datapoint corresponds to an individually processed and analyzed ice sample. The lines go through the average value for each depth. Temperature proxy $\delta^{18}O_{ice}$ (highest resolution available [*Grootes and Stuiver*, 1997]) is shown for reference. The full datasets for methane and δ^{15}N appear in the auxiliary material.

of the mean value for the two samples generally amounting to ~2 ppb. The mean values for each ice sample with their uncertainties are reported in the auxiliary material[1] and are archived at the National Snow and Ice Data Center (www.nsidc.org).

[12] Other highly resolved GISP2 records contain a dramatic reversal at around this time including $\delta^{18}O_{ice}$ (Figure 2), a local temperature proxy, and parameters related to climate change on regional scales (light scattering, electrical conductivity, several ions) [*Greenland Summit Ice Cores*, 1997]. A detailed $\delta^{18}O_{ice}$ record from the North GRIP core also contains the reversal prior to D-O 21 (*NGRIP Members* [2004], full version of the dataset). A similar reversal is found in a stalagmite from Dongge cave (South-eastern China), which is thought to record Asian monsoon strength [*Kelly et al.*, 2006a, 2006b]. The magnitude of the reversal is large in all records. In particular, reversals in methane and $\delta^{18}O_{ice}$ (Figure 2) are nearly as large as at the well known Younger Dryas reversal and are greater than changes at the 8.2-ka centennial-scale event [*Alley et al.*, 2003; *Spahni et al.*, 2003; *Kobashi et al.*, 2007].

[13] Ice core methane serves as a climate indicator for widespread regions and offers a way to determine if changes in Greenland and elsewhere were simultaneous. This is achieved by comparison of ice core methane to ice core N_2 and Ar isotopes, which circumvents the uncertainty in the age offset of gas records with records from the ice matrix [*Severinghaus et al.*, 1998]. We find that abrupt changes in methane are closely paralleled by changes in nitrogen isotopes of trapped air (Figure 2; data table is given in auxiliary material). The latter are influenced by change in local temperature and snow accumulation rate that affect thermal diffusion and gravitational settling of isotopes. The paired behavior of methane and δ^{15}N is similar to abrupt events studied previously (e.g., termination of Younger Dryas, onset of Bølling, D-O events 9–17 [*Severinghaus et al.*, 1998; *Severinghaus and Brook*, 1999; *Huber et al.*, 2006]). Therefore it appears likely that similar climate mechanisms were at work at the centennial abrupt sequence described here. The observed ~10-25 cm offset between changes in methane and in δ^{15}N corresponds to ~50 years (Figure 2); the latter value is uncertain because it is difficult to determine the depth-age relationship over such a small interval. The offset is partly due to slightly faster diffusion of CH_4 in the firn (1–3 years), nevertheless it appears that changes in Greenland temperature preceded changes in methane by at least a few years.

[14] The methane cycle is part of a larger climate and biogeochemical system, which can apparently switch extremely abruptly between states that support high and low methane concentrations. Potential mechanisms to enhance emissions include warming in boreal regions, intensified moisture balance over land in the tropics, or both, in either case stimulating methanogenesis in wetlands, the major natural methane source. Speleothem records from China suggest a connection between atmospheric methane changes and changes in moisture balance in this region [*Wang et al.*, 2001; *Kelly et al.*, 2006a, 2006b]. Changes in volatile organic carbon levels (VOC's), competitors for the OH radical, the major methane sink [*Valdes et al.*, 2005], might also be abrupt, perhaps due to climate-driven abrupt changes in plant VOC emissions. It seems unlikely that emissions from sea floor hydrates [*Kennett et al.*, 2003] could explain the sequence of changes we observe here, as this would require an abrupt increase in hydrate emissions, a decrease, then an increase again, all within ~650 years, then maintenance of high emissions for several thousand years during D-O 21. *Weitemeyer and Buffett* [2006] suggested in a modeling study that a subglacial clathrate source may cause short-lived elevated concentrations of methane during deglaciation. This clathrate source could be coupled to a temperature increase more tightly than the marine source (the latter requires time for heat to penetrate through the marine sediment column). However the observed paired behavior of methane and δ^{15}N is extremely systematic for all abrupt events studied regardless of ice sheet configuration, seeming incompatible with either one of these hydrate scenarios.

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/gl/2007GL029799.

[15] D-O 21 occurs during the transition to Marine Isotope Stage 5a, a time of higher sea level and warmer global temperatures than at the preceding MIS 5b. The reversal we describe here, at the onset of D-O 21, may be a consequence of climate instability during this transition, perhaps related to ice sheet retreat and input of meltwater to the ocean disrupting ocean heat transport, with attendant impacts on other parts of the climate system. Previous work on the last deglaciation suggests that the climate system is unstable when in transition [*Taylor et al.*, 1993]. Our findings support this notion for the MIS 5b to 5a transition with respect to methane source regions.

[16] It is not yet clear, however, how common events like this may have been, because the ice core methane record covering large climate transitions has not yet been examined completely with the resolution and precision described here. A sequence of abrupt, ~100 ppb oscillations in methane around D-O 16 and 17 is present in GISP2, NGRIP and Byrd ice cores [*Blunier and Brook*, 2001; *Flückiger et al.*, 2004; *Huber et al.*, 2006], and may similarly be associated with the transition from MIS 4 to MIS 3. Further high-resolution methane studies in this and other parts of the Greenland ice cores are needed to establish how ubiquitous the centennial instabilities in methane source regions were, and the interhemispheric methane gradient should be evaluated to decipher the tropical and boreal components of abrupt changes at methane source regions. This should be possible at a centennial scale with the new West Antarctic Ice Sheet (WAIS) Divide ice core from West Antarctica (modern ice accumulation 24 cm/yr) which is now being drilled (www.waisdivide.unh.edu).

4. Conclusions

[17] The abrupt reversal in atmospheric methane described here indicates that large climate switches can occur on centennial time scales, and further demonstrates how dynamic the methane cycle was during the late Quaternary. The abrupt reversal in the concentration increase at the start of D-O 21 is analogous to the reversal in methane concentration during the Younger Dryas, but happened on a much shorter time scale. It may be related to climate instability associated with the large climate transition from MIS 5b to 5a. A more complete high resolution, high-precision record will be needed to fully understand how common abrupt switches in methane were during the last glacial period.

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