

Relative timing and variability of atmospheric methane and GISP2 oxygen isotopes between 68 and 86 ka

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[1] The global biogeochemical cycle of methane has received wide attention because of methane's role as a greenhouse gas. Measurements of methane in air trapped in Greenland ice cores provide a high-resolution record of methane levels in the atmosphere over the past ~ 100 ka, providing clues about what controls the methane cycle on geologic timescales. Remarkable similarity between local temperature recorded in Greenland ice cores and changes in global methane concentrations has been noted in previous studies, with the inference that the local temperature variations have global significance, but the resolution of sampling and measurement precision limited fine-scale comparison of these variables. In this work a higher-precision (~ 2 ppb) methane data set was obtained from the Greenland Ice Sheet Project 2 (GISP2) ice core for the time interval between 86 and 68 ka, encompassing three large abrupt warming events early in the last glacial period: Dansgaard-Oeschger (D-O) events 19, 20, and 21. The new data set consists of duplicate measurements at 158 depths, with average time resolution of 120 years. Such detailed measurements over D-O 21, the longest in Greenland records, have not yet been reported for other ice cores. The new data set documents short-term variability (~ 20 ppb typical amplitude), which is remarkably persistent, and in many cases similar features are observed in the most detailed published $\delta^{18}\text{O}_{\text{ice}}$ record. High-precision GISP2 $\delta^{15}\text{N}$ data show that changes in Greenland temperature are synchronous with the methane variations at the onset of D-O events 19, 20, and 21, supporting previous results from the Greenland Ice Core Project ice core for D-O 19 and 20. Cross-spectral analysis quantifies the extremely close similarity between the new methane record and the $\delta^{18}\text{O}_{\text{ice}}$ record. Because methane sources are widely distributed over the globe, this work further validates $\delta^{18}\text{O}_{\text{ice}}$ at Greenland summit as a geographically broad climate indicator on millennial to multicentennial timescales.

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1. Introduction

[2] Reliable records of past climates are valuable because they illuminate key properties of the climate system. A proxy documenting and integrating climate variability over vast land areas is especially helpful because it circumvents the difficulties of interpreting numerous individual records that reflect local and regional conditions. Methane from ice cores [Chappellaz *et al.*, 1993; Brook *et al.*, 1996] serves as such an integrated proxy, since methane emitted into the atmosphere from widespread sources is quickly homogenized. Methane sources are located on land where anaerobic degradation of

organic matter takes place, most notably in tropical wetlands and in peatlands in the boreal regions. Increased temperature and moisture supply due to changing climate increase methane emissions [Frolking and Crill, 1994]. Therefore changes in concentration of atmospheric methane reflect changes of climate over vast landmasses where methane is produced. Two additional sources of methane need to be mentioned: aerobic production by land plants [Keppler *et al.*, 2006] and emissions resulting from destabilization of methane hydrates [Kennett *et al.*, 2003]. The possible contribution from these two sources is currently debated [e.g., Dueck *et al.*, 2007; Sowers, 2006], however was likely smaller than anaerobic production in wetlands and peatlands, at least for the time interval discussed here.

[3] One of the most prominent features of the ice core methane record is the pattern of abrupt increases in methane at the onset of warm periods known as Dansgaard-Oeschger (D-O) events [Chappellaz *et al.*, 1993; Brook *et al.*, 1996]. These are generally believed to reflect a geographically widespread impact of the D-O events on methane emissions due to changes in temperature and rainfall [Brook *et al.*, 2000].

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[4] A portion of the observed changes in methane might also be due to changes in sink strength. Methane is destroyed in the atmosphere primarily through reactions with the OH radical. Early work suggested that most of the observed CH_4 change in ice cores was due to changes in the global source strength and little was due to changes in available OH radical [Thompson *et al.*, 1993; Crutzen and Brühl, 1993]. Later work investigated the role of temperature change on the sink strength, showing that warmer climates should lead to increased sink strength [Thompson *et al.*, 1993; Harder *et al.*, 2007]. Source strength increases inferred from rising methane levels associated with warming would therefore be underestimated if calculated using a constant sink. Other recent work suggests that volatile organic hydrocarbons (VOC) emitted by vegetation could decrease the amount of available OH, changing methane sink strength [Valdes *et al.*, 2005]. Models that incorporate vegetation and VOC emissions suggest that vegetation and VOC emissions respond to climate. There are a number of studies on the increase in VOC emissions with temperature [e.g., Monson *et al.*, 1992; Sharkey *et al.*, 1996]. According to Valdes *et al.* [2005] up to 30% of the Last Glacial to Holocene change in methane may have been due to change in OH driven by change in VOC's [Valdes *et al.*, 2005]. However, recent work suggests that OH is recycled in reactions with VOCs, such that the effect of VOCs on methane sink strength may have been overestimated [Lelieveld *et al.*, 2008]. In addition, independent work on ice cores over D-O events 19 and 20 by Flückiger *et al.* [2004] found changes in N_2O with timing similar to the changes in methane. Since the N_2O signal is at least partly terrestrial this observation provides some support for the hypothesis that abrupt changes in methane are due to changes in terrestrial sources.

[5] Atmospheric air is continuously “sampled” by the newly forming ice on polar ice sheets, allowing reconstruction of past changes in atmospheric methane using ice cores. Previous work identified large (>50 ppb) changes associated with the D-O events. These measurements had precision of 10–20 ppb, so smaller variations could not be adequately constrained [Chappellaz *et al.*, 1993; Brook *et al.*, 1996; Huber *et al.*, 2006]. Detailed new measurements are reported here on the Greenland Ice Sheet Project 2 (GISP2) ice core using a refined methodology with precision improved to ~2 ppb. Therefore, more subtle variability can be traced from this work, since even a 10 ppb oscillation is confidently recorded with the new ice sample measurement protocol.

