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Greenland temperature, climate change, and human society during the last 11,600 years

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during the last 11,600 years

A dissertation submitted in partial satisfaction of the requirements for the degree of

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in

Oceanography

by

Takuro Kobashi

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2007
The Dissertation of Takuro Kobashi is approved, and it is acceptable in quality and form for publication on microfilm:

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Chair

University of California, San Diego

2007
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PUBLICATIONS

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ABSTRACT OF THE DISSERTATION

Greenland temperature, climate change, and human society during the last 11,600 years

by

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University of California, San Diego, 2007
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Following the last glaciation, the climate of the last 11,600 years (Holocene) has been warmer, wetter, and more stable, fostering development of human agriculture and civilization around the globe. This thesis focuses primarily on the climatic variation of the last 11,600 years based upon an ice core reconstruction of Greenland temperature and atmospheric gases. Then, prior studies of associated impacts on human society are briefly reviewed.

This study employs high-precision analyses of argon and nitrogen isotopes in air-bubbles in a central Greenland ice core (GISP2). With a new method to analyze nitrogen and argon isotopes simultaneously and a new algorithm to calculate surface temperature, various climatic changes during the past 11,600 years are revealed. A previously identified abrupt climate change around 8,200 years ago is characterized by
an abrupt cooling of $3.3 \pm 1.1 \, ^\circ C$ in less than 20 years with a simultaneous decrease of atmospheric methane concentration. A newly identified abrupt warming of $4 \pm 1.5 \, ^\circ C$ at 11,270 B.P. is found at the end of a cooling known as the Preboreal Oscillation, which was the last large abrupt warming event in the record. This may suggest that the oceanic circulation condition finally reached a warm and stable Holocene mode after this event. The Greenland temperature history of the last 1000 years clearly shows the “Medieval Warm Period” and “Little Ice Age” with persistent multidecadal temperature fluctuations. A strong correlation is observed between Northern Hemisphere temperature and Greenland temperature with a possible lag of Greenland temperature by 20-30 years, suggesting that the two share common causal factors such as volcanic and solar forcing for the last 1000 years.

It has been suggested that these climatic events had impacts on past human societies. As the Earth’s environment is expected to undergo a substantial change in the future, the past history of climate and society may provide valuable lessons.
Introduction
The last 11,600 years was a critical period for human society. After the last glaciation, the global environment rapidly improved for human habitation permitting the development of agriculture, which eventually led to accumulation of knowledge and urbanization. During this period, human societies around the globe developed quasi-continuously by increasing population and expanding their habitat. Although the basic relationship between nature and humans has not changed, human’s perception toward nature drastically changed through time. Current human society faces unprecedented environmental problems, making the study of the past particularly useful as a potential source of insight. This thesis explores the variation of past climate change through Greenland temperature as a main focus, using a new and more accurate temperature indicator, and it reviews published studies of climatic impacts on human society during the last 11,600 years. The thesis closes with a discussion of possible implications for human society.

Greenland temperature is reconstructed here using nitrogen and argon isotopes in air-bubbles in ice. The method was originally developed by Severinghaus et al. (1998), and it is modified here to measure these isotopes simultaneously in the same sample [Kobashi et al., submitted-b]. The precision of temperature estimates from these isotopic measurements is substantially improved [Kobashi et al., submitted-b]. Here, the basis of the methodology is explained.

Nitrogen and argon isotopes in the atmosphere are constant for $>10^5$ years [Allegre et al., 1987; Mariotti, 1983]. Therefore, the isotopic deviation observed in ice cores can be attributed to processes in the firn layer (unconsolidated snow). Isotopic fractionation by gravitation and temperature gradients at the top and bottom of the firn
layer is known to occur [Craig et al., 1988; Severinghaus et al., 1998]. Two independent isotopic measurements allow the separation of these two effects, thus providing information about the temperature gradient in the firn layer in the past [Severinghaus and Brook, 1999]. This gradient reveals temporal change in surface temperature due to the thermal inertia of the underlying ice. As a complicating issue, it is increasingly clear that those gases with smaller molecular diameters, including argon, leak out of ice during bubble close-off and during/after coring [Huber et al., 2006; Severinghaus and Battle, 2006]. Some evidence suggests that this process affects isotopic composition of gases [Severinghaus et al., 2003]. Although conclusive evidence for the gas-loss processes and impacts on isotopes are difficult to obtain at this point, robust climatic information can nonetheless be retrieved from the data and is presented in this thesis.

In the first chapter [Kobashi et al., submitted-b], which is a collaborative work with Jeff Severinghaus and Kenji Kawamura, a new method is described for simultaneous measurements of argon and nitrogen isotopes, and its application to records of the last 11,600 years. This chapter also includes descriptions of data quality, statistics, and discussion of impacts of gas loss on isotopes. This chapter is currently under revision for publication in the Journal of Geophysical Research -Atmospheres.

In the second chapter [Kobashi et al., 2007], which is a collaborative work with Jeff Severinghaus, Edward Brook, Jean-Marc Barnola, and Alexi Grachev, an abrupt climate change 8,200 years ago is investigated with ice core records of nitrogen isotopes and methane concentration. The high precision of the nitrogen and methane data permitted deconvolution of primary signals from the confounding effects of gas
diffusion and bubble close-off processes. These signals provide qualitative surface temperature and methane evolution during the event. The characterization of the timing of the event in Greenland and over a broad hemispheric area are made possible by combined interpretation of nitrogen and methane data. This chapter is in press in *Quaternary Science Reviews*.

In the third chapter [Kobashi et al., submitted-a], which is a collaborative work with Jeff Severinghaus and Jean-Marc Barnola, an abrupt climate change around 11,270 B.P. is described. This abrupt warming in Greenland occurs at the end of a century-long cooling trend. Notably, in this chapter a new method is introduced to calculate surface temperature from the temperature gradient derived from isotope measurements and accumulation rate. This paper is currently under revision for publication in *Earth and Planetary Science Letters*.

In the fourth chapter [Kobashi et al., submitted-c], which is a collaborative work with Jeff Severinghaus, Jean Marc Barnola, Kenji Kawamura, and Tara Carter, the last 1000 years of Greenland temperature is reconstructed at high resolution (10 yr). Special efforts are made in this chapter with replicate sampling to increase confidence and precision of data. Using the new method for surface temperature calculation, multidecadal to multi-centennial temperature fluctuations are clearly found, some of which are widely known as the “Little Ice Age” and the “Medieval Warm Period”. The documentary evidence is used to explore the relationship between climate and people in Greenland and Iceland. The chapter is in preparation for publication in a broad-interest journal.
The final chapter describes the general trend of climate for the last 11,600 years with isotopic data and explores the application to human society in the late Holocene. In addition, this chapter reviews previously studied climatic events, which are known to have caused societal impacts during the past 11,600 years. The relation between climate and people in the past, present, and future is explored. The chapter is concluded with possible implications for future human society.
References


Severinghaus, J.P., A. Grachev, B. Luz, and N. Caillon, A method for precise measurement of argon 40/36 and krypton/argon ratios in trapped air in polar

Chapter I

Argon and nitrogen isotopes of trapped air in the GISP2 ice core during the Holocene epoch (0-11,500 B.P.): Methodology and implications for gas loss processes
Abstract

Argon and nitrogen isotopes of air in polar ice cores provide constraints on past temperature and firn thickness, with relevance to past climate. We developed a method to simultaneously measure nitrogen and argon isotopes in trapped air from the same sample of polar ice. This method reduces the time required for analysis, allowing large numbers of measurements. We applied this method to the entire Holocene sequence of the GISP2 ice core (82.37m-1692.22m) with a 10-20 year sampling interval (670 depths). $\delta^{40}$Ar and $\delta^{15}$N show elevated values in the oldest part of the data set, consistent with a thicker firn layer and increased temperature gradient in the firn due to the legacy of the abrupt warming at the end of the Younger Dryas interval and the gradual warming during the Preboreal interval (11.5-10.0 ka). The Preboreal Oscillation and the 8.2k event are clearly recorded. The data show remarkable stability after the 8.2k event.

Available data suggests that post-coring gas loss involves two distinct types of fractionation. First, smaller molecules with less than a certain threshold size leak through the ice lattice with little isotopic fractionation. Second, gas composition changes via gas loss through microcracks, which induces isotopic fractionation. These two gas-loss processes can explain most trends in our data and in other ice core records. We also employed krypton isotopes ($^{86}$Kr/$^{82}$Kr) to further investigate gas-loss processes, because Kr is expected to be insensitive to gas loss fractionation due to its large atomic size. Preliminary data show less gas-loss fractionation in Kr than in Ar as expected, but more data are required to constrain gas-loss mechanisms.
1. Introduction

Polar ice core studies have provided much information about past climate change owing to their continuity and unique archive of past atmosphere (e.g., CO$_2$ and CH$_4$) [Siegenthaler et al., 2005; Spahni et al., 2005]. Nitrogen and argon isotopic ratios in air trapped in polar ice are relatively new proxies containing information about the past firn layer (unconsolidated snow), including the temperature gradient between top and bottom and the firn thickness [Craig et al., 1988; Caillon et al., 2003; Schwander, 1988; Severinghaus et al., 1998]. These parameters are especially powerful tools to investigate past abrupt climatic changes [Huber et al., 2006b; Kobashi et al., accepted; Landais et al., 2005; Leuenberger et al., 1999; Severinghaus and Brook, 1999; Severinghaus et al., 1998].

The firn layer can be subdivided into three sections in terms of gas flows [Severinghaus and Battle, 2006; Sowers et al., 1992]. The first one is a convective zone where gases are freely mixed with the atmosphere by wind pumping [Colbeck, 1989, Kawamura et al., 2006]. Thus, no gas fractionation occurs in this section. In the current central Greenland firn layer, the convective zone is estimated to be 0-2 m. The second section is a diffusive zone in which gases are nearly in diffusive equilibrium. In this section, gas movements are governed primarily by molecular diffusion, and gas fractionation occurs. At central Greenland, the diffusive zone is estimated to be 65-70m thick [Schwander et al., 1993]. The third section is a non-diffusive or lock-in zone. In this zone (~10m), the vertical mixing of the gas is inhibited by sealing of dense winter layers, but horizontal mixing still occurs in
summer layers (which are less dense than winter layers). Eventually, all the bubbles are closed at the bottom of the lock-in zone.

Gases in the firn layer are fractionated by two mechanisms, gravitational fractionation and thermal diffusion \cite{Severinghaus et al., 2003}. The gravitational fractionation is primarily governed by the depth of the diffusive column and the mass difference of gases \cite{Craig et al., 1988; Schwander, 1989}. On the other hand, thermal fractionation is caused by a temperature gradient between top and bottom of the diffusive column \cite{Severinghaus et al., 1998}. The magnitudes of fractionation for a given temperature gradient are gas-dependent, and can be calibrated by laboratory experiments \cite{Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b}. The measurements of nitrogen and argon isotopic ratios in trapped air in ice allow us to separate the two effects, and provide us with the past temperature gradient and thickness of firn diffusive column \cite{Caillon et al., 2003; Severinghaus and Brook, 1999}.

Recent studies \cite{Huber et al., 2006a; Severinghaus and Battle, 2006} introduced a third mechanism that alters the composition of gases in firn and ice core air. During the bubble close-off process, smaller molecules such as neon, oxygen, and argon with less than a certain threshold molecular size (~3.6 Å) leak out through the ice lattice with little isotopic fractionation. A similar gas loss process likely occurs during coring and storage \cite{Bender et al., 1995; Ikeda-Fukazawa et al., 2005}, which appears to be accompanied by isotopic fractionation of Ar and O₂ especially for poor quality ice samples with many fractures \cite{Severinghaus et al., 2003}. These fractionation effects can confound the temperature and firn thickness signals of
interest. Therefore it is critically important to understand the gas-loss process in order to use gases trapped in ice cores for paleoclimatic studies.

We investigate the potential impacts of gas loss on argon isotopes by measuring krypton isotopes, which have a larger molecular size and are thus less likely to leak out from ice [Severinghaus and Battle, 2006]. In this paper, we describe the method and report argon and nitrogen isotopic data and the argon/nitrogen ratio for the past 11,500 years. We pay special attention to the impacts of gas loss on isotopic composition. The climatic interpretations of these data are described in separate papers for the abrupt climate change 8,200 years ago [Kobashi et al., in press], and for the Preboreal Oscillation [Kobashi et al, submitted].

2. Material

We used the Greenland Ice Sheet Project 2 (GISP2) ice core in the depth range of 82.37m-1692.22m for this study. This range corresponds to the Holocene epoch (0-11,500 B.P.) on the gas-age scale (Meese/Sowers timescale; Meese et al. [1997]). The GISP2 ice core was drilled at central Greenland (72° 36’N 38° 30’W; 3203 masl) during the period 1989-1993, and since then the ice core has been stored at -35 °C in the National Ice Core Laboratory (NICL), Denver, Colorado USA. We cut ice samples in a cold room (-22°C) at NICL, and shipped samples in insulated boxes with eutectic packs to Scripps Institution of Oceanography (SIO), keeping the samples below -20 °C. The experiments were conducted in four different time periods, denoted Periods I-IV (see Table 1).
The resolution of the samples is 10-20 years. For the depth interval 1359.95m-1458.95m, in which the 8.2k climatic event is recorded [Kobashi et al., accepted], we conducted higher resolution analyses with a 10-year spacing. For this interval we measured up to six samples for each depth (Fig. 1). For the last millennium [Kobashi et al., in prep.], we also conducted high resolution analyses with a 10-year interval, and we analyzed ~3 samples for each depth (Fig. 1). For other periods, analyses were conducted with a 20-year interval and a single sample for each depth (Fig. 1). The total number of samples is 1006 for 670 depths.

3. Method

We developed a new method to measure argon and nitrogen isotopes in the same air sample (previously it was two separate experiments from two samples), substantially reducing the time required for analyses. The method uses a heated copper mesh (500 °C) to remove molecular oxygen, which contains an isotopomer ($^{18}$O$^{18}$O) that isobarically interferes with $^{36}$Ar during the mass spectrometric measurements (Fig. 2). Also, the simultaneous analyses substantially reduce the errors on the difference of nitrogen and argon isotopes, which is used to estimate the past temperature gradient ($\Delta T$) in the firm layer (see later discussion). Many steps in the experiment and apparatus are adapted and developed from previous studies [Caillon et al., 2002; Severinghaus and Brook, 1999; Severinghaus et al., 2003; Severinghaus et al., 1998]. The method for krypton isotopic measurement follows the getter method [Severinghaus et al., 2003] but with a larger amount of ice for each sample (~700 g).
We made significant changes to the method after Period I involving the sample size, extraction line, and mass spectrometer. First, we increased the size of ice samples from 50g to 100g. Second, we constructed a special vacuum extraction line with four evacuation ports, having a reduced dead volume and number of connections. Third, we changed the mass spectrometer from a ThermoFinnigan DeltaPlus XP to a MAT252. We found that the DeltaPlus XP has worse linearity than the MAT252, which introduced larger corrections and so errors in the data. With these and other improvements, we obtained better precision (see later discussion).