[6] The new detailed methane record reported here also helps to address the nature of small short-term variability in the detailed record of $\delta^{18}\text{O}$ of H_2O in the ice matrix, the original ice core paleothermometer [Dansgaard *et al.*, 1969]. It has been argued that this isotopic ratio may reflect not only temperature changes, but also shifts in sources of precipitation, amount of winter versus summer snowfall, and other nontemperature factors [Jouzel *et al.*, 1997; Wunsch, 2006]. Independent methods established the exact link between $\delta^{18}\text{O}_{\text{ice}}$ and local temperature change over the average glacial versus average Holocene conditions (the borehole method) [Cuffey and Clow, 1997] and over the abrupt changes (the thermal diffusion method) [Severinghaus *et al.*, 1998]. However, a close look at the detailed $\delta^{18}\text{O}_{\text{ice}}$ record [Groote and

Stuiver, 1997] reveals many short-term changes in between large events, which could be a result of smaller local temperature variability, nontemperature factors, or more significant large-scale phenomena. It is hard to establish the background nonclimate noise level of such a record, because its variability comes mostly not from the analytical measurement but from variability in the factors that govern the $\delta^{18}\text{O}$ values of local precipitation. In that sense the new detailed methane record is valuable as an independent cross-check on the possible climatic significance of various small oscillations that appear quite persistent from the $\delta^{18}\text{O}_{\text{ice}}$ record. The analysis of coherence between the two records performed in this work serves to help address the criticism of spatially broad conclusions being drawn from the Greenland $\delta^{18}\text{O}_{\text{ice}}$ record alone, since its relevance to large-scale climates is hard to pinpoint [Wunsch, 2006].

[7] An immediate problem arises when trying to directly compare the ice core methane record to the $\delta^{18}\text{O}_{\text{ice}}$ record because the age scale for gases is derived from the age scale for the ice with important additional assumptions. The air is trapped in the ice at some ~70 m below the surface of the ice sheet. Trapped air is younger than the surrounding ice because it has had recent diffusive exchange with the atmosphere via pores and channels in the firn. The ice at the close-off depth is a few centuries old, since that is how long it takes for ~70 m of snow to accumulate. As a result of this age mismatch, any attempt to match short-term oscillations in the $\delta^{18}\text{O}_{\text{ice}}$ record and in the methane record is difficult since the age assignments, even though they are from the same ice core, are uncertain by a century or more. This problem can be circumvented at times of abrupt climate change where $\delta^{15}\text{N}$ records of entrapped air are available [Severinghaus and Brook, 1999]. It has been confirmed that abrupt temperature change creates a temperature difference across the firn layer, which in turn drives separation of isotopes in air by thermal diffusion, depending on the magnitude of temperature difference across the firn [Severinghaus *et al.*, 1998, 2001; Grachev and Severinghaus, 2005]. Thus an isotopic marker of abrupt climate change is present in the gas phase and therefore can be directly compared to methane, regardless of the age scale. Published results show that the two characteristics of trapped air (methane concentration and $\delta^{15}\text{N}$) are synchronous to within 1–5 decades for all of the abrupt change events studied so far [Severinghaus *et al.*, 1998; Severinghaus and Brook, 1999; Huber *et al.*, 2006; Flückiger *et al.*, 2004; Grachev *et al.*, 2007]. Since the abrupt temperature change at the onset of a D-O event in Greenland causes not only $\delta^{18}\text{O}_{\text{ice}}$ of the ice matrix to change dramatically, but also creates an anomaly in $\delta^{15}\text{N}$ of the entrapped gas, methane and $\delta^{18}\text{O}_{\text{ice}}$ can be synchronized where $\delta^{15}\text{N}$ and methane are known to be synchronous.

[8] The general similarity between the GISP2 methane and $\delta^{18}\text{O}_{\text{ice}}$ records has been noted previously in the context of the full GISP2 methane record [Brook *et al.*, 1996], original work on this topic on the Greenland Ice Core Project (GRIP) ice core [Chappellaz *et al.*, 1993], and subsequent studies [Huber *et al.*, 2006; Wunsch, 2006]. It should be noted that the data set reported here supercedes the original GISP2 methane data set of Brook *et al.* [1996] in the time interval between 68 and 86 ka. The original data set correctly pointed

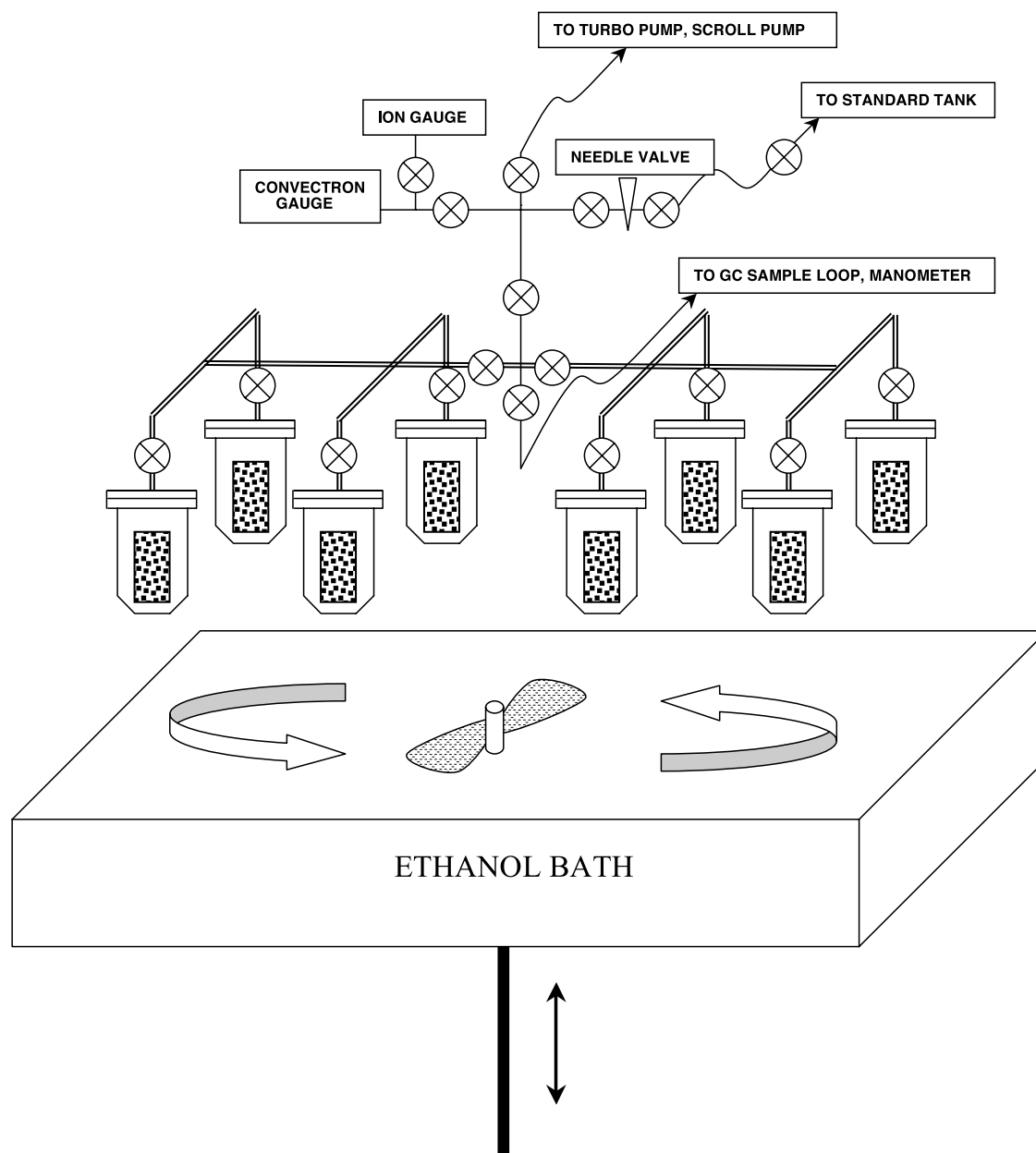


Figure 1. Schematic of the extraction line employed for making ice core measurements.

out large features in the data; however, its precision and resolution were insufficient to document smaller features discussed here. It is the goal of this paper to extract new climate information by comparing the published detailed GISP2 $\delta^{18}\text{O}_{\text{ice}}$ record and the new detailed high-precision GISP2 methane record, with the onsets of three large abrupt warmings serving as synchronization markers via the available $\delta^{15}\text{N}$ records.

2. Experimental Methods

[9] The experimental procedure employed in this work follows *Brook et al.* [2000] but has been modified extensively to improve precision. Figure 1 is a schematic of the

vacuum line employed. The valves are pneumatically actuated Swagelok valves with Kel-F stem tips, and were operated via a computer interface. Vacuum was established with a turbomolecular pump (Alcatel ATP 80) backed by a dry pump (ULVAC scroll pump). The vacuum line was connected directly to a 6-port Valco gas sampling valve mounted in an Agilent Technologies 6890N gas chromatograph with a flame ionization detector (FID) and electronic pressure control for the detector gases (ultrazero air and hydrogen). Carrier gas (N_2 , Airgas BIP grade) flow was regulated with the Agilent manual pressure control system. Pressure in the sample loop ($\sim 10\text{ cm}^3$) was measured with a capacitance manometer (MKS Baratron, range 0 to 100 torr, 0.15% accuracy). Settings of the gas chromatograph, spec-

Table 1. Equipment and Settings Employed for the Gas Chromatographic Measurement

Equipment/Parameters	Specifications/Settings
Instrument, Agilent 6890N	FID detector, ChemStation software
Temperatures	
Valve box	50°C
Oven	50°C
Front inlet	50°C
Settings of the detector	
FID temperature	150°C
H ₂ flow rate (EPC controller)	35.0
Air flow rate (EPC controller)	345.0
Make up gas flow rate	off
Carrier gas column head pressure/flow rate (manually adjusted, no EPC on carrier gas)	26 psi/ ~30 ml/min
Purity of gases	
Carrier gas (N ₂)	>99,999 (BIP grade from Airgas)
Air	Ultra-zero air from Airgas
Hydrogen	Research grade from Airgas
Column, Hayesep-D	(80/100 6' × 1/8" × 0.085")
Integration settings for Agilent ChemStation: slope sensitivity	0.7 (the only parameter set)
Rotation of 6-port valve	
On	0.1 min
Off	1.1 min
Sample loop	10 cm ³ , 1/8" stainless steel
Pressure measurement	0 to 100 torr MKS Baratron capacitance manometer, 0.15% accuracy

ifications of the column, and the purity of input gases are given in Table 1. The manometer and sample loop together with the column were kept inside the oven for precise constant temperature control. The glass flasks (Figure 1) had a total volume of ~ 125 cm³ and terminated in a glass stainless steel transition which was welded to a 2 3/4" stainless steel Conflat flange. A stainless steel vacuum-insulated adjustable-height bath was used to chill the sample flasks using ethanol. The bath was stirred with an air-powered adjustable-speed stirrer. Constant temperature was maintained with an FTS Systems chiller (MFC 100821) with immersion probe coiled around the stirrer in the center of the bath. Temperature in the bath was monitored using a digital thermometer and was $\sim -64.5^\circ\text{C}$ at equilibrium. An air standard with a methane concentration of 380.2 ppb (NOAA04 scale) [Dlugokencky *et al.*, 2005] was run multiple times on each day to establish a calibration line consisting of peak area versus input pressure in the sample loop. A needle valve (Figure 1) and the bellows valve on the standard gas tank were employed to gradually admit gas into the line until the pressure reached the desired range.