About 50g of ice (for Period I) or 100g of ice (for Period II-IV) was cut for each sample. We found that precision was improved by having similar sample size for each analysis during mass spectrometry. To average out slight gas differences between summer and winter layers (Severinghaus and Battle, 2006), the samples are taken as a 30cm long piece for shallower depths (above ~820m), which is slightly more than the average annual layer thickness of shallow core in central Greenland [Alley et al., 1993]. We used a 10-20 cm long ice sample for the deeper part of the core. About 5mm of the outer layer of the ice sample is shaved off with a clean bandsaw prior to analysis, because gas composition may be altered in this layer during/after coring. Then, the samples are cut into small pieces to fit into a pre-cooled vacuum extraction vessel. These steps are conducted in a cold room with temperature below -20 °C at SIO. Then, samples in a cold box are brought to the laboratory for extraction. Two pre-cooled glass-covered magnetic stirrers are placed in the vessels to agitate the water during the subsequent gas extraction process.
Four vacuum extraction vessels, each with ice samples, are bolted on Conflat evacuation ports with copper gaskets. All four samples are simultaneously evacuated for 40 minutes as vessels are kept cooled at -20 °C by cold ethanol. Sublimation during this evacuation process cleans the surface of the ice samples. Then, four valves connected to the vessels are closed, and the cold ethanol bath is removed. One vessel is warmed with hot water to melt the ice and to release trapped air. Before the ice completely melts, the hot water is removed to keep melt water at or below room temperature to avoid boiling during sample air transfer. After the melting is completed, the pressure of the line is checked for leaks, and the sample air transfer is started by opening the valve connected to the vessel. The magnetic stirrers in the vessel are used to agitate the water to facilitate degassing. During the transfer, air samples pass first through two cryotrap, heated copper, and then a third cryo trap in sequence (Fig. 2). The first trap (Trap 1 in Fig. 2) is at about -100 °C with a mixture of ethanol and liquid nitrogen, and removes water vapor from the sample. The second trap (Trap 2 in Fig. 2) at -196 °C with liquid nitrogen removes organic contaminants and CO₂. Next, the sample air passes through 5 linear cm of heated copper wool (Fisher) in a 9mm O.D. quartz tube at ~500 °C, which removes oxygen (O₂). The last trap (Trap 3 in Fig. 2) at -196 °C with liquid nitrogen, removes potential contaminants generated by the heated copper including CO₂. We found that the mass spectrometer (Finnigan MAT252) became unstable without the last trap, probably due to unknown contaminants. Importantly, the cryotrap are made of glass, to minimize surface adsorption of nitrogen and argon; we found that stainless steel traps at -196 °C adsorbed an unacceptable amount of gas and retained heavier isotopes preferentially. The sample
air is collected in a stainless dip tube immersed in a dewar of liquid helium at 4 °K. The transfer takes 25 minutes. During the transfer, we maintain pressure below 0.5 torr before the last trap by adjusting air flow. This permits full removal of the oxygen; higher pressures were observed to cause oxygen breakthrough. The residual pressure (normally <1*10^{-3} torr) is checked after the 25-minute transfer. After the transfer, the valve on the stainless dip tube is closed, and the dip tube is removed from the liquid helium. The dip tube with ~10cc (STP) of sample air is kept overnight for the complete homogenization of gases. After four samples, the copper wool is regenerated by exposing it to hydrogen gas at 500 °C, and the water produced is pumped away.

The argon isotopic ratio (mass 40/36), nitrogen isotopic ratio (mass 29/28), and the argon/nitrogen ratio (mass 40/29) were measured with mass spectrometers at SIO (ThermoFinnigan DeltaPlus XP for Period I, and ThermoFinnigan MAT 252 for Periods II-IV). The mass spectrometry follows Severinghaus et al. [2003], with slight modifications to accommodate the large amount of nitrogen in the samples. The mass 28 beam amplifier is fitted with a 10^7 ohm ceramic resistor (Caddock) with a low coefficient of temperature sensitivity, and an appropriate capacitor (provided by Hans-Jürgen Schlüter of ThermoFinnigan, Bremen, Germany). Typical beam currents for masses 28 and 40 were 100 and 2.5 nA, respectively.

Slight corrections to the data were made for pressure differences between sample and standard sides, and for the sensitivity of isotopic measurements to the elemental ratios (the so-called “chemical slope”), following Severinghaus et al. [2003]. One small difference from the technique of Severinghaus et al. [2003] is that research
grade N$_2$ was used for the “chemical slope” calibration, in which tank N$_2$ is added to successive aliquots of Ar, and the $\delta^{40}$Ar is measured.

Isotopic ratios and elemental gas ratios are expressed as a deviation from the present atmosphere with the conventional delta notation for nitrogen, argon, and krypton isotopes and argon/nitrogen ratio, as follows:

$$\delta^{40}\text{Ar} = \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}_{\text{sample}}}/\frac{^{40}\text{Ar}}{^{36}\text{Ar}_{\text{standard}}}-1\right) \times 10^3 \%$$
$$\delta^{15}\text{N} = \left(\frac{^{15}\text{N}}{^{14}\text{N}_{\text{sample}}}/\frac{^{15}\text{N}}{^{14}\text{N}_{\text{standard}}}-1\right) \times 10^3 \%$$
$$\delta^{86}\text{Kr}= \left(\frac{^{86}\text{Kr}}{^{82}\text{Kr}_{\text{sample}}}/\frac{^{86}\text{Kr}}{^{82}\text{Kr}_{\text{standard}}}-1\right) \times 10^3 \%$$
$$\delta\text{Ar/N}_2 = \left(\frac{^{40}\text{Ar}}{^{29}\text{N}_2_{\text{sample}}}/\frac{^{40}\text{Ar}}{^{29}\text{N}_2_{\text{standard}}}-1\right) \times 10^3 \%$$

For routine measurements, we use a standard gas made of commercial tank N$_2$ and Ar in approximately atmospheric proportions [Severinghaus et al., 2003]. Then, the isotopic ratios are normalized to atmospheric composition by a weekly measurement of outside atmospheric air at La Jolla. La Jolla air (LJA) measurements are done similarly to ice core analyses so that any small fractionations during sample measurements should be canceled out during the normalization [Severinghaus et al., 2003].

4. Results

4.1. Reproducibility

The reproducibility of the measurement with this method can be estimated from the weekly atmospheric measurements, and also the pooled standard deviation
(PSD or $S_{pooled}$) of replicate ice samples cut from the same depth in the core

[Severinghaus et al., 2003]. $S_{pooled}$ is defined as the square root of the summed squared deviations of replicates $\delta_i$ from their respective means, divided by the degrees of freedom.

$$S_{pooled} = \sqrt{\frac{\sum_{i,j=1}^{n,m} (\delta_i - \bar{\delta}_j)^2}{n - m}}$$

where $n$ is the number of samples and $m$ is the number of reported means.

Precision for $\delta^{15}$N is comparable to the previous method, ranging from 0.003‰ to 0.005‰, and the precision stayed in this range for all measurement periods (Table 2). The PSD of replicate ice samples appeared to be better than LJA data (Table 2), suggesting that the outside air sampling technique may have introduced a small and variable isotopic fractionation. Precisions for $\delta^{40}$Ar for both LJA and PSD improved after Period I. Several reasons for the improvement can be considered. From Period II onward, we used a special extraction port with fewer connections, and other modifications to reduce the potential for leaks. In addition, we used a different mass spectrometer (ThermoFinnigan MAT252) because the ThermoFinnigan DeltaPlus XP had worse linearity, which imposed a larger correction on $\delta^{40}$Ar data (typical correction for $\delta^{40}$Ar is 0.1-0.2‰, which is one order larger than the value for the MAT 252). From Period II onward, we used twice as much as ice for each analysis. These improvements likely contributed to the better precision. The $\delta^{40}$Ar precision for Period III and IV are as good as the conventional method (Severinghaus et al., 2003). The
precision of $\delta$Ar/N$_2$ for LJA was roughly constant around 0.09‰ throughout the project.

4.2. All data (82.37m-1692.22m)

The very high $\delta^{15}$N and $\delta^{40}$Ar values at the deepest part of the record are a result of an abrupt warming at the end of Younger Dryas [Severinghaus et al., 1998]. The abrupt warming created substantially warmer temperatures at the surface than the bottom of the firn, with the temperature difference reaching ~8 °C [Grachev and Severinghaus, 2005]. From 1700m to 1400m, $\delta^{15}$N and $\delta^{40}$Ar show a gradual decrease, and stabilize from 1400m to 80m. These trends suggest that the temperature gradient in the firn decreased as the bottom of the firn warmed up and approached thermal equilibrium. Warming also caused thinning of the firn layer, reducing the magnitude of isotopic fractionation by gravitational settling. All of these factors caused a gradual decrease of $\delta^{15}$N and $\delta^{40}$Ar. The later stabilities of $\delta^{15}$N and $\delta^{40}$Ar are an indication of the Holocene climatic stability since the last glaciation. Two distinct abrupt climate changes during the Holocene, ‘the 8.2k event’ and ‘the Preboreal Oscillation’ are clearly shown as anomalies in the otherwise smooth $\delta^{15}$N and $\delta^{40}$Ar profiles (Fig. 1).

The $\delta$Ar/N$_2$ data show mostly slightly negative values, as seen in previous work [Severinghaus et al., 2003; Bender et al., 1995]. This is consistent with preferential leakage of Ar relative to N$_2$ during the bubble close-off process [Severinghaus and Battle, 2006] and during core retrieval and storage [Bender et al., 1995]. Notably, the data exhibit a substantial increase to positive values and an enhanced variability between 1100m and 1500m. This can be explained, as described
for other cores by Bender et al. [1995], as being due to gas loss from ice with partially formed clathrates during core retrieval. Gases in ice cores transform their state from gas to solid (clathrate) owing to increasing pressure with depth [Shoji and Langway, 1982]. The transition from gas to clathrate is gradual, due to kinetic or nucleation limitation at the low temperature of the ice, and extends over a transition zone of several hundred meters [Ikeda et al. 1999; Ikeda-Fukazawa et al., 2005; Uchida and Hondoh, 2000]. Within the transition zone, both gas and solid phases coexist in the ice core. Because gases exert so much pressure on the surrounding ice, ice becomes brittle in this zone during core recovery, creating many fractures in ice samples. Deeper ice with gas purely in the clathrate phase is much more stable. Argon gas dissociates from clathrate at a lower pressure than nitrogen gas [Saito and Kobayashi, 1965]. Furthermore, O₂ and by implication argon diffuse through the ice lattice to the growing clathrate more rapidly than nitrogen [Ikeda et al., 1999; Uchida and Hondoh, 2000]. Therefore, in the transition zone the gas becomes nitrogen-rich and the clathrate becomes argon-rich.

The substantial δAr/N₂ increase and enhanced variability from 1100m to 1500m can be explained by the fact that during the gas loss process nitrogen leaks out from the nitrogen-rich gas phase, and so the total gas (gas + clathrate) becomes argon-rich in this zone. Especially high fracture concentrations in this zone likely contribute to mass-dependent fractionation, rather than size-dependent fractionation by permeation through the ice lattice (see later discussion). The increases in variability of δAr/N₂ suggest that the nature of the gas loss process in this depth range is highly variable. This abnormal increase of δAr/N₂ and also δO₂/N₂ in the gas-clathrate
transition zone is also found in other ice cores [Bender et al., 1995; Ikeda-Fuakzawa et al., 2005].

Total air content (TAC) in ice cores is known to be affected by the altitude of the ice sheet [Raynaud et al., 1997], and the temperature [Martinerie et al., 1992] among other variables. Our TAC data set shows several small shifts with depth (Fig. 1). As these shifts coincide with different periods of measurements, they are likely artifacts caused by calibration problems. As we did not intend to use the TAC data for purposes other than assessing the quality of the data, we do not proceed to interpret the data. However, we note that at shallow depths (80-100m) air content decreases by 20-30% due to incomplete closure of bubbles in the ice-firn transition zone (Fig. 1). These samples may have been affected by artifactual enrichment of heavy isotopes due to partial gas loss during pumping under vacuum, and so isotopic data from these samples should be interpreted with caution.

We made multiple replicate analyses for some depth intervals because of their climatic importance. These replicates provide an opportunity to assess the data quality. The depth range 82.2m-316.77m corresponds to the last millennium (the climatic interpretation is in [Kobashi et al., in prep.]), and the depth range 1359.95m-1458.95m corresponds to the 8.2k event (the climatic interpretation is in [Kobashi et al., in press]). We made duplicate analyses sporadically in the depth range of 1245.1m-1346.88m.
4.3. Depths from 1359.95m-1458.95m

Samples in this depth range were analyzed during Period I when the method was first applied. \( \delta^{15}\text{N} \) and \( \delta^{40}\text{Ar} \) clearly depict the abrupt climate change 8,200 years ago (Fig. 1 and 3) [Kobashi et al., submitted]. However, \( \delta^{40}\text{Ar} \) data are noisier than for the other periods as discussed previously. One way to check the quality of data is to look at the differences in duplicate (or replicate) data [Severinghaus et al., 2003]. We expect that the gas composition of ice from the same depth in the core should be the same. Therefore, variations of data from the same depth are likely introduced during/after the coring process or in the analysis procedure.

The replicate difference plots (\( \delta^{40}\text{Ar} \) vs. \( \delta\text{Ar}/\text{N}_2 \) and \( \delta^{15}\text{N} \) vs. \( \delta\text{Ar}/\text{N}_2 \)) show significant negative correlations (Fig. 4). These negative correlations together with anomalously high \( \delta\text{Ar}/\text{N}_2 \) values can be explained by the fact that these depths are in the clathrate-gas transition and brittle ice zone as discussed previously. We suggest that mass-dependent isotope fractionation occurs during gas leakage via microcracks. This process occurs along with the previously described size-dependent preferential loss of Ar relative to \( \text{N}_2 \) due to the smaller molecular size of Ar (Bender et al., 1995; Craig et al., 1988; Severinghaus et al., 2003). The combination of these two processes thus causes the observed negative correlation between \( \delta\text{Ar}/\text{N}_2 \) and \( \delta^{15}\text{N} \) (\( \delta^{40}\text{Ar} \)). The correlation between \( \delta^{40}\text{Ar} \) and \( \delta^{15}\text{N} \) is likely a residual of gravitational and thermal fractionation in the firn.

To illuminate the sources of errors, we reanalyzed \( \delta^{40}\text{Ar} \) with the conventional “getter method” (Severinghaus et al., 2003) in the depth range of 1410.1m-1424.24m. The \( \delta^{40}\text{Ar} \) with the conventional method shows higher values by a constant \(-0.025\%\)
than the values with the copper method (Fig.5), and it produced better precision ($\delta^{40}{\text{Ar}}/4 = \text{pooled standard deviation of } 0.014$). No Ar/N$_2$ data are obtained with the conventional method as the getter destroys all the nitrogen. This experiment illustrates that the larger errors with the copper method in Period I originate from the analytical procedure rather than from the ice itself. However, the cause of the shift is unknown (see later discussion).

4.4. Depths from 1245.1m-1346.88m

Samples in this depth range were analyzed during Period II, and are located in the middle of the gas-clathrate transition zone (Fig. 6). As we started using a new extraction line and a different mass spectrometer (MAT252) after Period I, the data in this depth range provide a good comparison to understand the larger errors in Period I. We analyzed 12 duplicate samples in this depth range. The reproducibility of $\delta^{40}{\text{Ar}}$ improved compared with Period I (Table 2), corroborating the earlier conclusion that the source of the variability in Period I is largely due to the analytical method. The replicate difference plot ($\delta{\text{Ar/N}}_2$ vs. $\delta^{40}{\text{Ar}}$ and $\delta{\text{Ar/N}}_2$ vs. $\delta^{15}{\text{N}}$) shows similar trends as the Period I result, confirming that the trends in the Period I data are not because of the method, but because of the ice itself. The negative correlation of $\delta^{40}{\text{Ar}}$ and $\delta{\text{Ar/N}}_2$ is consistent with an isotopic fractionation during gas loss. An important observation regarding ice samples in this depth zone is that when some samples in the vessel were evacuated and checked for gas leaks by closing the valve to the pump, the pressure in the vessel did not stabilize owing to substantial gas leaks from the ice itself. Ice in this
depth zone is highly fractured. This suggests that a fair amount of gas was leaking through microcracks during the evacuation process.

4.3. Depths from 82.37m-316.62m

During the spring (Period III) and fall (Period IV) 2005, we analyzed air trapped in the GISP2 ice core over the past millennium (950-1950 A.D.) for argon and nitrogen isotopes, and argon/nitrogen ratio using the copper method with the Finnigan MAT252 mass spectrometer (Fig. 7). For Period III (4/15/2005-5/28/2005), we analyzed 140 ice samples at 50 depths (~20 year interval; 89.69m-313.48m). For Period IV (11/1/2005-11/17/2005), we analyzed 149 ice samples at 52 depths (~20 year interval; 82.37m-316.62m). Therefore, the final sampling resolution is a 10-year interval. The two experiments were conducted independently from separate samplings at NICL. Thus, the dataset provides an opportunity to test the reproducibility of isotopic compositions, and elemental ratios. A caveat is that ice was not cut from exactly the same depths, but rather offset by 10 years, so it is not clear that exactly the same mean can be expected.