[10] Ice samples were cut the same day they were processed and analyzed. Samples were cut using a band saw in a walk-in freezer (-25°C) from original larger pieces having ~ 10 cm vertical dimension and weighing ~ 400 g. The surfaces on samples that were not freshly cut were trimmed off by ~ 2 mm. Final ice samples for analysis typically had dimensions of ~ 9.5 cm (vertical) $\times 2.5$ cm $\times 3.5$ cm and a weight of ~ 62 g. Ice samples were paired to replicate the results, with two adjacent samples cut from each larger piece. A total of 8 samples were typically cut on a given day. Samples were individually placed in labeled plastic bags inside an insulated cooler that was transported to a lab freezer (-25°C).

[11] For each sample an empty dry flask was prechilled to -64.5°C in the cold bath for 2 min, after which an ice sample

was placed inside it. The flask was sealed to the line with a copper gasket. The other seven sample flasks were loaded with ice samples and attached in a similar fashion. Throughout the procedure flasks on the line were kept at least partially submerged in the bath.

[12] Flasks containing ice samples were evacuated for 1 h, after which the line pressure was typically 1.2×10^{-2} torr. Three tests for leaks were performed with the pump closed off: with both arrays open (Figure 1, left and right), and with one array open, the other closed. The system was freshly evacuated in between the tests. Typical results were as follows: a rise in pressure in 60 s to 4.6×10^{-2} torr for a test with both arrays open, and to $\sim 4.0 \times 10^{-2}$ torr for a test with one of the arrays closed. After the tests the system was freshly evacuated for a few minutes and all eight flask valves were closed off.

[13] Plastic containers with tap water ($\sim 55^\circ\text{C}$) were employed to melt ice samples. The goal was to not allow samples to warm up above room temperature and to remove warm water promptly from under a sample that was almost completely melted. It typically took ~ 18 min for the last sample to complete melting.

[14] The cold bath was then lifted to submerge flasks close to the glass-to-metal transition, and at least 40 min was allowed for meltwater to refreeze. Calibration was run during that time as follows: a total of eight methane measurements were performed on the standard tank at each of the target pressures: ~ 15 , 20 (x2), 25, 30, 35, and 40 (x2) torr. During a calibration run both arrays of the line remained open. Prior to calibration runs at least three "warm-up" runs were performed with 40 torr of gas admitted in the sample loop. These runs served to condition the gas chromatograph and to flush the system prior to actual runs.

[15] Samples were measured in order 1 through 8, with four measurements for each sample; that is, each sample was measured four times before shifting to the next sample. To

maximize sample yield on repeated measurements, the remaining gas from a sample was kept behind the left (or right) array valve (Figure 1), while the rest of the line was evacuated. Sample or standard injections were typically spaced by ~ 3.5 min, which was sufficient to complete one run and evacuate the system. A typical yield for a sample was ~ 40 torr on the first run and ~ 35 , 25 and 15 torr on the subsequent runs.

[16] To test for contamination a block of blank ice was prepared as follows. A cylindrical stainless steel container with Conflat flange top was filled with deionized water. A copper gasket was placed on the flange on the flask, which was then attached to the top flange with bolts. The top flange was connected to a Swagelok valve and 1/8" stainless steel tubing on the outlet. Water was boiled for ~ 1 h with the valve open and steam released through the tubing. The valve was then closed and the container was chilled and submerged into a cold bath to freeze the water. The amount by which the container was submerged was gradually increased to ensure slow ice formation. After freezing was complete, typically over the course of 6–8 h, the container was placed under running tap water to make it possible to remove the ice block from the container. Typically a crack formed across the ice block at that point.

[17] Blank ice tests were performed as follows. Samples of the same dimensions as the actual samples were cut from a block of blank ice. A block of blank ice yielded two samples. All the processing and measurement steps remained the same, except that after evacuating the flasks a known amount of standard gas was added into the flasks after which they were closed off. This amount of gas (~ 45 torr) was intended to be similar to the amount of air in a sample. The ice was then melted and refrozen as for the actual samples, followed by measurements.

[18] Uncertainty of the ice core methane measurements arises from two factors: the measurement itself and the gas extraction from the ice. The measurement uncertainties are due to the noise in the gas chromatograph, integration of the peak area, measurement of the pressure of gas in the sample loop, and uncertainty of the peak area/pressure calibration. Gas extracted from each piece of ice was measured four times, yielding an overall precision of ~ 2 ppb. A calibration line based on eight points was established independently each day yielding an R^2 value of ~ 0.9999 . Because measurements for the duplicate pieces of ice agree between each other also within ~ 2 ppb, it can be concluded that (1) our extraction procedure does not introduce additional random noise and (2) methane in ice is homogenous; that is, there are no real offsets in methane concentrations horizontally.

[19] Blank experiments showed a mean value of ~ 4 ppb, which indicates that our absolute methane concentration values may be uniformly off by 4 ppb, perhaps due to adsorbed methane on the walls of the line or some other subtle effect. We did not apply a correction for that effect

because we felt the technique of the blank experiments themselves needed to be refined. The concern is that we cannot be totally sure that all methane was removed during the preparation of the air-free ice used in blank experiments.