The comparison of datasets suggests that the means of all data for $\delta^{40}$Ar, $\delta^{15}$N, and $\delta$Ar/N$_2$ are significantly different in the two periods at the 95% confidence level (Table 3), although the differences are rather small (~0.002‰) for isotopes. The means are lighter in the spring data, and $\delta$Ar/N$_2$ shows the largest difference (0.57‰) between the two periods. Pooled standard deviations of $\delta^{15}$N and $\delta^{40}$Ar are good in the two periods, but the precision of $\delta$Ar/N$_2$ became significantly better in the fall (see later discussion). An important observation comes from $\delta^{15}$N$_{excess}$, which is calculated
as \( \delta^{15}N_{\text{excess}} = \delta^{15}N - \delta^{40}\text{Ar} \) (a proxy for the temperature difference across the diffusive part of the firn) [Severinghaus and Brook, 1999]. Because the offsets of \( \delta^{40}\text{Ar}/4 \) and \( \delta^{15}N \) in the two periods are identical at -0.002\‰, \( \delta^{15}N_{\text{excess}} \) shows no change (\( p \)-value = 0.373; Table 3). This suggests that \( \delta^{15}N_{\text{excess}} \) is relatively insensitive to fractionation of \( \delta^{40}\text{Ar}, \delta^{15}N, \) and \( \delta\text{Ar}/N_2 \). The possible causes of the offsets are discussed later.

The replicate difference plots (\( \delta^{40}\text{Ar} \) vs. \( \delta\text{Ar}/N_2 \) and \( \delta^{40}\text{Ar} \) vs. \( \delta^{15}N \)) are shown in Figure 8. The \( \delta^{40}\text{Ar} \) vs. \( \delta\text{Ar}/N_2 \) plot for spring shows a weak but significant positive correlation in contrast to the negative correlation seen in the deeper, more fractured ice. On the other hand, the plot for fall does not show a significant correlation. The observation of larger variation of \( \delta\text{Ar}/N_2 \) in the spring dataset (Table 3) suggests that the spring dataset may have experienced additional fractionation (see later discussion). The strong correlation between \( \delta^{40}\text{Ar} \) vs. \( \delta^{15}N \) (Fig. 4) suggests that part of the variability in these data is likely related to some kind of mass dependent fractionation, which may have occurred during experiments or in the firn.

One important observation is that some of the spring ice samples were warmed during the shipment from NICL to SIO. Normally, ice samples are kept under -20 °C during shipment, but one box experienced warmer temperature (-15 °C) during shipment in spring 2005 for unknown reasons. We are not sure how many samples in the box experienced warmer temperature, as the temperature logger was located on the top of the ice samples. The lighter \( \delta\text{Ar}/N_2 \) value and more variable \( \delta\text{Ar}/N_2 \) in the spring dataset suggests that argon gas preferentially leaked out of the ice in the spring samples, which is consistent with size-dependent fractionation and its temperature dependent nature [Ikeda-Fukazawa et al., 2005]. Overall, the comparison of the two
datasets suggests that the reproducibility of $\delta^{40}\text{Ar}$ and $\delta^{15}\text{N}$ is good in spite of possible gas loss by warming of ice samples. Notably, the temperature difference proxy $\delta^{15}\text{N}_{\text{excess}}$ is shown to be a very conservative proxy.

4.6. Comparison with modeling study

Firn conditions such as density, temperature profile, and bubble close-off depth change in known ways with surface temperature and precipitation variations. Therefore, the past firn condition can be explicitly calculated from empirical glaciological models if the surface temperature and accumulation histories are known [Schwander, 1989; Barnola et al., 1991; Schwander et al., 1997; Goujon et al., 2003]. Goujon et al. [2003] developed such a model for firn-densification and heat diffusion to calculate the past firn condition. The model also calculates nitrogen and argon fractionation ($\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$), which are derived from the firn thickness and temperature profile in the model. The model [Goujon et al., 2003] is applied to the central Greenland ice core (GISP2) with the past surface temperature (Fig. 9) reconstructed from calibrated oxygen isotopes of ice, and the past precipitation reconstructed from the measured layer thicknesses corrected for thinning with an ice flow model [Cuffey and Clow, 1997; Cuffey et al., 1995]. The Goujon et al. model results for $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}/4$ are slightly lower (-0.006‰) than observed, suggesting that the model underestimates actual firn thickness by 1-2m. We simply add 0.006‰ to the model $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}/4$, as it is expected that the relative change is more accurate than the absolute number.
Model results and data for $\delta^{40}\text{Ar}$ and $\delta^{15}\text{N}$ show a general agreement (Fig. 10a,b) suggesting that the surface temperature reconstruction by Cuffey et al. [1995] is accurate to describe the general trend of the past 11,500 years. Observed and modeled $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}/4$ correlate strongly ($r^2=0.83$) if all the data are included. However, the correlations on centennial to millennial time scales are very weak ($r^2<0.01$ for 80m-1300m), and the model result fluctuations on these time scales are larger than those seen in the observations. This is likely due to overestimation of the amplitude of centennial temperature fluctuations by the $\delta^{18}\text{O}_{\text{ice}}$-based surface temperature (Fig. 10a,b). The Preboreal Oscillation and the 8.2ka event are the only events in which observations and model show a clear correlation (Fig. 10a,b). The residual plots between model and observation (fig. 10c) suggest that the high $\delta^{40}\text{Ar}$ and $\delta^{15}\text{N}$ values in the early Holocene and subsequent decreases are well represented in the model. However, the observed $\delta^{40}\text{Ar}$ and $\delta^{15}\text{N}$ oscillations on a shorter time scale are not represented in the model, which may suggest that oxygen isotopes of ice are not a good indicator of small temperature changes when climate is relatively stable.

The residual $[(\delta^{15}\text{N}_{\text{observation}} - \delta^{15}\text{N}_{\text{model}}) - (\delta^{40}\text{Ar}_{\text{observation}} - \delta^{40}\text{Ar}_{\text{model}})]$ of the residual plots (Fig. 10d) suggests that the mismatches of model and data are due either to an inaccurate temperature gradient in the model, or artifactually biased isotopic measurements by gas-loss or errors in the normalization process. The plot shows that most data are within the range of 0.0 ‰ to -0.010‰ (fig.10d). The negative values are suggestive of artificially high $\delta^{40}\text{Ar}$ or low $\delta^{15}\text{N}$ (see later discussion). A correlation with $\delta\text{Ar}/\text{N}_2$ (gravitationally corrected) is not observed (Fig. 10d,e), which may
suggest that gas-loss imprints on isotopes are due to a separate process from that which causes most Ar/N$_2$ fractionation.

4.7. Krypton isotopes

Krypton is a noble gas with a larger atomic size than argon. For this reason, and based on firn air profiles that clearly show argon fractionation but not krypton fractionation during bubble close-off, the krypton atom is expected to be immune to size-dependent fractionation [Huber et al., 2006a; Severinghaus and Battle, 2006]. As argon isotopic values might have undergone fractionation during gas loss, krypton isotopes may provide independent information on the firn condition in the past. Kawamura and Severinghaus [in prep.] developed a method to measure krypton isotopic values ($^{86}\text{Kr}/^{82}\text{Kr}$) with a relatively large volume of ice (0.7-1 kg). Although the number of measurements is quite small, the $^{86}\text{Kr}/4$ trends are similar to the $^{15}\text{N}$ and $^{40}\text{Ar}$ trends (Fig. 11). To investigate potential gas loss impacts on $^{40}\text{Ar}$, it is useful to calculate temperature differences ($\Delta T$) from both $^{86}\text{Kr}/4$ combined with $^{15}\text{N}$ and $^{40}\text{Ar}$ combined with $^{15}\text{N}$. The past temperature difference ($\Delta T$) in the firn can be reconstructed using the difference in thermal response of $^{15}\text{N}$, $^{40}\text{Ar}$, and $^{86}\text{Kr}$ [Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b; Severinghaus et al., 1998].

$$\Delta T_{\text{Ar}} = (\delta^{15}\text{N}-\delta^{40}\text{Ar}/4)/(\Omega^{15} - \Omega^{40}/4)$$

$$\Delta T_{\text{Kr}} = (\delta^{15}\text{N}-\delta^{86}\text{Kr}/4)/(\Omega^{15} - \Omega^{86}/4)$$
where $\Omega^{15} = 0.0147$ (‰/°C) at -31 °C [Grachev and Severinghaus, 2003b], $\Omega^{40}/4 = 0.010$ (‰/°C) at -31 °C [Grachev and Severinghaus, 2003a], and $\Omega^{86}/4 = 0.0027$ (‰/°C) in the temperature range of -60 to -40 °C [Kawamura and Severinghaus, in prep]. Ideally, $\Delta T_{Ar}$ should equal $\Delta T_{Kr}$. However, it is found that $\Delta T_{Ar}$ is consistently lower than $\Delta T_{Kr}$ (Fig. 12). The difference centers around -3.5 °C, but the data variations are too large to make a robust conclusion regarding whether or not the difference is constant. More krypton analyses would certainly help to understand gas loss and its impacts on isotopes. Nonetheless, these data confirm that $\delta^{40}Ar$ is probably enriched by gas loss.

5. Implication for gas loss processes

Recent firn air studies [Huber et al., 2006a; Severinghaus and Battle, 2006] reveal that during the bubble close-off smaller molecules (e.g., neon, oxygen and argon) with less than a certain threshold size (~3.6 Angstroms) leak out from newly formed bubbles through the ice lattice. This size-dependent process appears to not affect the isotopic composition of argon measurably, which is a plausible finding because isotopes have similar molecular sizes [Severinghaus and Battle, 2006]. This size-dependent fractionation causes bubble air to be depleted in smaller molecules, and the remaining air in firn to be enriched in smaller molecules. This is consistent with the observed fact that oxygen and argon concentrations are normally less than expected in air trapped in ice cores. However, the magnitude of the observed depletion in ice samples is more than expected from a mass balance calculation based
on the firn air profiles [Severinghaus and Battle, 2006], suggesting that small molecules also leak out during/after coring.

The δO₂/N₂ of air trapped in ice core samples is known to decrease with storage time because the oxygen molecule preferentially leaks through the ice lattice [Kawamura, 2000; Ikeda-Fukazawa et al., 2005]. The impacts of this mode of gas loss on isotopes are not completely clear, as evidence is somewhat contradictory. Some studies show no change in δ¹⁸O with decreasing δO₂/N₂ (Fig. 13) [Suwa and Bender, submitted], whereas other studies have found enrichments of δ¹⁸O and δ⁴⁰Ar associated with low oxygen and argon concentrations in ice that was stored for >5 years at –20 °C (Grachev, 2004). The gas loss process is likely to be temperature-dependent, based on the observation that samples kept at colder temperature (e.g., -50°C) experience less gas-loss [Ikeda-Fukazawa et al., 2005]. Our data from 82.37m-316.62m also suggest that warming of ice samples caused argon loss, but the isotopic composition seems unaffected. These observations may suggest that during/after coring smaller molecules leak out from air trapped in ice with little influence on isotopic composition, as during the bubble close-off process in firn.

In contrast, other observations indicate clearly that some gas loss process affects isotopic composition [Grachev, 2004; Severinghaus et al., 2003]. It is found that very negative δO₂/N₂ data in Siple Dome ice core samples (Severinghaus et al., 2006) are usually associated with higher δ¹⁸O values, suggesting that oxygen leakage is linked with isotopic fractionation. The Siple Dome ice is highly fractured, and the most fractured pieces are generally associated with more negative δO₂/N₂. As discussed previously, our data at the gas-clathrate transition (also brittle) zone show
that the gas leak involves nitrogen gas, and the leak is associated with detectable isotopic fractionation for both $\delta^{40}\text{Ar}$ and $\delta^{15}\text{N}$ (Fig. 4).

These observations imply that at least two types of gas fractionation may be involved during/after the coring process [Bender et al., 1995]. The first one is the size-dependent fractionation with little isotopic fractionation, which was observed in the firn air study. The second one is a mass dependent fractionation, which we hypothesize is caused by gas loss from microcracks as observed especially in samples from the gas-clathrate transition zone and/or brittle ice. Ice samples with many microcracks create shorter pathways for gas to leak through the ice lattice, which may explain why a size-fractionated gas abundance pattern has been observed when pumping on highly fractured ice in the laboratory [Craig et al., 1988]. At the same time, sample evacuation may not be able to remove all the gases out of fractures, so the remaining air in fractures could become enriched in heavier gases. The combination of the various mechanisms could explain why we observe both enrichments in isotopes and depletion in smaller molecules [Bender et al., 1995; Craig et al., 1988].

The difference between $\delta^{40}\text{Ar}/4$ and $\delta^{15}\text{N}$ for the last 11,500 years does not show any particular trends similar to $\delta\text{Ar}/\text{N}_2$ (Fig. 10), although other processes related to clathrate formation might obscure the relationship between $\delta\text{Ar}/\text{N}_2$ and $\delta^{40}\text{Ar}$. It is not clear why $\delta^{40}\text{Ar}/4$ is higher than $\delta^{15}\text{N}$, which is physically inconsistent with the borehole temperature record. One explanation might be gas loss and resultant argon isotopic enrichments [Severinghaus et al., 2003] as a recent model and data comparison for the last 1000 years suggests [Kobashi et al., submitted]. Another
explanation might be normalization problems, due perhaps to fractionation during the sampling of La Jolla air. Further krypton isotope analyses should provide insights on this important but complicated issue.

6. Conclusion

We developed a method to analyze argon and nitrogen isotopes from the same sample, which reduced the uncertainty of estimates of past temperature difference across the firn layer, and substantially reduced the time required for analyses. The method is applied to the Holocene section of the GISP2 ice core. We achieved precisions for $\delta^{15}$N and $\delta^{40}$Ar that are similar to conventional methods, but with improvement in $\delta^{15}$N$_{excess}$ due to cancellation of correlated errors. The $\delta^{15}$N and $\delta^{40}$Ar data show a very similar trend of a gradual decrease from 1700m to 1400m due to the response of the firn to the warming at the start of the Holocene, followed by relatively constant values from 1400m to 80m. The general trends agree well with previous modeling studies [Goujon et al., 2003], although model fluctuations on shorter time scales do not match with observed results, suggesting that borehole-calibrated $\delta^{18}$O$_{ice}$ is not a reliable temperature indicator on these time scales.

Available data suggests that two types of fractionation occur during/after coring, which affect the gas composition in ice cores. The smaller molecules such as oxygen and argon leak through the ice lattice with little isotopic fractionation as observed in firn air studies [Severinghaus and Battle, 2006]. Mass-dependent fractionation of $^{40}$Ar/$^{36}$Ar occurs during gas loss through cracks especially in the brittle ice, affecting isotopic composition. Krypton isotopes show a very similar trend
as argon and nitrogen isotopes, and due to their large atomic diameter may provide a constraint on the gas-loss process in the future.

**Acknowledgement**

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This chapter, in part, has been submitted for publication of the material as it appears in Journal of Geophysical Research –Atmospheres, 2007, Takuro Kobashi; Jeff Severinghaus; Kenji Kawamura. The dissertation author was the primary investigator and author of this paper.
Table 1.1. Time periods in which experiments were conducted and sample depths.

<table>
<thead>
<tr>
<th></th>
<th>Period I</th>
<th>Period II</th>
<th>Period III</th>
<th>Period IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>1359.95-1458.95</td>
<td>827.95-1357.9</td>
<td>89.69-820.555</td>
<td>82.37-316.62</td>
</tr>
<tr>
<td></td>
<td>1459.29-1584.1</td>
<td>1585.15-1692.22</td>
<td></td>
<td></td>
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</tbody>
</table>
Table 1.2. Precision of La Jolla Air (LJA) and sample pooled standard deviation (PSD). Number in parentheses in second and third columns is the number of samples used in the calculation. PSDs are calculated only if two or more samples are analyzed for a depth.

<table>
<thead>
<tr>
<th></th>
<th>LJA</th>
<th>PSD</th>
<th>LJA</th>
<th>PSD</th>
<th>LJA</th>
<th>PSD</th>
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<tbody>
<tr>
<td><strong>δ¹⁵N (‰)</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Period I</td>
<td>0.005 (17)</td>
<td>0.004 (238)</td>
<td>0.044</td>
<td>0.036</td>
<td>0.069</td>
<td>4.12</td>
</tr>
<tr>
<td>Period II</td>
<td>0.003 (14)</td>
<td>0.003 (22)</td>
<td>0.009</td>
<td>0.022</td>
<td>0.069</td>
<td>3.01</td>
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<tr>
<td>Period III</td>
<td>0.005 (23)</td>
<td>0.004 (138)</td>
<td>0.016</td>
<td>0.016</td>
<td>0.086</td>
<td>0.78</td>
</tr>
<tr>
<td>Period IV</td>
<td>0.004 (17)</td>
<td>0.004 (148)</td>
<td>0.014</td>
<td>0.016</td>
<td>0.137</td>
<td>0.53</td>
</tr>
</tbody>
</table>
**Table 1.3.** Comparisons of two experiments in spring and fall 2005. H$_0$ is the null hypothesis that the fall dataset equals the spring dataset.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{40}$Ar/4 (‰)</th>
<th>$\delta^{15}$N (‰)</th>
<th>$\delta$Ar/N$_2$ (‰)</th>
<th>$\delta^{15}$N$_{excess}$ (‰)</th>
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<tbody>
<tr>
<td><strong>Spring</strong></td>
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<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.317</td>
<td>0.308</td>
<td>-1.24</td>
<td>-0.009</td>
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<tr>
<td>4/15-5/28</td>
<td>0.004</td>
<td>0.004</td>
<td>0.78</td>
<td>0.004</td>
</tr>
<tr>
<td><strong>Fall</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.319</td>
<td>0.310</td>
<td>-0.67</td>
<td>-0.009</td>
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<td>11/1-11/17</td>
<td>0.004</td>
<td>0.004</td>
<td>0.53</td>
<td>0.004</td>
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<tr>
<td><strong>Diff. of means</strong></td>
<td><strong>(spring-fall)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.002</td>
<td>-0.002</td>
<td>-0.57</td>
<td>0.000</td>
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<tr>
<td>$p$-values for H$_0$: spring=fall</td>
<td>0.011</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.373</td>
</tr>
</tbody>
</table>
Figure 1.1. Data from the last 11,500 years including $\delta^{15}$N, $\delta^{40}$Ar, $\delta$Ar/N$_2$, total air content, and number of samples analyzed for each depth. Shaded area represents the gas-clathrate transition zone [Gow et al., 1997]. Total air content values are relative to mean of all data. Double red lines represent depths in which we analyzed samples with a 10-year interval. Other depths were analyzed with a 20-year interval.
Figure 1.2. Simplified schematic of the extraction line.
Figure 1.3. $\delta^{15}N$, $\delta^{40}Ar$, and $\delta Ar/N_2$ records for the depth range 1470-1350m. The large dip in $\delta^{15}N$ and $\delta^{40}Ar$ corresponds to the abrupt climate change 8,200 years ago [Kobashi et al., in press].
Figure 1.4. Replicate difference plots of $\delta^{40}$Ar vs. $\delta$Ar/N$_2$, $\delta^{15}$N vs. $\delta$Ar/N$_2$, and $\delta^{40}$Ar vs. $\delta^{15}$N for the depth range 1470-1350m. Equations are for linear trend lines.
Figure 1.5. Argon isotopic values for the depth range 1405-1430m by two different methods.
Figure 1.6. Replicate difference plots of $\delta^{40}$Ar vs. $\delta$Ar/N$_2$ and $\delta^{40}$Ar vs. $\delta^{15}$N for the depth range 1245.1-1346.88m. Equations are for linear trend lines.

- For $\delta^{40}$Ar vs. $\delta$Ar/N$_2$:
  \[ y = -0.006x + 0.018 \]
  \[ r^2 = 0.53 \]
  \[ p = 0.008 \]

- For $\delta^{40}$Ar vs. $\delta^{15}$N:
  \[ y = 4.3x + 0.004 \]
  \[ r^2 = 0.25 \]
  \[ p = 0.098 \]
Figure 1.7. δ¹⁵N, δ⁴₀Ar/4, and δAr/N₂ for the depth range 82.22m-316.47m. This depth range corresponds to the last 1000 years (Kobashi et al., submitted). Error bars are standard errors of means. Red data are obtained during the fall 2005, and blue data are obtained during the spring 2005.
Figure 1.8. Replicate difference plots of $\delta^{40}$Ar vs. $\delta$Ar/N$_2$ for spring and fall 2005, and $\delta^{40}$Ar vs. $\delta^{15}$N for the depth range 82.22m-316.47m. Equations are for linear trend lines.
Figure 1.9. Surface temperature reconstruction in central Greenland for the last 11,500 years from borehole temperature-calibrated oxygen isotopes of ice (Cuffey and Clow, 1997).
Figure 1.10. Observation and model (Goujon et al., 2003) comparison. (a) Modeled and observed $\delta^{40}$Ar/4. (b) Modeled and observed $\delta^{15}$N. (c) Difference between modeled and observed $\delta^{15}$N and $\delta^{40}$Ar/4. (d) the difference of (c) between $\delta^{15}$N and $\delta^{40}$Ar. (e) $\delta$Ar/N$_2$ gravitationally corrected by $\delta^{15}$N.
Figure 1.11. Plot showing $\delta^{40}$Kr, $\delta^{40}$Ar and $\delta^{15}$N data from the experiments on krypton isotopes.
Figure 1.12. Plot of difference ($\Delta T_{Ar} - \Delta T_{Kr}$) between temperature gradient reconstructed using isotopes of Ar and N₂, and Kr and N₂.
Figure 1.13. $\delta^{18}O$ and $\delta^{15}O$ (‰) in GISP2 ice core (Suwa and Bender, submitted). Samples were analyzed in 1994 and 2006. $\delta^{18}O$ decreases 7.3‰ after 12 years presumably due to storage in a relatively warm freezer, but $\delta^{15}O$ shows no change (0.021±0.074‰ lighter in 2006).
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Chapter II

Precise timing and characterization of abrupt climate change

8,200 years ago from air trapped in polar ice
Abstract

How fast and how much climate can change has significant implications for concerns about future climate changes and their potential impacts on society. An abrupt climate change 8,200 years ago (8.2ka event) provides a test case to understand possible future climatic variability. Here, methane concentration (taken as an indicator for terrestrial hydrology) and nitrogen isotopes (Greenland temperature) in trapped air in a Greenland ice core (GISP2) are employed to scrutinize the evolution of the 8.2ka event. The synchronous change in methane and nitrogen implies that the 8.2ka event was a synchronous event (within ±4 years) at a hemispheric scale, as indicated by recent climate model results (LeGrande et al., 2006). The event began with a large-scale general cooling and drying around ~8175±30 years B.P. (Before Present, where Present is 1950 AD). Greenland temperature cooled by 3.3±1.1 ºC (decadal average) in less than ~20 years, and atmospheric methane concentration decreased by ~80±25ppb over ~40 years, corresponding to a 15±10% emission reduction. Hemispheric scale cooling and drying, inferred from many paleoclimate proxies, likely contributed to this emission reduction. In central Greenland, the coldest period lasted for ~60 years, interrupted by a milder interval of a few decades, and temperature subsequently warmed in several steps over ~70 years. The total duration of the 8.2ka event was roughly 150 years.

Keywords: abrupt climate change, ice core, nitrogen isotopes, methane, Holocene, Greenland
1. Introduction

Future climatic change associated with anthropogenic greenhouse gases is a primary concern for human society. Climate models and paleoclimatic records suggest that future climate change may involve large and abrupt changes (IPCC, 2001; Manabe and Stouffer, 1993; National Research Council (U.S.). Committee on Abrupt Climate Change., 2002; Stocker and Schmittner, 1997). One way to quantify possible impacts of future abrupt climate change amid model uncertainties is to look back to the past, and find the closest possible analog (Alley and Agustsdottir, 2005; National Research Council (U.S.). Committee on Abrupt Climate Change., 2002). The abrupt climate change ~8200 years ago, the largest abrupt climatic event in the past 10,000 years (Fig.1), occurred at a time when the background climate was much like the present (the Holocene, a relatively warm period after the last glacial period, Fig. 1). The event was characterized by generally cool, dry, and windy climate, which affected ecosystems and early human societies (Alley et al., 1997a; Weiss, 2000). The widespread evidence for the 8.2ka event, combined with a rapid decrease of atmospheric methane concentration (Spahni et al., 2003; this study) suggests that the event was at least hemispheric or “near-global” in its geographical extent (Alley and Agustsdottir, 2005; Morrill and Jacobsen, 2005; Wiersma and Renssen, 2006). The cause of the event may have been the largest proglacial lake (Lake Agassiz) outburst of the last deglaciation (Clarke et al., 2004), which has been dated to 8470±300 (1σ) B.P. (Barber et al., 1999; Rohling and Palike, 2005). This hypothesis holds that a massive outflow of fresh water ran out the Hudson Strait, to the North Atlantic, causing a slowdown of the meridional overturning circulation, which enabled
wintertime sea ice cover to expand with consequent hemispheric cooling and drying especially surrounding the North Atlantic area (Alley and Agustsdottir, 2005; Ellison et al., 2006). An alternative hypothesis is that a millennial-scale cooling trend started a few centuries earlier than the 8.2ka event (Rohling and Palike, 2005). A minor solar minimum coinciding with the 8.2ka event (Muscheler et al., 2004) as a third hypothesis, may have forced the system to cross a threshold and may have triggered the 8.2ka event (Bond et al., 2001; Bond et al., 1997).

In this study, we address the detailed timing and evolution of the 8.2ka event by measuring nitrogen isotope ratios and methane concentration in trapped air in the GISP2 ice core. Atmospheric methane concentration can be viewed as a qualitative indicator of integrated terrestrial hydrological conditions in methane-producing regions, owing to the dominant methane source from wetland areas (~75% of natural emissions (Houweling et al., 2000)). Nitrogen isotopes in trapped air in an ice core provide a signal of local temperature changes in Greenland (Goujon et al., 2003; Landais et al., 2004; Severinghaus et al., 1998). This method (Severinghaus and Brook, 1999; Severinghaus et al., 1998) provides an opportunity to precisely and directly assess the timing of abrupt climate change in Greenland with respect to changes in atmospheric methane, by comparing two gases in the same core. We also provide an improved estimate of the magnitude of the temperature change in central Greenland.
2. Materials and methods

We used the GISP2 ice core for our analyses. The resolution of nitrogen isotope data is 1 m (~10 year) from 1359.95 m to 1458.95 m depth, corresponding to a gas age range of 7600 B.P – 8600 B.P. (see below for the basis for this chronology). Replicate analyses (2-3 for each depth) were conducted for the entire record. Additional replicates were done in the intervals 1412.95-1416.95 m (6 replicates per depth) and 1417.97-1423.95 m (4 replicates per depth) to increase the confidence level of the temperature estimate for the 8.2ka event. The total number of sampling depths is 96, and the total number of samples is 238. Ice samples were analyzed for nitrogen isotope ratios following the method described in Severinghaus et al. (2003) with some modifications described here. We (Kobashi et al., submitted) developed a new method (“copper method”) for the simultaneous analysis of nitrogen and argon isotopes in air proportions, with oxygen removed from the air sample by exposure to hot copper. We used a new mass spectrometer with 8 Faraday cups for simultaneous collection of the mass 28, 29, 36, and 40 beams (Finnigan Delta XP). For comparison purposes we also measured some argon data with a Finnigan MAT 252 (10 kV) by conventional methods as in Severinghaus et al. (2003).

Our sampling depths are located in the transition zone between air bubbles and air clathrates (Bender et al., 1995). Unusual gas loss fractionation can be seen in the Ar/N2 data as δAr/N2 values are abnormally enriched due to the partial formation of clathrates combined with gas loss from the bubbles (Bender et al., 1995) (Fig. 2). The higher variability of δ40Ar may be partially introduced by the poorer linearity of the Finnigan Delta XP. The δ40Ar data measured with the conventional method and with
a modified “copper method” employing the Finnigan MAT 252 show better precision (Kobashi et al., submitted). As the precision of $\delta^{40}$Ar is so low, we do not attempt to interpret the argon data here (Fig. 2). However, the magnitude of the argon isotope shift for the 8.2ka event is consistent with our temperature estimate within its uncertainty (Fig. 2). An additional difference from the Severinghaus (2003) method is that the N$_2$:Ar ratio is 83, the air ratio, rather than 10. This higher ratio may have also contributed to lower $\delta^{40}$Ar precision. In order to obtain a strong argon beam, the samples were run at an elevated inlet pressure of 208 mbar. These modifications degraded the linearity somewhat, as expected for this (3 kV) mass spectrometer source.

Two to six ~50 g ice samples from each depth are cut for isotopic analyses. The ice sample is placed in a glass flask with a comflat flange and evacuated for 40 minutes while keeping the flask at -20 °C. Samples are then melted and warmed to room temperature (~22°C) releasing the trapped air. The released air samples are transferred into a dip tube, cooled to 4K using liquid helium. During the transfer, water vapor is removed by a glass water trap at -100 °C, and potential organic contaminants and CO$_2$ are removed by another glasstrap at -196 °C. Then, air passes through a copper mesh heated to 500 °C to remove the oxygen, which has an isotopic species ($^{18}$O$^{18}$O) with the same mass as $^{36}$Ar. Finally, the last glass trap at -196 °C removes remaining CO$_2$ produced by the copper. Then, the air sample is introduced to the mass spectrometer for the measurement of argon and nitrogen isotopes, and Ar/N$_2$.

The pooled standard deviation of all of replicated ice samples (samples taken from the same depth in the core) is 0.004 ‰ for $\delta^{15}$N. The estimated standard error of the mean of nitrogen isotope data ranges from 0.0028-0.0016‰ depending on the number of
samples analyzed. Two data points were rejected owing to experimental reasons (large residual pressure after the gas extraction and a change in the location of the heated copper during the gas transfer).

For methane analyses, the resolution is 2 m (~20-year) from 1360.03 m to 1460.03 m, except depths from 1410.03 m to 1426.03 m, where resolution was increased to ~50 cm (~5-year). The method for methane analysis is described in Brook et al. (2000) with a slightly different extraction technique. We used a 6-port line with glass instead of stainless steel vessels, and a Shimadzu Gas chromatograph (GC). For each depth, we conducted duplicate analyses. Whenever the difference between the duplicates was more than 40 ppb we ran another set of duplicates, rejecting the first set. This occurred three times out of 77 duplicate runs. For two more samples one of the replicates was lost due to operator error. The mean difference between the replicates and the pooled standard deviation are 14 and 17 ppb, respectively. 20 blanks were analyzed during the experiments, and the mean is 11.4 ± 8.4 ppb. The data agree with a lower resolution methane record (Spahni et al., 2003) for the 8.2ka event from the GRIP ice core within its uncertainty.

The recent finding of a possible new methane source from terrestrial plants (Keppler et al., 2006) may change our understanding of the relative contribution of various atmospheric methane sources. As methane emissions from terrestrial plants are expected to positively correlate with temperature, the significance of concentration changes in this study would not substantially change if a large plant methane source is verified.
In this study, we use the GISP2 visual-stratigraphic age scale (Alley et al., 1997b) for the ice age scale with minor modifications. By correlating the GRIP \(^{10}\text{Be}\) ice-core data and tree ring \(^{14}\text{C}\), Muscheler et al. (2004) found that the minimum of the oxygen isotope record of ice for the 8.2ka event occurred at an absolute age of \(\sim 8,150 \pm 20\) years B.P.. To adjust our time scale to match this observation, the entire time scale is shifted by 110 years toward younger age. After this correction, we estimate that the uncertainty of the absolute ages of ice is \(\pm 30\) years from 7600-8600 B.P. However, relative age uncertainty, as applies to inferred duration in this study, should be much smaller (1\%) (Alley et al., 1997b). The gas time scale is calculated from a firn densification model (Goujon et al., 2003). The gas-ice age difference (\(\Delta\text{age}\)) uncertainty is estimated to be \(\sim 10\%\) (\(\sim 20\) years).