[20] Later work (E. Brook et al., manuscript in preparation, 2009) established that a small correction to the absolute methane concentration data is needed to account for the greater solubility of methane versus the main constituents of air, N_2 , O_2 , and Ar. This correction is currently determined to be 1.017 ± 0.006 (i.e., measured concentration should be increased by 1.7%) to compare to true atmospheric values. The data are internally consistent though, and changes in concentration determined from the data are not affected by the correction. We do not make this correction at this time because its absolute magnitude is being constrained further with additional experiments. None of the conclusions of this paper are influenced by not making the correction. Gravitational correction is small ($<1\%$) and not essential for these measurements, and is also omitted here.

3. Results and Discussion

[21] The methane record obtained in this work is shown in Figure 2. We employ the gas age scale from the work of Schwander et al. [1997] as discussed below. We quantify the changes in GISP2 methane at the D-O events 19, 20, and 21 at 90, 114, and 224 ppb (a 20, 26, and 45% increase, respectively) (Table 2). Our choice of reference points for this calculation is shown by arrows in Figure 3, which shows the methane data versus depth at those transitions. If the reference points are accepted the uncertainty of the above values for the methane changes are small, about 2 ppb (equivalent to $\sim 2\%$ or less). These data confirm previous suggestions of a substantial difference between methane change at D-O 21 versus D-O 19 and D-O 20 [Brook et al., 1996] despite roughly similar magnitude of the ice isotopic signals for these events (Figure 2). Published results based on gas isotopes from GRIP and NGRIP ice cores report that the magnitudes of D-O events 19 and 20 were 16°C and 11°C respectively [Lang et al., 1999; Landais et al., 2004]. If the same $\delta^{18}\text{O}_{\text{ice}}$ -temperature relationship held during the neighboring D-O 21, its $\delta^{18}\text{O}_{\text{ice}}$ change would translate into a magnitude of temperature change similar to D-O 20. Brook et al. [1996] suggested that the methane response to D-O events was modulated by insolation changes, explaining the weak response to D-O 19 and D-O 20 as a result of declining Northern Hemisphere insolation, and presumably weakening impact on the Asian monsoon and high-latitude summer warmth. The exact mechanism of interaction between the orbital and millennial timescales is unclear, however.

[22] These results are in general agreement with the previous work done on the GRIP ice core for D-O 19 and 20 [Flückiger et al., 2004]. The methane change at D-O 21 has not been measured in great detail in other ice cores. The small

Figure 2. Methane record obtained in this work and the most detailed published $\delta^{18}\text{O}_{\text{ice}}$ record [Grootes and Stuiver, 1997]. Also shown are residuals for methane and $\delta^{18}\text{O}_{\text{ice}}$ when the main trend is subtracted out. Note that duplicate points are shown for methane and not just the averages. Gaussian smoothing was employed to obtain residuals. A portion of this full methane data set (between 82 and 86 ka) has been reported previously in a paper that discussed a previously unknown abrupt event in methane at ~ 84.5 ka [Grachev et al., 2007].

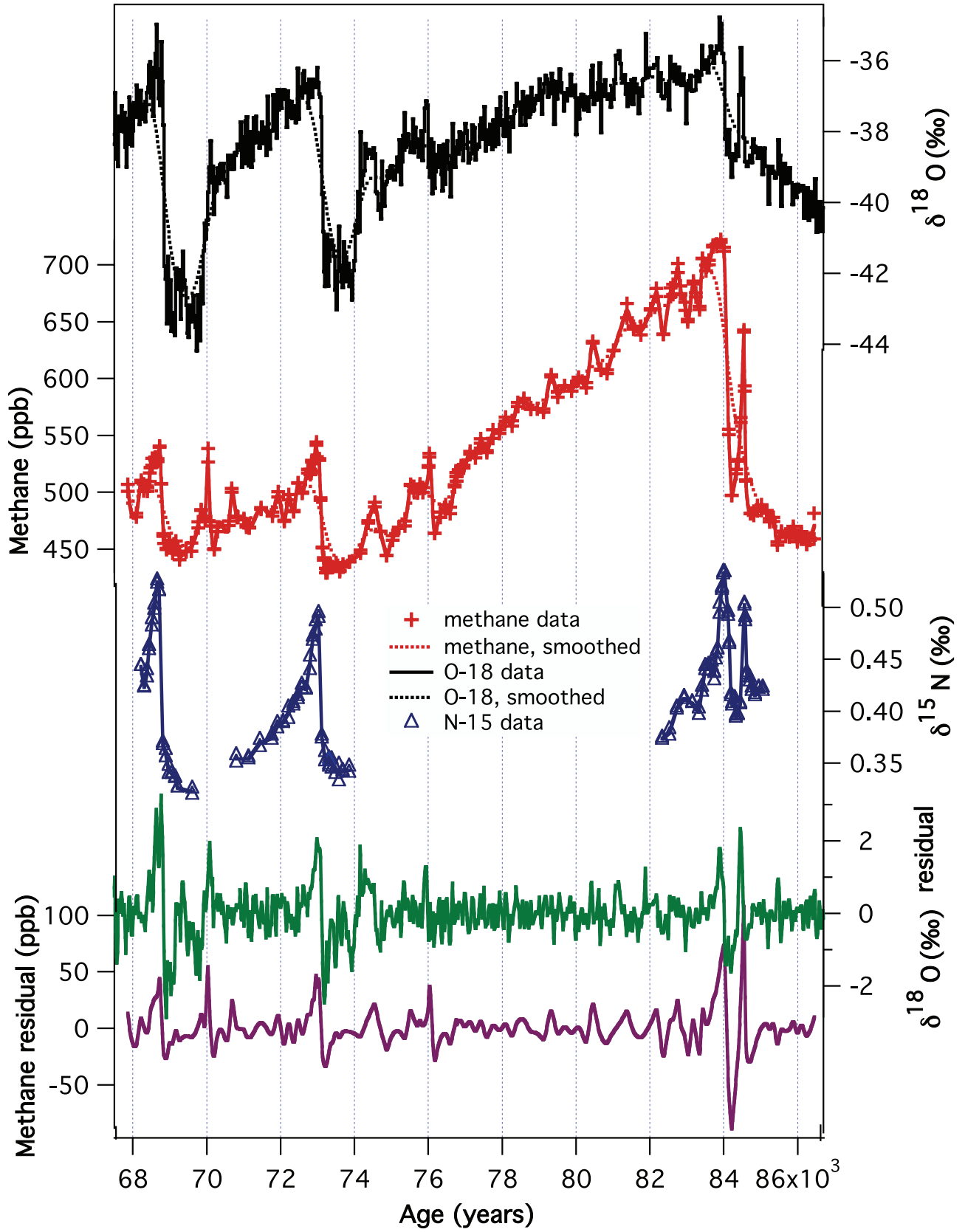


Figure 2

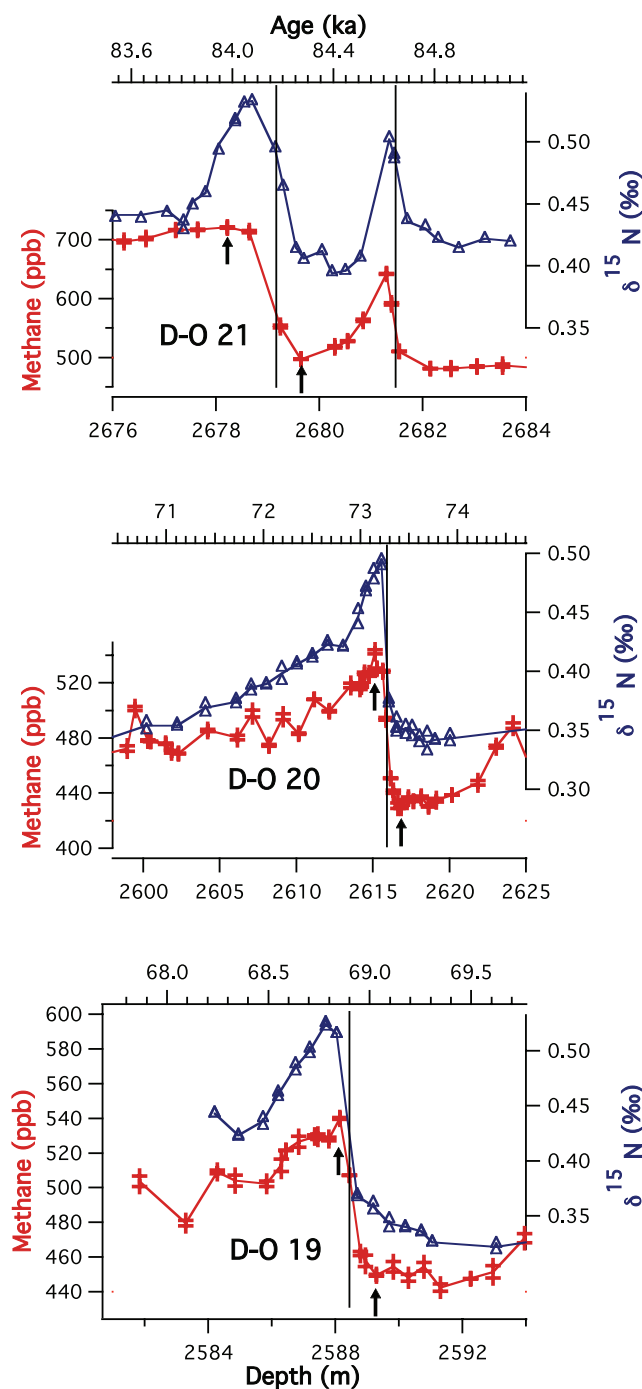


Figure 3. Methane and $\delta^{15}\text{N}$ versus depth at times of abrupt transitions associated with the onset of D-O events 19, 20, and 21. Procedure of $\delta^{15}\text{N}$ measurements for D-O events 19 and 20 is reported in detail by Grachev [2004]. Data for the onset of D-O 21 are from Grachev *et al.* [2007].

section of GISP2 containing the methane reversal at the onset of D-O 21 was described previously by Grachev *et al.* [2007].

[23] The measurement uncertainty of this study is generally small compared to the typical changes observed in Figure 2 (~ 20 ppb or more), and therefore the small short-term changes can be identified with confidence. The new data

reported here allow identification of three abrupt methane increases in addition to the ones associated with the onsets of D-O events 19, 20, and 21. In Table 2 we identify the timing, duration, and magnitude of the six abrupt methane increases. We define duration as the time it takes to reach the full amplitude of the change, but emphasize that half or more of the change usually occurs much faster than that full duration. It should also be kept in mind that, for example, doubling of the global methane source does not lead immediately to the doubling of methane concentration owing to the time required for the atmospheric methane concentration to reach new steady state following a source change. In addition, the firm induces smoothing of abrupt atmospheric changes, because air of different ages mixes by diffusion prior to being entrapped in the ice [Schwander *et al.*, 1988]. Therefore, the actual changes in methane emissions probably happened substantially faster than what is observed for even the fastest abrupt events seen in Figure 2. The existence of three large abrupt climate warmings and associated methane fluctuations during the time period of this study that are not associated with recognized D-O events suggests that such events are more common than the classic definition of D-O event stratigraphy implies. In addition to the significance of this variability for understanding links between climate and biogeochemistry, these variations should be useful for high-resolution correlation of ice core chronologies on submillennial timescales.

[24] A close look at the new methane record suggests a persistent short-term variability. Changes of ~ 20 ppb are superimposed on larger features and permeate the entire record (Figure 2). The abrupt changes noted above appear to be manifestations of this more general variability, perhaps amplified by some unknown mechanism.