3. Evolution of Greenland temperature

3.1 Magnitude of Greenland cooling

The magnitude of temperature changes is often used as the most important climatic indicator and as a target for climate model simulations (LeGrande et al., 2006). There have been many attempts to quantify the magnitude of the temperature change for the 8.2ka event in central Greenland. A conventional method uses oxygen isotopes of ice (\(\delta^{18}\text{O}_{\text{ice}}\)) calibrated by the empirical modern spatial relationship of temperature and \(\delta^{18}\text{O}\) of precipitation. This slope of the temperature-isotope relationship so derived is called the “spatial slope” or spatial sensitivity. Several studies, however, have shown that the temporal isotope-temperature sensitivity is quite variable and different from the spatial sensitivity (Cuffey et al., 1995; Jouzel et al.,
1997). The 1.8 ‰ change of δ¹⁸O (decadal average) during the event in the GISP2 and GRIP ice cores corresponds to 2.7 °C cooling, using the spatial calibration (Johnsen, 1989). Alley et al. (1997a) calibrated the oxygen isotope record (GISP2) using the borehole-temperature estimate for the Holocene (Cuffey et al., 1995) assuming that the temperature sensitivity at a millennial time scale is valid for the decadal time scale, and estimated the magnitude of 8.2ka cooling to be 6±2 °C. Leuenberger et al. (Leuenberger et al., 1999) estimated the magnitude of the 8.2ka cooling as 7.4 °C with a range of 5.4-11.7 °C using δ¹⁵N, a similar method as described here (See later discussion).

We used the nitrogen isotope data in trapped air in the GISP2 ice core (Fig. 2) to quantify the magnitude of temperature change in combination with a heat diffusion and firn densification model (Goujon et al., 2003). The nitrogen isotopic ratio (¹⁵N/¹⁴N) in the atmosphere is known to be constant for millions of years (Mariotti, 1983; Severinghaus et al., 1998). Thus, any isotopic deviations from atmosphere in trapped air in an ice core can be attributed to isotopic fractionation in the firn layer (porous top layer of ice sheet ~80m thick). Two important processes cause fractionation in the firn, gravitational fractionation and thermal diffusion. Gravitational fractionation in the firn layer (Craig et al., 1988; Schwander, 1989) is mainly controlled by the thickness of the firn layer and the mass difference of the gas pair (typically δ¹⁵N = -0.31‰ for our samples). Fractionation due to thermal diffusion occurs during abrupt warming or cooling, when a temperature gradient is generated between the top and base of the firn (Severinghaus et al., 1998). The magnitude of the fractionation is gas-dependent, and
is calibrated with laboratory experiments (Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b).

The variations in firn condition (e.g., firn thickness, density, and temperature profile) and associated isotopic fractionation can be explicitly calculated using a firn densification model (Goujon et al., 2003; Schwander, 1988; Schwander et al., 1993) if surface temperature and accumulation rate are known. The model used here (Goujon et al., 2003) includes heat transfer through the firn and the ice down to the bottom of the ice sheet. The model uses as inputs the oxygen isotopes of ice (Stuiver et al., 1995) with an adjustable scaling $\alpha$ as a surface temperature proxy, and independently estimated accumulation rate from annual layer-counting with ice-flow corrections (Alley et al., 1997b; Cuffey and Clow, 1997). It calculates both firn thickness and thermal gradient in the firn and thus allows us to predict the nitrogen fractionation (Fig. 3). The best fit of our data with the modeled nitrogen isotope ratios (Fig. 3) was found with a decadal average cooling of $3.3 \pm 0.5 ^\circ$C, corresponding to an oxygen isotope temperature sensitivity $\alpha=0.55 \pm 0.05 \text{‰/°C}$ and $\beta=17.34$ (range: 15.69-19)‰ $[T( ^\circ \text{C})=({\delta^{18}}O+\beta)/\alpha]$. An important uncertainty regarding this temperature estimate comes from a possible change in the thickness of a near-surface layer known as the convective zone, where gases mix with the atmosphere by wind pumping (Colbeck, 1989; Kawamura et al., 2006). Although we believe that the convective zone stayed relatively constant for the past 10,000 years in central Greenland, we cannot rule out an increase in convective zone thickness due to intensified wind during the event, which would bias the temperature estimate. A $\pm 2 \text{ m}$ change in the thickness of the convective zone during the cooling period corresponds to a $\delta^{15}$N signal of $\pm 0.009 \text{‰}$,
and we therefore add ±1 °C uncertainty to the cooling estimate (thermal response of δ¹⁵N is ~-0.015‰ for 1°C temperature gradient at ~ -31°C: Grachev and Severinghaus, 2003b). Overall, we estimate that the magnitude of the cooling at central Greenland was 3.3±1.1 °C in the decadal average (difference between decadal averages before and after the cooling event). In particular, the magnitude of the cooling was twice as large as the Little Ice Age cooling (~1.6 °C after the Medieval Warm Period) (Dahl-Jensen et al., 1998), which took a few centuries to reach minimum temperature, but had substantial impacts on European society (Fagan, 2000). The magnitude of the 8.2ka cooling on shorter time scales (1-5 years) may have been larger, but cannot be addressed by our technique due to smoothing of the gas record (Severinghaus et al., 1998).

This temperature change estimate is smaller than previously published estimates. Notably, our estimate of temperature change is significantly smaller than that of Leuenberger et al. (1999) who used a similar technique with δ¹⁵N data from the GRIP ice core to estimate that temperature changed by 7.4°C with a range of 5.4-11.7 °C (Fig. 4). The experimental uncertainty of their data (pooled standard deviation for duplicate data=0.030‰) is about 7-fold larger than our uncertainty of 0.004‰ (Fig. 4), and contains high values that are physically unrealistic. Clearly, the differences in experimental procedures introduced larger errors into Leuenberger et al.’s dataset, such as by air leaks during the gas extraction process or water introduced into the mass spectrometer (N₂H⁺ forms in the presence of water and isobarically interferes with ¹⁵N₁⁴N⁺). As the signal for the 8.2k event (0.035‰) is rather small, the precision of the Leuenberger et al. dataset should make identification of the 8.2k event difficult. It
is possible that the magnitudes of the 8.2ka cooling at the GISP2 and GRIP sites are different. However, to draw such a conclusion, it would be necessary to reanalyze the GRIP ice core with higher precision.

Climate models employed for the 8.2ka event produce cooling. Using the ECBILT-CLIO model, Renssen et al. (2001) estimated the cooling to be 2 to 5 °C in Greenland, similar to that found here. Using CLIMBER-2, Bauer et al. (2004) estimated 3.6 °C in the North Atlantic sector (60-80°N). LeGrande et al. (2006) found 1.4 °C with a range of 1.9 to 1.1 °C cooling with a coupled model (Goddard Institute for Space Studies MODELE).

3.2 Time-evolution of Greenland temperature change

As mentioned above, the oxygen isotopes of ice may have a significant influence from changes in seasonal precipitation and storm tracks, as well as other phenomena (Jouzel et al., 1997). The nitrogen isotopes provide an independent means to qualitatively assess the time-evolution of Greenland temperature under two plausible assumptions. The first assumption is that nitrogen signals mostly consist of the thermal signal from the temperature gradient $\Delta T$ between top and bottom of the firn layer. This is validated by the firn densification model, which shows that the thermal signal is about 10 times larger than the gravitational signal due to firn thickness changes (Fig. 3). The second assumption is that the change in the temperature gradient $\Delta T$ in the firn layer is similar to the change in surface temperature. Because the heat conductivity of snow is much smaller than that of ice and the heat capacity of the ice sheet is quite large (Yen, 1981), $\Delta T$ should mimic
surface temperature evolution on a decadal to centennial time scale. The firn densification-heat diffusion model (Goujon et al., 2003) with oxygen isotopes of ice as a surface temperature proxy supports the assertion that surface temperature changes should be qualitatively represented in nitrogen signals for the 8.2ka event.

The surface temperature signal in the nitrogen isotope record is smoothed by gas diffusion and bubble close-off in the firn layer (Severinghaus et al., 1998). To reconstruct the surface temperature signals from smoothed signals in nitrogen isotope record, we need to deconvolve the nitrogen record using some assumed smoothing function. The effect of the smoothing process can be represented by an age distribution (hereafter we call it a smoothing function). Spahni et al. (2003) developed smoothing functions for the central Greenland methane record (GRIP) for the 8.2 ka event, with two solutions, ‘narrow’ and ‘wide’ (referring to the width of the smoothing function) intended to represent the range of uncertainty. We adopt these functions for analysis of our data, under the plausible assumption that conditions at GRIP and GISP2 were similar. Smoothing functions for nitrogen gas are obtained by modifying the smoothing functions (‘wide’ and ‘narrow’) for methane (Spahni et al., 2003) (methane diffuses 7% faster than nitrogen; Severinghaus et al., 1998). We can express the nitrogen isotope record $M$ as $M(t) = \int_0^\infty C(\tau)A(t-\tau)d\tau$, where $A$ is a qualitative surface temperature history, $C$ is a smoothing function, $t$ is time, and $\tau$ is a time index (Bendat and Piersol, 2000). Alternatively, we can write $\mathcal{F}(M(\nu)) = \mathcal{F}(C(\nu))\mathcal{F}(A(\nu))$, where $\mathcal{F}$ represents Fourier transform, and $\nu$ is frequency (Bendat and Piersol, 2000). Thus, qualitative surface temperature history $A(t)$ can be calculated as $A(t) = \mathcal{F}^{-1}(\mathcal{F}(M(\nu)) / \mathcal{F}(C(\nu)))$, where $\mathcal{F}^{-1}$ represents the inverse Fourier transform.
This Fourier transform method assumes perfect data; to account for experimental error we use the following technique.

To estimate the uncertainty of the deconvolution process, 100 realizations of synthetic nitrogen isotope records are generated by Monte Carlo simulation by adding white noise to the δ\textsuperscript{15}N data with a standard deviation of 0.004‰. These synthetic records are then linearly interpolated to obtain 1-yr-resolution time series. Then, these realizations are deconvolved with the two smoothing functions (‘wide’ and ‘narrow’). The solutions are smoothed with a spline fit (Enting, 1987) with a 30-year cutoff period to eliminate higher frequency fluctuations (these ice core gas records do not possess high frequency climate information because of the smoothing processes), and the mean and standard deviation (1σ) of the 100 realizations at each time step are calculated for each smoothing function. This deconvolution process shifts the signals toward older ages, as expected, because the surface signals are recorded in ice with a time lag owing to the gas diffusion in the firn layer. To obtain a proper timing for the surface temperature history from the nitrogen isotope record, the deconvolved record needs to be shifted toward younger age. The magnitude of the shift can be calculated by integrating the smoothing functions. Accordingly, the age of data is shifted to younger age by 34 years for ‘wide’ and 22 years for ‘short’. Upper and lower bounds (1σ) are presented (Fig. 5).

The deconvolved δ\textsuperscript{15}N (qualitative temperature history) suggests that the 8.2ka event at Greenland started around 8175 B.P. on our timescale, and the cooling took ~20 years to reach the temperature minimum (Fig. 5). We emphasize that the cooling could have been faster than this due to uncertainty in the smoothing functions and the
inverse method. The decadal oxygen isotope record (thick blue line in Fig. 5e) shows a pattern with timings similar to the deconvolved nitrogen record ($r^2=0.63$; Fig. 5), which suggests that the oxygen isotopes of ice faithfully record the decadal surface temperature change during the 8.2ka event. The coldest period lasted for ~60 years with one warm period of a few decades. Then, the temperature gradually increased for ~70 years with a brief period of rapid warming (Fig. 5). Thomas et al. (2006) found a similar duration of the event by compiling oxygen isotope and chemistry of ice data from Greenland ice cores.

4. Evolution of the near-global 8.2ka event

4.1 Methane concentration and emission history

How the 8.2ka event evolved with time and space is important for understanding the mechanism of the event. The atmospheric methane concentration record provides a hint about the temporal evolution of the 8.2ka event, because methane emissions are strongly affected by climate (Brook et al., 2000). The methane record thus can help to interpret the regional climatic signals found in other paleoclimate records. However, the ice-core methane record does not directly reflect atmospheric methane concentration; rather it is a smoothed record of atmospheric methane history due to diffusion and gradual bubble close-off. To reconstruct the atmospheric methane history, the ice-core methane record is deconvolved with the smoothing functions by the same procedure as for nitrogen isotopes (Fig. 5).

To reconstruct the methane emission history, we constructed a simple one-box model (the atmospheric methane concentration is calculated according to the equation
\[ \frac{dM}{dt} = Q-S = Q-M/\tau \] with a constant atmospheric methane lifetime \( \tau \) of 8 years). Here, we assume that the total methane emission before the event was the same as the estimated preindustrial methane emission of 221±30 Tg (CH4)/yr, where 163 ± 32 is from wetlands, and 58.5 is from other natural sources (termites, wildfires, and wild animals) (Houweling et al., 2000). The preindustrial methane concentration (~700ppb; Houweling et al., 2000) was higher than that prior to the 8.2ka event. Therefore, the estimated emissions should be considered to be upper bounds. We note that recent discovery of aerobic methane production from plants (Keppler et al., 2006) may account for a large fraction of this “wetland” source, but our conclusion is little affected by this discovery. The methane lifetime of ~8±1 years is estimated from the total atmospheric methane loading before the event of 1757 Tg (=2.767[Tg/ppb] × 635[ppb]) (Etheridge et al., 1998; Fung et al., 1991) divided by the total methane emission, with the ±1 yr uncertainty obtained from the emissions uncertainty. We assume that the lifetime stayed constant through the event. This atmospheric mixing process can be represented as a smoothing function derived by inputting a pulse (delta function) to the model. Two smoothing functions of the atmospheric mixing \( B \) and firn diffusion \( C \) are derived and convolved to produce one smoothing function \( D: \)

\[ \Imath(D(v)) = \Imath(B(v))\Imath(C(v)). \]

The deconvolution of the ice-core methane record with this combined function \( D \) is conducted with the same procedure as for the nitrogen isotope record. The deconvolved results are converted to methane emissions under the assumption of a constant lifetime of methane.

Results show that during the event, the atmospheric methane concentration decreased by 80±25 p.p.b., from 635 to 555±18 p.p.b.. The firn layer smoothing
reduced this magnitude by ~15% in the ice core record. The model suggests that methane emissions decreased by 32±14 Tg (CH₄)/yr, from 220 to 188±10 Tg (CH₄)/yr or by 15±10%. The reduction started around 8175 B.P., coincident with the temperature cooling at Greenland (Fig. 5). It took about 40 years to reach minimum methane emission values, although large uncertainty makes this conclusion tentative, and soon after atmospheric methane concentration started to increase (Fig. 5). During the period of gradual increase, reconstructed atmospheric methane concentration shows a spike-like increase around 8070 B.P. (Fig. 5), suggesting a brief period of increased methane emission, and by extension, warming and wetting. The spike is also observed in the Greenland temperature record suggesting that the short term warmer and wetter event was a large scale climatic excursion during the 8.2ka event (Fig. 5). The total length of the 8.2ka event was roughly 150 years (Fig. 5). Note that the magnitude or speed of methane concentration change on shorter time scales (such as interannual) may have been larger or faster, but cannot be addressed by our technique due to the inherent information loss by smoothing of the gas record.

4.2 Geographical area of methane sources changes

An important question concerns the actual locations where changes in natural methane emissions occurred. Recent studies (Christensen et al., 2003; Walter et al., 2001a) suggest that methane emission is strongly controlled by temperature change. Walter et al. (2001a) found that a global temperature change of ±1°C leads to ~20% changes in methane emission. Christensen et al. (2003) estimate that a 2 °C change of summer temperature over the area where most of the northern wetlands are located
results in a 45 % change in methane emission. Both studies with different approaches agree that emission sensitivity to temperature is roughly ~20% for a 1 °C change. However, the recent finding of possibly large methane emissions from terrestrial plants (Keppler et al., 2006) may significantly revise the figures described here.