[25] We now turn to comparing the new methane record to the most detailed available published $\delta^{18}\text{O}_{\text{ice}}$ record (Figure 2). To enable the comparison we used a modified version of the GISP2 gas age scale. We used the gas age-ice age difference determined by Schwander *et al.* [1997] assuming the lower value of the sensitivity coefficient of $\delta^{18}\text{O}_{\text{ice}}$ to temperature used in that study ($\alpha = 0.33$ ‰/°C), which we believe is a better average value for this time than the canonical spatial value of 0.67 ‰/°C. The age scale was then further adjusted by -160 years (gas ages reduced by 160 years) to provide a better match between timing of changes between methane and $\delta^{18}\text{O}_{\text{ice}}$ at the onset of events D-O 19, 20, and 21. This correction is derived from the relationship between $\delta^{15}\text{N}$ of N_2 and $\delta^{18}\text{O}_{\text{ice}}$, the former a recorder of abrupt temperature change in the gas phase, the latter a recorder of the same events in the ice matrix [Severinghaus *et al.*, 1998; Severinghaus and Brook, 1999]. The 160 year offset is not surprising given uncertainties in the gas age scale [Schwander *et al.*, 1997]. To illustrate the point that nitrogen isotope data show that the Greenland temperature and methane changed essentially synchronously at that time, we plot $\delta^{15}\text{N}$ of N_2 and methane for these time intervals on a depth scale (Figure 3), which bypasses the interrelated unknowns needed to construct a gas age scale.

[26] Previous work on the GRIP ice core [Flückiger *et al.*, 2004] has already shown that the onset of D-O events 19 and 20 was synchronous in trapped air $\delta^{15}\text{N}$ (Greenland

Table 2. Abrupt Increases in Methane From This Study Between 86 and 68 ka

Onset of Abrupt Increase (ka)	Initial Methane Concentration (ppb)	Amount of Increase (ppb)	Amount of Increase (%)	Duration (years)
84.7	481	160	33	210
84.2 (D-O 21)	497	224	45	350
76.2	462	71	15	140
73.2 (D-O 20)	430	114	26	280
70.2	450	81	18	140
69.0 (D-O 19)	450	90	20	210

temperature) and in methane. Here and in the discussion below the word synchronous implies synchronous within sampling resolution, i.e., within one to a few decades. Our previous paper [Grachev *et al.*, 2007] reported that the changes at the onset of D-O 21 and at the preceding sharp climate event were synchronous as well. The present study confirms from high-precision $\delta^{15}\text{N}$ data that events 19 and 20 were indeed very nearly synchronous with the methane shifts. The wealth of combined $\delta^{15}\text{N}$ /methane data gathered for the Last Glacial [Severinghaus *et al.*, 1998; Severinghaus and Brook, 1999; Flückiger *et al.*, 2004; Huber *et al.*, 2006; Grachev *et al.*, 2007] indicates very systematic behavior for all abrupt events of the last glacial showing that methane and $\delta^{15}\text{N}$ change nearly synchronously. Both are measured in air extracted from ice and have the same age (except for a ~ 1 year difference owing to the different diffusivities of

methane and nitrogen) [Severinghaus *et al.*, 1998], therefore it is certain that the observed signals are synchronous. Hence, a picture appears of widespread geographical areas transitioning into a different climate regime all at once. Independent work of Ruth *et al.* [2007] based on high-resolution records of $\delta^{18}\text{O}_{\text{ice}}$ and dust from the NGRIP ice core indicates that “during Dansgaard-Oeschger events North Atlantic region temperature and east Asian storminess were tightly coupled and changed synchronously within 5–10 years with no systematic lead or lag.”

[27] In addition to the obvious visual matches between variations in the new methane record and $\delta^{18}\text{O}_{\text{ice}}$ (Figure 2), cross-spectral analysis shows significant coherence. As also shown by Wunsch [2006] for GRIP ice core and methane data for 10–50 ka the power spectrum for both variables is red (Figure 4). Significant coherence is found for periods longer

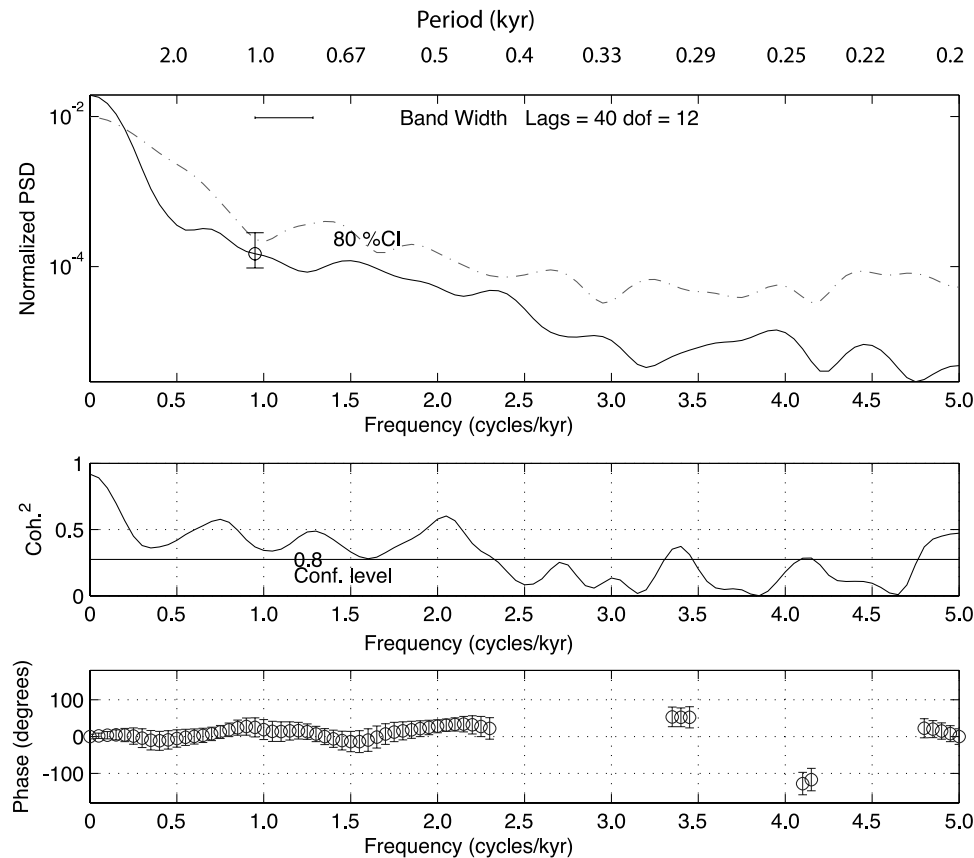


Figure 4. Cross-spectral analysis of the methane record and $\delta^{18}\text{O}_{\text{ice}}$ records using a lagged cross-correlation function with 40 lags and 12 degrees of freedom [Jenkins and Watts, 1968]. The (top) error bar and (middle) horizontal line indicate the 80% confidence interval for the power spectrum and coherence, respectively. Dashed line is methane; solid line is $\delta^{18}\text{O}_{\text{ice}}$.

than about 500 years, also similar to findings of *Wunsch* [2006], and demonstrating the connection between millennial variability in methane and $\delta^{18}\text{O}_{\text{ice}}$. This coherence supports the hypothesis of a connection between local temperature variations in Greenland and the broader climate-related factors that control the methane budget, underscoring the large-scale reach of the events recorded in the ice core $\delta^{18}\text{O}_{\text{ice}}$ isotopic record. The phase plot (Figure 4) shows essentially zero phase offset between the records for periods greater than ~ 500 years, consistent with the $\delta^{15}\text{N}$ of N_2 evidence discussed above, but providing a description of the whole record rather than discrete sections. Figure 2 (bottom) shows the residuals of both records when the main trend is subtracted out, helping to illustrate the persistence of short-term variability in both records.

[28] Inferences of a connection between events in the ice cores and climate change in areas remote from Greenland have also been drawn from speleothem deposits in central China and elsewhere, and the similarity of the Chinese speleothem oxygen isotope records and the ice core methane record has been noted by several authors [e.g., *Jiang et al.*, 2005; *Kelly et al.*, 2006a]. There are few high-resolution speleothem records that cover the time interval of this study, but those that do [*Xia et al.*, 2007; *Johnson et al.*, 2006; *Kelly et al.*, 2006b; *Wang et al.*, 2008] clearly show the main features associated with the D-O events 19, 20, and 21, with even possibly the few smaller features of our record being manifested. In contrast to the Greenland ice core $\delta^{18}\text{O}_{\text{ice}}$ record, but similar to the methane record, the Chinese cave deposits show a clear decrease in amplitude of the $\delta^{18}\text{O}$ rainfall proxy progressing from events A21-A19 (the D-O 21–19 equivalents in the cave records) [*Wang et al.*, 2008]. This suggests an interaction between the orbital forcing and hydrological response to the D-O events. A similar pattern is evident in the West African monsoon proxy data from *Weldeab et al.* [2007], which can be interpreted as an indication that the response of river runoff from western equatorial Africa to D-O events 21–19 declined over this interval. A possible mechanism for these common observations is the gradual displacement of the intertropical convergence zone (ITCZ) rainfall belts southward as Northern Hemisphere summer insolation decreased, perhaps related to ice sheet growth and impacts on atmospheric circulation [*Chiang et al.*, 2003]. How the abrupt warming in Greenland interacts with this more gradual timescale due to orbital forcing is not clear, but perhaps warming in the North Atlantic drives a reversal in the overall ITCZ migration, and/or influences summer monsoon rainfall by lowering sea level pressure over Asia [*Hostetler et al.*, 1999], with the response set by the overall insolation state.

4. Conclusions

[29] 1. We documented extremely tight correspondence between methane and $\delta^{18}\text{O}_{\text{ice}}$ at millennial to multicentennial timescales. This observation suggests that the climatic link between Greenland (local temperature, reflected by $\delta^{18}\text{O}_{\text{ice}}$) and broad methane-producing regions (boreal regions, tropics, or both) is extremely sensitive: rather small, short-term changes in one are paralleled closely by the other, and

the link between the two apparently persists throughout the entire $\sim 18,000$ years of this study in spite of the fact that the background climate conditions (ice sheet extent, sea level, insolation, etc.) varied dramatically.

[30] 2. We provide additional confirmation that Greenland temperature and methane at abrupt transitions change essentially synchronously at the onset of D-O 19 and 20 (this work), in agreement with *Flückiger et al.* [2004]. A similar result was reported recently for the onset of D-O 21 and the preceding short-lived sharp warming at ~ 84.5 ka [*Grachev et al.*, 2007]. Therefore, it appears that the early glacial period, which in itself was characterized by greatly differing climates for the times of D-O 21 versus D-O 19 and 20, was subject to the same climatic mechanism that drove abrupt changes at deglaciation [*Severinghaus et al.*, 1998; *Severinghaus and Brook*, 1999] and at full glacial conditions [*Huber et al.*, 2006], when changes were also found to be near synchronous.

[31] 3. Methane signals are modulated as was suggested by *Brook et al.* [1996], in that the size of the D-O events in methane is not directly related to their size in $\delta^{18}\text{O}$, but is modulated according to the value of the Northern Hemisphere summer insolation. Climate records that record the Asian and African monsoon show similar patterns.

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