At present, ~70% of natural wetland methane emissions come from low latitudes, and only 25% of methane emissions come from wetlands north of 30°N, despite larger wetland areas in the north (Hein et al., 1997; Walter et al., 2001a; Walter et al., 2001b). The past inter-hemispheric gradient of atmospheric methane concentration from two polar ice cores (Greenland and Antarctica) can provide constraints on the locations of past methane emissions (Brook et al., 2000; Ethridge et al., 1998, Chappellaz et al., 1997). Chappellaz et al. (1997) found that during the early Holocene the northern (90°-30°N) contribution may have been slightly higher (~30%) and the tropical (30°N-30°S) contribution smaller (~60%; the numbers are average values of two different periods of 5,000-7,000 and 9,500-11,500). This corresponds to ~50 Tg/yr from the north and ~100 Tg/yr from the tropics, and the rest (10 Tg/yr) from the south.

If we assume that during the 8.2ka event average northern (90°-30°N) temperature cooled by 1-2 °C as inferred from much paleo-evidence from Europe (Wiersma and Renssen, 2006), this would correspond to a 10-20 Tg/yr methane emission reduction from the northern area, which is smaller than our estimate for the methane emission reduction during the 8.2ka event. Although large uncertainty for our methane emissions estimates precludes a firm conclusion, this may imply that the impacts of the event extended beyond the northern area. Furthermore, recent
compilations of paleoclimate data from around the globe (Alley and Agustsdottir, 2005; Morrill and Jacobsen, 2005; Wierma and Renssen, 2006) suggest a near-global cooling and drying event. The European region experienced strong cooling and hydrologic changes, and the Sahara and western Asian monsoon region experienced drying. Cooling probably occurred in North America, with drying in the US Great Plains (Alley and Agustsdottir, 2005; Morrill and Jacobsen, 2005). The southward shift of the intertropical convergence zone (ITCZ) as inferred from the Cariaco Basin record (Haug et al., 2001; Hughen et al., 1996) may indicate that a large tropical area experienced changes in precipitation (Alley and Agustsdottir, 2005; Morrill and Jacobsen, 2005). A recent study showed a weakened Asian Monsoon during the 8.2ka event from oxygen isotopes of stalagmites from Dongge Cave in southern China (Wang et al., 2005). LeGrande et al. (2006) calculated methane changes for the 8.2ka event using local regression models coupled with the general circulation model (GCM). They found significant methane emission reduction over North America and Europe by 11% (8%) with North Atlantic Deep Water formation reduced by 60% (40%). Their estimate is slightly less than our estimate of 15±10% but within the uncertainty. As a conclusion, our methane data are consistent with this widespread footprint and model result of the event’s impact on temperature and precipitation.
5. Timing of the 8.2ka event

Although many high-resolution proxy data for the early Holocene reveal an abrupt event at around 8.2ka, the apparent age and duration are different in different locations, probably owing to the difficulties of all paleoclimate records with age uncertainty, continuity, and regional climatic influences (Alley and Agustsdottir, 2005; Morrill and Jacobsen, 2005; Rohling and Palike, 2005). Therefore, it is difficult to assess the relative timing of climatic events between different regions inferred from paleoclimatic proxies. The simultaneous analysis of nitrogen isotopes and methane in a single ice core circumvents these problems, and allows us to compare the timing of northern high-latitude and large-scale climate change in methane source regions (Severinghaus and Brook, 1999; Severinghaus et al., 1998).

The methane and nitrogen isotope records show very similar timing through the 8.2ka event ($r=0.91$ for the period of 8000-8250 B.P., Fig. 6). We found that the maximum correlation coefficient ($r=0.95$) occurs when the methane age is shifted by 7.6±4 (1σ) years toward older ages, suggesting that the methane signal lags the nitrogen signal. Uncertainty was estimated using a Monte Carlo procedure. We carried out 5000 realizations in which we added white noise to the data with a standard deviation of 17 ppb for methane and 0.004 per mil for $\delta^{15}$N, and found the maximum of the lagged correlation.

However, to compare accurately the near-global climate signal in methane and the Greenland climate signal in nitrogen isotopes, we have to account for two non-climatic processes that can create differences in phasing of the two gases in an ice core. The first is the atmospheric methane reservoir effect. Owing to the large load of
methane in the atmosphere, a change in methane emissions takes time to be reflected in the atmospheric methane concentration (e-folding time of ~8 years). The second is due to differences in the diffusion rate of methane and nitrogen gases. As these gases diffuse through the firn layer, a change at the surface takes 20-30 years on average to be recorded in the ice (Spahni et al., 2003). The difference in the speed of diffusion between methane and nitrogen creates an apparent methane lead relative to the nitrogen signal by 1-2 years (Severinghaus et al., 1998; Spahni et al., 2003).

To more precisely evaluate the timing of climatic changes in methane and nitrogen isotopes, we process the data so that both signals experience the same filtering (Fig. 6). Because climatic signals in methane experience two filtering processes before being trapped in ice, and the signal to noise ratio of data are lower than for nitrogen isotopes, it is more difficult to obtain a precise climatic signal (emission change) by deconvolution. Instead, we process the nitrogen isotope signal to be comparable to the methane signal by the following method. First, the age of the nitrogen signal is shifted by 1-2 year toward older age to account for the difference in speed of diffusion. Second, an atmospheric reservoir effect was added to the nitrogen isotope signal. To do so, the nitrogen signal is scaled to be comparable with the methane record so that we can access the timing of different quantities (Fig. 7). Then, the scaled nitrogen signal is converted to methane emission using the relationship

\[
\text{Modeled methane emission (Tg/yr)} = 2.767 \times \left[ \text{the scaled nitrogen signal} \right] / 8 \text{ yr (methane lifetime)}.
\]

Then, the emission scenario derived from the nitrogen record is smoothed with an atmospheric mixing model of the form \( \frac{dM}{dt} = Q - S = Q - \frac{M}{\tau}, \) where \( M \) represents total mass of CH\textsubscript{4} in atmosphere, \( Q = \) source strength, \( S = \) sink
strength, and $\tau$=a constant atmospheric methane lifetime of 8 years). The methane and adjusted nitrogen isotope signals show synchronous timing with a maximum correlation coefficient of $r = 0.96$ with 0-1 year shift (Fig. 7). Thus we conclude that cooling and drying in many parts of the globe occurred within $\pm 4$ years of climate changes in Greenland recorded by the nitrogen isotope record.

6. Conclusion

A large number of paleoclimatic records over a near-global area show a large and abrupt climate change around 8,200 years B.P. However, the duration, magnitude and general character of the event have been ambiguous. Here, we provide a general character and timing of the event precisely using methane and nitrogen isotopes in trapped air in a Greenland ice core. Climate change in Greenland and at a near-global scale was simultaneous (within $\pm 4$ years) as supported by the GCM model results (LeGrande et al., 2006). The event started around 8175±30 years B.P., and it took less than $\sim 20$ years to reach the coldest period, with a magnitude of cooling of 3.3±1.1 °C in central Greenland. After $\sim 60$ years of the coldest period, climate gradually recovered for $\sim 70$ years to a similar state as before the event. The duration of the event was roughly 150 years.

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Figure 2.1. Greenland ice core records covering the past 16,000 years (oxygen isotopes of ice and methane). Note that the 8.2ka event punctuates the relatively warm and stable past ~11,000 years since the end of the last glaciation. (Top) GISP2 oxygen isotope record (Stuiver et al., 1995) with a 50-year moving average. The oxygen isotope record can be considered as a qualitative temperature record on this time scale. (Bottom) Methane concentration in ice cores. Owing to the different resolution and precision of methane records in GISP2 and GRIP, we used records from 175-7530 B.P. and 8762-9891 B.P. from GRIP (Blunier et al., 1995), and records from 7612 B.P.-8617 B.P. (this study) and 10153 B.P.-16507 B.P. from GISP2 (Brook et al., 2000).
Figure 2.2. Methane concentration, $\delta^{15}$N, $\delta^{36}$Ar/4, and $\delta$Ar/N$_2$ data. Circles represent average values. Error bars are $1\sigma$. For methane and $\delta^{15}$N data, blue lines are $1\sigma$ error range after spline fit (Enting, 1987) with 10-year cutoff period for $\delta^{15}$N and 30-year cutoff period for methane. For $\delta^{36}$Ar/4 data, red line represents modeled $\delta^{36}$Ar/4 value (see text).
Figure 2.3. Modeling results of the rapid cooling (see text). Black lines ($\delta^{15}$N_{therm}, $\delta^{15}$N_{grav}, and $\delta^{15}$N_{total}) are model results. Red dots are data and average values, and error bars are standard errors of mean (1σ).
Figure 2.4. Nitrogen isotope data from Leuenberger et al. (1999) and this study. Diamonds are individual data points, and blue solid lines represent average values.
Figure 2.5. Evolution of Greenland temperature and near-global wetland condition as inferred from $\delta^{15}$N and methane. The blue area represents the duration of the event from 8175-8025 B.P., and the dark blue area is the coldest period. (a) Methane record as for Fig. 2. The lines for the error range are calculated by Monte Carlo simulation and spline-fitted with a 30 year cutoff period spline fit (Enting, 1987). (b) Reconstructed atmospheric methane concentration. Lines are mean and range of error (1σ) (see text for detail). (c) $\delta^{15}$N record as for Fig. 2. The lines for error range are calculated by Monte Carlo simulation and spline-fitted with 10 year cutoff period (Enting, 1987). (d) Deconvolved $\delta^{15}$N record. This qualitatively represents surface temperature change in central Greenland (see text). Lines are range of error (1σ). (e) Surface temperature change reconstructed from oxygen isotope record of ice (Stuiver et al., 1995). Thin and thick lines represent raw and smoothed (20-year running mean) records.
Figure 2.6. Filtering processes for nitrogen isotopes and methane. The climatic signal (emission change) in methane goes through two natural filtering processes while the climatic signal (surface temperature change) in nitrogen isotopes goes through only one filtering process. Red rectangles indicate the places where climatic signals start. To obtain the same timing, nitrogen signals are processed by a fictitious atmospheric reservoir (see text).
Figure 2.7. Timing of the 8.2ka event. (a) Red and blue lines represent methane concentration and scaled nitrogen isotope data, respectively, after a spline fit (Enting, 1987) with cut-off period of 10 yr, corresponding to the resolution of data. (b) Same as (a) except the nitrogen signal has been processed to mimic the methane atmospheric reservoir effect (see text). Red and blue lines represent the methane and the processed nitrogen signal, respectively. Dotted lines are error range (1σ) for methane data. Note that the methane signal lags the nitrogen signal by 7.6±4 years in the ice core record, but after the nitrogen signal is processed to account for the 8-year lifetime of methane, the two signals show almost identical timing (see text).
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Chapter III

Evidence for abrupt warming in the Earliest Holocene

11,270 years ago
Abstract

Nitrogen and argon isotopes in air trapped in a Greenland ice core (GISP2) show two prominent peaks in the interval 11,800-10,800 B.P., which indicate two large abrupt warming events. The first abrupt warming (10±4°C) is the widely documented event at the end of the Younger Dryas. Here, we report on the second abrupt warming (4 ±1.5°C), which occurred at the end of a short lived cooler interval known as the Preboreal Oscillation (11,270±30 B.P.). A rapid snow accumulation increase suggests that the climatic transition may have occurred within a few years. The character of the Preboreal Oscillation and the subsequent abrupt warming is similar to the Dansgaard-Oeschger (D/O) events in the last glacial period, suggestive of a common mechanism, but different from another large climate change at 8,200 B.P., in which cooling was abrupt but subsequent warming was gradual. The large abrupt warming at 11,270 B.P. may be considered to be the final D/O event prior to the arrival of the present stable and warm epoch.

1. Introduction

1.1. The Early Holocene and Preboreal Oscillation

After an abrupt warming at the end of the Younger Dryas interval [Severinghaus et al., 1998], Greenland temperature gradually rose by ~5 °C for ~2000 years and accumulation rate increased by >40 % [Cuffey and Clow, 1997]. This temperature increase was interrupted by a brief cold event (the Preboreal Oscillation) at 11,400-11,270 B.P. (yr Before Present, where present means C.E. 1950; Fig. 1) [Bjorck et al., 1996; Bjorck et al., 1997]. Atmospheric methane concentration
decreased during the Preboreal Oscillation by 8% or 60 ppb [Brook et al., 2000] and the tropical Atlantic had stronger trade winds and lower precipitation [Hughen et al., 1996], suggesting that a broad geographic area experienced this cooling [Brook et al., 2000]. Many European pollen studies show that vegetation responded to this cool event [Bjorck et al., 1997]. At the time of the Preboreal Oscillation, sea level was still about 50 m lower than present [Bard et al., 1996]. A large meltwater pulse (MWP-1B) is inferred to have occurred around this time from an observed rapid sea level rise around this time, potentially causing this brief cool event [Bard et al., 1996; Fairbanks, 1989].

The rapid environmental changes around this time had major impacts on ecosystems including human society [Bar-Yosef, 2001; Byrd, 2005]. The first large settled villages based on intentional cultivation (agriculture) emerged in Southwest Asia around this time likely due to a warmer and wetter environment [Bar-Yosef, 2001; Byrd, 2005]. Therefore, the precise understanding of climate change around this time may provide an important framework to understand the formative states of human society [Bar-Yosef, 2001; Byrd, 2005].

1.2. Nitrogen and argon isotopes and temperature reconstruction

Over the last decade, isotopic compositions of inert gases in ice cores such as nitrogen and argon have been extensively used to reconstruct past abrupt temperature changes [Grachev and Severinghaus, 2005; Huber et al., 2006b; Kobashi et al., submitted-a; Landais et al., 2004a; Landais et al., 2004b; Lang et al., 1999; Leuenberger et al., 1999; Severinghaus and Brook, 1999; Severinghaus et al., 1998].
Recent advances in measurement techniques have further sharpened the precision of estimates of temperature change [Kobashi et al., submitted-b], and a recently completed high resolution Holocene record (10-20 year interval) from GISP2 provides opportunities to understand past climate change during the period when human society went through major changes [Kobashi et al., in preparation; Kobashi et al., submitted-a; Kobashi et al., submitted-b].

The basic principles of the method rest on the fact that the isotopic ratios of these gases in the atmosphere are constant for $>10^5$ years [Allegre et al., 1987; Mariotti, 1983]. Therefore, any deviations of isotopic composition in ice cores from atmospheric values are the result of isotopic fractionation in the firn layer (unconsolidated snow on top of glacial ice). The firn layer can be subdivided into three sections in terms of isotopic fractionation [Sowers et al., 1992]. The upper few meters of firn is called the “convective zone”, in which air freely exchanges with the atmosphere by wind pumping [Colbeck, 1989; Kawamura et al., 2006]. Therefore, air in this zone has the same gas composition as the atmosphere [Colbeck, 1989]. Below this layer, there is a stagnant layer called the “diffusive air column”, where gas is nearly in diffusive equilibrium and transport is dominantly by molecular diffusion [Sowers et al., 1992]. Isotopic fractionation occurs in this layer by gravitational settling and thermal diffusion [Severinghaus and Brook, 1999; Severinghaus et al., 2001; Severinghaus et al., 1998]. The last layer is called the “non-diffusive zone” or “lock-in-zone”, where vertical air movement ceases owing to the existence of impermeable layers of higher-density firn [Sowers et al., 1992]. The thickness of the convective zone and non-diffusive zone are likely constant during the Holocene in
Greenland, as a model study reproduces gas isotope signals well with an assumption of constant thickness of these two layers [Goujon et al., 2003]. Therefore, henceforth we call the thickness of the diffusive air column the “firn thickness”.

Gases in the diffusive air column fractionate by at least two mechanisms. First, a change in firn thickness induces a change in gravitational fractionation [Caillon et al., 2003; Sowers et al., 1992]. Second, a temperature gradient (ΔT) between the top and bottom of the firn induces thermal fractionation [Severinghaus et al., 1998]. Measurements of both nitrogen and argon isotopes allow a deconvolution of these two effects, and can be used to infer past firn thickness and ΔT [Landais et al., 2004a; Landais et al., 2004b; Severinghaus and Brook, 1999]. The method is most effective for investigating abrupt climate changes, which create a large ΔT and thus large isotopic signals [Landais et al., 2004a; Landais et al., 2004b; Severinghaus and Brook, 1999].

The surface temperature reconstruction from ΔT is not straightforward for higher frequencies because there is no single unique solution, due to smoothing of the record by gas diffusion and bubble close-off. As various surface temperature histories can satisfy the observed gas-isotopic signals, oxygen isotope records of ice (δ¹⁸O ice) have been used by some studies to provide constraints on the “shape” and rate of surface temperature change [Huber et al., 2006b; Kobashi et al., submitted-a; Landais et al., 2004a]. However, δ¹⁸O ice is not only a proxy of temperature. It may vary without temperature change, or it may be biased by other climatic variables such as the evaporative origins of the moisture, or changes in the seasonality of precipitation [Charles et al., 1994; Jouzel et al., 1997; White et al., 1997]. For these reasons, direct
methods of temperature reconstruction without $\delta^{18}\text{O}_{\text{ice}}$ have been explored, thus far with limited success [Landais et al., 2004b]. In this study, we developed a new method to reconstruct a surface temperature history without using $\delta^{18}\text{O}_{\text{ice}}$, based on simultaneous measurements of nitrogen and argon isotopes.

2. Methodology

2.1. Chronology

A precise chronology is critical to compare climate information in ice cores with other paleoclimatic archives, for example those dated by $^{14}\text{C}$. Recent advances in the tree-ring chronology provide an absolutely dated tree-ring chronology back to 12,410 B.P. [Friedrich et al., 2004]. Therefore, it is now possible to correlate regional climate changes with unprecedented accuracy for the early Holocene [Friedrich et al., 2004; Reimer et al., 2004].

We used an ice core (GISP2) from central Greenland (72° 36’N 38° 30’W; 3203 masl), with a layer-counted time scale from visual stratigraphy [Alley et al., 1997b; Cuffey and Clow, 1997]. This chronology may be too old in the early to middle Holocene by ~100 years, as inferred from a correlation between $^{10}\text{Be}$ in the ice cores and $^{14}\text{C}$ from tree-rings [Finkel and Nishiizumi, 1997; Kobashi et al., submitted-a]. Therefore, it requires some adjustment. A recent Greenland ice core chronology (GICC05) for GRIP, NGRIP, and DYE-3 places the termination of the Younger Dryas at 11653 B.P. [Vinther et al., 2006]. However, the correlation of $^{10}\text{Be}$ from the ice core and $^{14}\text{C}$ from tree-rings shows that this chronology is ~80 years too old in the early Holocene (R. Muscheler, personal communication), which suggests that the age
of the Younger Dryas termination should be ~11,573 B.P. As another piece of evidence for the age of the Younger Dryas termination, the German tree ring chronology exhibits a rapid increase in tree ring width at 11,590 B.P [Friedrich et al., 1999; Friedrich et al., 2004]. As the uncertainty of dendrochronology is estimated to be less than 1 year for this interval (M. Friedrich, personal communication), the year 11,590 B.P. should be the best estimate for the age of the Younger Dryas termination. The GISP2 visual stratigraphy timescale has the age of the Younger Dryas termination at 11,705 B.P inferred from the rapid increase of accumulation rate [Alley et al., 1997b; Cuffey and Clow, 1997]. Therefore, we subtracted 115 years from the GISP2 chronology to align it with the tree-ring age of the Younger Dryas termination.

We used a firn densification-heat transfer model [Goujon et al., 2003] to estimate a preliminary gas age from input temperature and accumulation rate. These inputs were obtained from the borehole-calibrated $\delta^{18}$O ice and ice-flow corrected layer thickness records of Cuffey et al. (1997) [Cuffey and Clow, 1997]. The uncertainty of the gas-ice age difference (~450 years around 11,270 B.P.) calculation is estimated to be 10% or ±45 years [Goujon et al., 2003]. We find a rapid increase in accumulation rate, and oxygen isotope ratio of ice, at 11,270 B.P. (Fig. 1), which should correspond to the rapid increase observed in $\Delta T$ at 11,245 B.P. in the preliminary gas age. Therefore, we added 25 years to the calculated gas age to align the gas signal with the ice signal of the warming (Fig. 1). Relative ice-age uncertainty at century scales in the early Holocene is estimated to be ~1% [Alley et al., 1997b]. Therefore, the age difference of 320 years between the termination of the Younger Dryas and the abrupt warming at 11,270 B.P. yields ~4 years relative uncertainty.
Although it is difficult to identify all the uncertainties, we estimate the absolute uncertainty of reported calendar ages herein to be ±30 years from the above information.

2.2. Inert gas isotopes and isotopic fractionation in firn layer

We analyzed argon (mass 40 and 36) and nitrogen (mass 15 and 14) isotope ratios ($\delta^{15}$N and $\delta^{40}$Ar) in air trapped in the GISP2 ice core (Fig. 1) [Kobashi et al., submitted-b]. Data before 11,446 B.P. are from Severinghaus et al. [Severinghaus et al., 1998], and data in the later part is from Kobashi et al. [Kobashi et al., submitted-b]. The two datasets for $\delta^{15}$N show good agreement for the overlapping four points (Fig. 2.). From 11,466 B.P. to 10,000 B.P. the data resolution is about 20 years, and each data point is from a single sample [Kobashi et al., submitted-b]. We only use data from Kobashi et al. [Kobashi et al., submitted-b] for surface temperature calculation because of its continuity and precision. The isotopic ratios are presented as a deviation from the present atmospheric composition (which is the standard) by conventional notation as follows.

$$\delta^{40}\text{Ar} = \left(\frac{^{40}\text{Ar}^{36}\text{Ar}_{\text{sample}}}{^{40}\text{Ar}^{36}\text{Ar}_{\text{standard}}} - 1\right) \times 10^3 \text{‰}$$  (1)
$$\delta^{15}\text{N} = \left(\frac{^{15}\text{N}^{14}\text{N}_{\text{sample}}}{^{15}\text{N}^{14}\text{N}_{\text{standard}}} - 1\right) \times 10^3 \text{‰}$$  (2)

The analytical method and precision are described elsewhere [Kobashi et al., submitted-b]. Each observed $\delta^{15}$N and $\delta^{40}$Ar value can be decomposed into two
components as discussed previously. Therefore, the observed $\delta^{15}N$ ($\delta^{15}N_{obs}$) and $\delta^{40}Ar$ ($\delta^{40}Ar_{obs}$) may be written as

$$\delta^{15}N_{obs} = \delta^{15}N_{grav} + \delta^{15}N_{therm} = \delta^{15}N_{grav} + \Delta T^{15}\Omega^{15} \gamma \quad (3)$$

$$\delta^{40}Ar_{obs} = \delta^{40}Ar_{grav} + \delta^{40}Ar_{therm} = \delta^{40}Ar_{grav} + \Delta T^{40}\Omega^{40} \gamma \quad (4)$$

$$^{15}\gamma \cong ^{40}\gamma \quad (5)$$

where the subscripts ‘therm’ and ‘grav’ represent thermal and gravitational components, respectively, $^{15}\gamma$ is a disequilibrium term, and $^{15}\Omega$ is the thermal diffusion sensitivity of $\delta^{15}N$ [Grachev and Severinghaus, 2003b]. The disequilibrium terms are negligible for timescales longer than the firn diffusion time of ~10 years [Schwander et al., 1993], and are ignored in this study. The gravitational component depends on the absolute mass difference, which is 4.007 times larger for $\delta^{40}Ar$ than for $\delta^{15}N$ [Craig et al., 1988]. Therefore, we can express it as $\delta^{15}N_{grav} \cong \delta^{40}Ar_{grav}/4$.

$$\delta^{40}Ar_{obs} = \delta^{15}N_{grav} \times 4 + \Delta T^{40}\Omega^{15} \gamma \quad (6)$$

For simplicity, we use $\delta^{40}Ar/4$ rather than $\delta^{40}Ar$ in the following discussion so that the gravitational signals for nitrogen and argon isotopes are on the same scale. The past firn temperature gradient $\Delta T$ can be calculated from the difference ($\delta^{15}N_{excess} = \delta^{15}N_{obs} - \delta^{40}Ar_{obs}/4$), which is sensitive to the differing thermal responses of $\delta^{15}N$ and $\delta^{40}Ar/4$.

Grachev and Severinghaus [2003a; 2003b] conducted laboratory experiments to obtain the thermal coefficients of $\delta^{15}N$ and $\delta^{40}Ar$ in air, which are a prerequisite for precise
estimates of temperature changes. With these numbers, $\Delta T$ ($^\circ$C) can be calculated simply as $\Delta T$ ($^\circ$C) = $\delta^{15}$N$_{excess}$ ($^\circ$C) / 0.0047 ± 0.0005 ($^\circ$C/‰) \cite{Grachev2003a,Grachev2003b,Severinghaus1999}.

\[
\delta^{15}$N$_{obs} - \delta^{40}$Ar/4$_{obs}) = \Delta T \cdot 15 \gamma (15 \Omega - 40 \Omega/4) \equiv \delta^{15}$N$_{excess} \tag{7}
\]

$15 \Omega - 40 \Omega/4 = 0.0047 ± 0.0005$ ‰ K$^{-1}$ \tag{8}

The gravitational component can be calculated as a residual of observed $\delta^{15}$N corrected for the thermal component \cite{Severinghaus2003}. So, $\delta^{15}$N$_{grav} = \delta^{15}$N - $15 \Omega \cdot \Delta T$ where $15 \Omega = 0.0145$ ‰/°C at 240 K, the thermal diffusion sensitivity of $\delta^{15}$N \cite{Grachev2003b}. Note that the thermal coefficients are temperature dependent, but in the temperature range of -34 °C to -42 °C their difference is nearly constant within analytical uncertainty \cite{Grachev2003a,Grachev2003b}. Diffusive column height (DCH) or firn thickness can be calculated from $\delta^{15}$N$_{grav}$ \cite{Schwander1997,Severinghaus2003}.

\[
\text{DCH (m)} = \frac{RT}{(g \Delta m)} \left(\ln(\delta^{15}$N$_{grav}/1000+1)\right) \tag{9}
\]

where $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is temperature (K), $g$ is the acceleration due to gravity (9.82 m s$^{-2}$), and $\Delta m$ is the mass difference between $^{15}$N and $^{14}$N (0.001 kg mol$^{-1}$).
2.3. Gas loss and normalization problems

Recent studies show that gas composition in ice cores may change during/after the coring process \cite{Bender1995, KobashiSubmitted, Severinghaus2003}. At least two mechanisms may affect gas composition \cite{KobashiSubmitted}. First, smaller molecules with less than a certain threshold size (\(~3.6\text{Å}\)) leak out of the ice lattice with little isotopic fractionation, as observed in firn air and ice core studies \cite{Bender1995, Huber2006, KobashiSubmitted, Severinghaus2006}. This mechanism appears nearly independent of mass. Second, gases in ice leak through microcracks causing mass-dependent fractionation, which is often observed in poor quality ice and the gas-clathrate transition zone where ice samples are typically fractured \cite{Bender1995, KobashiSubmitted}. As the GISP2 ice core at the depth of our study is of good quality and is out of the gas-clathrate transition \cite{KobashiSubmitted}, it is less likely that argon and nitrogen isotopic compositions are affected. Potential minor impacts on isotopes of mass dependent fractionation should be cancelled out during the calculation of $\delta^{15}\text{N}_{\text{excess}}$, because nitrogen and argon isotopes are measured in the same sample \cite{KobashiSubmitted, Severinghaus2006}.

Prior work has found that both $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}/4$ may shift slightly and systematically on the order of 0.005-0.010‰ owing to analytical problems during the normalization of data to present atmosphere, the standard used \cite{Grachev2004, KobashiSubmitted, Severinghaus1999}. This slight shift creates a constant offset in the $\Delta T$ estimates, and affects the surface temperature calculation as
described below. Without any further information, the normalization problems are difficult to constrain. As we discuss later, we attempt to calibrate for the normalization problem by matching model results with observed isotope records. For the last-millennium temperature calculation done by Kobashi et al. [Kobashi et al., in preparation], $\Delta T$ was calibrated with the borehole temperature record. Kobashi et al. [Kobashi et al., in preparation] found that the $\Delta T$ (top minus bottom) data may be too negative by 1-2 °C. The dataset in this study was obtained with the same method and at the same time as the dataset for the last 1000 years [Kobashi et al., submitted-b]. Therefore, any normalization offset is expected to be similar.

2.4. Surface temperature calculation – a new method

Since Severinghaus et al.’s [1998] original study, there have been many attempts to quantify surface temperature changes with gas isotope records [Grachev and Severinghaus, 2005; Huber et al., 2006b; Landais et al., 2004a; Landais et al., 2004b; Lang et al., 1999; Leuenberger et al., 1999; Severinghaus and Brook, 1999]. To reconstruct surface temperature changes, it is necessary to understand changes in the firn condition such as heat diffusion and advection, densification, and the bubble close-off process. The firn condition and associated change can be explicitly calculated from empirical glaciological models if surface temperature and accumulation rate histories are known [Goujon et al., 2003; Schwander et al., 1997]. By combining gas-isotope data with firn-densification models, various methods have been developed to reconstruct surface temperature changes. A few studies used prescribed shapes of temperature histories, such as a step function, to estimate
magnitudes of temperature changes [Severinghaus and Brook, 1999; Severinghaus et al., 1998] Others reconstructed the surface temperature change by calibrating $\delta^{18}$O$_{\text{ice}}$ [Huber et al., 2006b; Kobashi et al., submitted-a; Landais et al., 2004a; Lang et al., 1999; Leuenberger et al., 1999]. Landais et al. [Landais et al., 2004b] explored a full range of the potential magnitude of temperature change from isotope records.

A rapid surface temperature change, if it is instantaneous or much faster than heat diffusion in firm, equals the temperature gradient ($\Delta T$) in the firm layer (assuming an isothermal initial state). If it happens gradually (over a few decades or longer), the temperature gradient ($\Delta T$) in firm progressively becomes smaller than the surface temperature change owing to heat transfer in the firm. To calculate surface temperature, the heat transfer in firm needs to be considered, which is also a function of $\Delta T$. In light of these circumstances, we modified the firm densification-heat transfer model to calculate surface temperature from the $\Delta T$ history and accumulation rate [Goujon et al., 2003]. We used an accumulation rate history obtained from visual layer counting [Alley et al., 1997b] coupled with ice-flow correction from a glaciological model [Cuffey and Clow, 1997].

After the modification, the model calculation proceeds as follows. In a model year, a new firm state is forced by a new surface temperature and accumulation rate. With the new forcing from the surface, heat diffusion/advection and firm densification is calculated. In the next model year, a new surface temperature ($T_s$) is obtained by adding the calculated temperature ($T_b$) at the bottom of firm in the previous model-year to $\Delta T$ obtained from observed $\delta^{15}$N and $\delta^{40}$Ar.
\[ T_s = T_b \text{ (model output from the previous model year)} + \Delta T \text{ (observation)} \]

By repeating this process, the surface temperature history can be calculated recursively. In the actual model run, it uses calibrated $\delta^{18}O_{\text{ice}}$ as surface temperature [Cuffey and Clow, 1997] until 11,417 B.P., and from that point on it switches to the method described above. Annual-resolution $\Delta T$ data are obtained by linearly interpolating the original data (~20-year resolution).

One modification from the original Goujon model [Goujon et al., 2003] is made to the calculation of isotopic fractionation. The firn condition is calculated with two different coordinate systems in the model [Goujon et al., 2003]. A Lagrangian coordinate system is used to calculate the temperature field in the firn, and an Eulerian coordinate system is used for the calculation of the age of the gas. We found that the results from the two coordinate systems disagree slightly, with the changes in firn thickness in the Eulerian coordinate showing a slight lag to the Lagrangian coordinate system. To be consistent between the temperature field and firn thickness, we modified the original code to use the Eulerian coordinate for the calculation of gravitational fractionation, which is a function of firn thickness.

3 Results

3.1. Isotope Data

The isotope records show two prominent peaks in the interval 11,800 B.P. to 10,700 B.P. (Fig. 1). The combined analysis of nitrogen and argon isotopes suggests that two large abrupt warming events occurred during this period. The first warming
occurred at 11,590 B.P., marking the end of the Younger Dryas [Alley et al., 1993; Severinghaus et al., 1998]. The second one occurred at 11,270 B.P. at the end of the Preboreal Oscillation. Rather abrupt changes are also clear in the $\delta^{18}O_{\text{ice}}$ and snow accumulation rate (Fig. 1). The magnitudes of the two peaks in $\delta^{15}N$ and $\delta^{40}\text{Ar}/4$ are 0.14 ‰ and 0.11 ‰ for the Younger Dryas termination, and 0.06 ‰ and 0.04 ‰ for the termination of the Preboreal Oscillation, respectively. The ratios $(\Delta\delta^{40}\text{Ar}/4)/\Delta\delta^{15}N$ of these changes are 0.78 for the Younger Dryas and 0.67 for the Preboreal Oscillation.

As the ratio $(\Delta\delta^{40}\text{Ar}/4)/\Delta\delta^{15}N$ of thermal responses of $\delta^{15}N$ and $\delta^{40}\text{Ar}$ to a temperature change is 0.68 [Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b], it can be inferred that the peak at the terminal Younger Dryas event consists of ~85 % thermal and ~15 % gravitational signals. The peak at the end of the Preboreal Oscillation nearly all comes from a thermal signal. The $\Delta T$ shows an abrupt increase of 4.1 °C at 11,271 B.P. (Fig. 3), which is about half of the observed $\Delta T$ (8 °C) at the Younger Dryas termination [Grachev and Severinghaus, 2005]. $\delta^{15}N$ shows two other smaller oscillations around 10,940 B.P. and 10,800 B.P. with amplitudes of ~0.02 ‰ and 0.015 ‰, respectively (numbered as 3 and 4 in Fig 1), which are also interpreted here as small abrupt warming events. The intervals between one abrupt warming and the next decrease progressively from 320, to 290, to 150, and to 50 years, an interesting fact that will be discussed below.

3.2. Surface temperature reconstruction

3.2.1. 11,417 B.P. to 10,000 B.P.
As mentioned in the data description, our approach to surface temperature reconstruction using $\Delta T$ requires an adequate calibration, due to possible artifacts. Therefore, we conducted three model experiments to find the best fit between model and observed data ($\delta^{15}\text{N}$ and firn thickness) by adjusting a correction to $\Delta T$. The temperature calculation depends on an initial temperature profile of the firn and ice sheet, especially for the first few hundred years of the integration. We assume that a temperature history before 11,417 B.P. can be reconstructed from the calibrated $\delta^{18}\text{O}_{\text{ice}}$ with the borehole temperature [Cuffey and Clow, 1997], and we force the model with this temperature until 11,417 B.P. Although a $\delta^{18}\text{O}_{\text{ice}}$-based surface temperature with a single calibration equation is clearly problematic [Huber et al., 2006b; Landais et al., 2004a], a model driven with the $\delta^{18}\text{O}$-based surface temperature reproduces $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$ sufficiently well [Goujon et al., 2003; Kobashi et al., submitted-b]. Therefore, the use of the calibrated $\delta^{18}\text{O}_{\text{ice}}$ should be valid in the first order and as a starting point for our method [Goujon et al., 2003; Kobashi et al., submitted-b].

The model experiments are conducted with three different $\Delta T$ time series corrected by +0.0 °C, +1.0 °C, and +2.0 °C (Fig. 3). The shifts are accommodated into the isotopic values by subtracting a constant value of 0.0047 (‰/°C) ×0.0 °C, ×1.0 °C, and ×2.0 °C from $\delta^{40}\text{Ar}/4$, respectively. [The value of 0.0047 (‰/°C) is the sensitivity of $\delta^{15}\text{N}_{\text{excess}}$ to a 1 °C temperature gradient [Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b]]. Figure 4 shows the three model results of $\Delta T$-based surface temperature reconstructions along with the $\delta^{18}\text{O}_{\text{ice}}$-based temperature reconstruction. The reconstruction with no $\Delta T$ shift (blue) shows a
gradual cooling after the Preboreal Oscillation. The reconstruction with +1 °C shift (green) shows a modest temperature increase after the Preboreal Oscillation. The reconstruction with +2 °C shift (red) shows a large temperature increase after the Preboreal Oscillation reaching almost -25 °C at 10,000 B.P. The δ¹⁸O_ice-based reconstruction (brown) shows a temperature history similar to the 0 °C-shift until 10,800 B.P., when it starts to fit better with ΔT shifted by +1 °C (Fig. 4).

Figure 5 shows the model results and the observed δ¹⁵N. The overall gradual decrease of δ¹⁵N after ~11,500 B.P. reflects decreasing firn thickness and firn temperature gradient as the firn adjusts to Holocene warmth. The reconstruction with ΔT shifted by +1 °C (green) shows the closest agreement with the observed δ¹⁵N. The modeled δ¹⁵N in general shows more fluctuation than the measurements, partly owing to the poorer precision of ΔT. Figure 6 shows the model results for DCH (or firn thickness) and the observed DCH, which is calculated from δ¹⁵N_grav (smoothed with a 5-point running mean). At 11,600-11,400 B.P., the modeled DCH shows the highest value of ~90 m in this interval. Then, it rapidly decreases as a response to the enhanced densification caused by the abrupt warming at the Younger Dryas termination. The DCH turns upwards around 11,250 B.P. as a response to the cooling during the Preboreal Oscillation, and then the DCH starts decreasing around 11,210 B.P owing to the surface warming at 11,270-11,250 B.P. The time lag is found to be ~50 years between the changes in surface temperature and DCH, owing to the slow heat transfer in the firn. The model results seem to correctly reconstruct the time lag for the Preboreal Oscillation, although later fluctuations in the observed DCH are not
reproduced well by the model results. The DCH reconstruction with $\Delta T$ shifted by +1 °C (green) again shows the closest agreement with observation (Fig. 6).

Recent studies [Li et al., 2003; Zwally and Jun, 2002] found that interannual variation of firn thickness was 40-80 cm during the period of 1992-1999 and seasonal variation was nearly 1 m at central Greenland, due to changes in temperature and accumulation. These magnitudes are much higher than expected by conventional firn densification models [Zwally and Jun, 2002]. The discrepancy between the observations and the conventional models is likely due to a higher dependency of the firnification process on temperature than accounted for in the conventional models [Zwally and Jun, 2002]. The low centennial fluctuations in the model DCH may suggest that the shallow firn densification parameterization in the Goujon model [Goujon et al., 2003] may need to be revised.

Temperature signals in gas isotope data are opposite in $\delta^{15}N_{grav}$ and $\delta^{15}N_{therm}$, because a surface warming creates a positive $\delta^{15}N_{therm}$ signal, and a negative $\delta^{15}N_{grav}$ signal due to thinning firn. Therefore, small surface temperature fluctuations, generating near-simultaneous changes in the shallow firn thickness and temperature gradient, can be canceled in the observed $\delta^{15}N$. To reconstruct observed isotope signals, it is important to have a realistic model representation of shallow firn densification processes, which are currently poorly understood. Future work with a higher resolution and precision isotopic dataset for the last 1000 years [Kobashi et al., in preparation; Kobashi et al., submitted-b] will address these issues further.

3.2.1. Preboreal Oscillation and abrupt warming at 11,270 B.P.
The reconstructed surface temperature with the $\Delta T$-based method shows a gradual cooling after the abrupt warming at the Younger Dryas termination, and then abruptly warms by 4±1.5 °C (decadal average) at the end of the Preboreal Oscillation (11,271±30 years B.P.; Fig. 1 and 7). The $\Delta T$ time series shows that the temperatures increased by 4.1±1.5 °C in only one sample interval between 11,271 B.P. (1681.21 m) and 11,257 B.P. (1680.32 m). Considering that gas diffusion and bubble close-off processes smooth isotopic signals, this warming very likely occurred in less time than the sample interval of 14 years. The fact that accumulation rate increased by 30 % in a few years (Fig. 7) suggests the climate reorganization was very rapid, similar to the Younger Dryas termination [Alley et al., 1993]. The results of the three model experiments produce nearly same temperature change of 4°C because of its rapidity, which confirms the robustness of the temperature estimate. Interestingly, the model produces a slightly smaller surface temperature change than the observed $\Delta T$ change, which is most pronounced in the temperature reconstruction with a zero $\Delta T$-shift but also with a 1 °C $\Delta T$-shift (Fig. 8). This can be explained as a result of the fact that the cold wave from the cooling during the Preboreal Oscillation continued to diffuse deeper during the surface warming (temperature inversion in Fig. 8). This points to the fact that an estimation of abrupt temperature changes from a $\Delta T$ record requires understanding of the preceding temperature trend.

Cuffey et al. [Cuffey and Clow, 1997; Cuffey et al., 1995] reconstructed past temperature by calibrating $\delta^{18}$O$_{\text{ice}}$ with borehole temperature. They found a calibration of $T (\degree C) = [\delta^{18}$O$_{\text{ice}} (\%o) + 24.72] / 0.328$ for times older than 8,000 B.P. The $\delta^{18}$O$_{\text{ice}}$-based surface temperature [Cuffey and Clow, 1997] shows a rapid temperature
decrease at 11,350 B.P, with sustained cold for ~80 years (Fig. 7). This trend creates a symmetrical shape (rapid cooling and warming) in the decadal climate change, which is different from our $\Delta T$-based surface temperature history. The $\Delta T$-based temperature record shows that the temperature after the Preboreal Oscillation was warmer than prior to the event (Fig. 4 and 7). This may be consistent with observations of a two step warming from the Younger Dryas to the Preboreal as some European paleoclimate evidence suggests (see later discussion) [Seppa et al., 2002].

4. Discussion

4.1. Comparison with other paleoclimate data

4.1.1. Atmospheric methane concentration

Atmospheric methane concentration can be considered as a crude hemispheric climate integrator, as the main sources of methane are wetlands [Walter et al., 2001] and plants [Keppler et al., 2006], which appear to respond to temperature directly and indirectly. Methane source changes appear relatively quickly in the atmospheric concentration because of its lifetime of ~8 years [Brook et al., 2000; Kobashi et al., submitted-a]. Therefore, methane records from ice cores are a useful qualitative tool to characterize near-hemispheric climate changes [Brook et al., 2000; Kobashi et al., submitted-a]. In addition, methane concentration and gas isotope records in a single ice core do not suffer from uncertainty introduced by the gas-ice age difference, allowing a direct comparison of the timing between local and large scale climate changes [Huber et al., 2006b; Kobashi et al., submitted-a; Severinghaus and Brook, 1999].
Methane concentration reached 769 ppb at 11,479 B.P. [Brook et al., 2000], which is the highest methane concentration throughout the preindustrial Holocene. The atmospheric methane increase was likely due in large part to rapidly developing circumarctic peatlands after the terminal Younger Dryas warming [MacDonald et al., 2006]. Then, it gradually decreased toward a minimum at 11,253 B.P. owing to cooler and/or drier climate, and rose by 58 ppb in one data interval at the end of the Preboreal Oscillation (Fig. 7). The character of methane change during the Preboreal Oscillation is more similar to the ΔT-based surface temperature than the δ18O-ice-based temperature (Fig. 7), although the lower resolution of methane data precludes any firm conclusions. The lowest methane concentration of 680 ppb during the Preboreal Oscillation occurs at 11,253 B.P or 1680.12 m in the depth scale, which is later than the end of the abrupt warming at 11,257 B.P. (1680.32 m) (Fig. 7). This observation suggests that the Greenland temperature rise preceded the atmospheric methane rise by at least 4 years (0.20 m). However, atmospheric methane change is expected to lag climate change (methane emission change) by 5-10 years owing to the atmospheric reservoir effect [Kobashi et al., submitted-a]. Therefore, the climate change or methane emission change over a broad area could have been synchronous, as observed during the abrupt climate change at 8,200 year B.P. [Kobashi et al., submitted-a]. We cannot exclude the possibility that the methane emission change actually lagged the Greenland temperature change by several decades. A higher resolution methane record will shed light on this issue.

4.1.2. Other evidence
Abundant evidence of the Preboreal Oscillation has been found in the North Atlantic region from low to high latitudes, but more evidence is now being found beyond the North Atlantic. Bond et al. [Bond et al., 1997] found that ice-bearing waters were advected toward the south in the North Atlantic during the Preboreal Oscillation (named as Event 8) and during similar events throughout the Holocene with a periodicity of 1470±500 years.

European researchers have long recognized the Preboreal Oscillation, especially in northwestern and central Europe (as reviewed by Bjorck et al. [Bjorck et al., 1997]). The event was characterized by a cool and humid (or dry in some regions) condition as evidenced by vegetation changes, decreased aquatic production, increased soil erosion, and advance of ice sheets [Bjorck et al., 1997]. The total terrestrial pollen concentration in Iceland shows a gradual decrease followed by an abrupt rise similar to the pattern seen in our gas isotope records [Bjorck et al., 1997]. In Greenland, the end of the Preboreal Oscillation was characterized by a rapid ice–margin retreat, suggesting that temperature finally became high enough to melt land-based ice [Bjorck et al., 1997]. This observation agrees with the $\Delta T$-based temperature reconstruction, showing that the post-Preboreal Oscillation climate was warmer than the condition prior to the Preboreal Oscillation. A pollen-based quantitative July temperature reconstruction was conducted in lake sediments at the Norwegian Barents Sea coast [Seppa et al., 2002]. The record shows that the transition from the Younger Dryas cold climate to the Holocene warmth consisted of two steps. The second step shows a gradual cooling and abrupt warming of 4 °C at 11,200B.P, which may correspond to the Preboreal Oscillation and the subsequent abrupt warming in our record [Seppa et
al., 2002]. The establishment of a birch forest suggests that oceanic conditions became similar to the present after the rapid warming at ~11,200 B.P. [Seppa et al., 2002]. Reduced sea surface salinity was inferred during the Preboreal Oscillation from Nordic sea sediment cores, potentially related to the cause of the cooling (see later discussion) [Hald and Hagen, 1998]. The oxygen isotope records of lake marl in Leysin, Switzerland show a clear decrease during the Preboreal Oscillation with striking resemblance to the $\delta^{18}O_{\text{ice}}$ of Greenland ice cores [Schwander et al., 2000]. Lake level studies [Magny, 2004; Magny et al., 2003] show that during the Preboreal Oscillation and during other similar cold events in the Holocene, Europe in the middle latitudes (50-43° N) experienced a wetter climate (high lake-level), and in southern and northern latitudes experienced a drier climate (low lake-level).

The grey scale from a sediment core in the tropical Atlantic (Cariaco basin off northern Venezuelan coast) shows clear evidence of the Preboreal Oscillation, suggestive of stronger winds and dry conditions [Hughen et al., 1996]. However, the character of the Preboreal Oscillation from the Cariaco basin is somewhat different from the Greenland records, showing a longer duration of ~250 years, and a more rapid onset of the event. From central North America, two Ontario lake sediment records (pollen and oxygen isotopes of carbonate) also show a clear cooling event during the Preboreal Oscillation [Yu and Eicher, 1998]. From the North Pacific, southwestern Alaska lake records [Hu et al., 2006] show a clear period of cold climate after the Younger Dryas termination, which could be the Preboreal Oscillation.

4.2. Causes of abrupt climate changes
4.2.1. Ocean circulation modes

The cause of the Preboreal Oscillation cooling has been hypothesized to be melt water input (maximum 21,000 km$^3$ for 1.5-3 year) to the Arctic Ocean caused by a flood at ~11,335 B.P. from Lake Agassiz [Fisher et al., 2002]. The fresher surface seawater might have enabled expanded winter sea ice cover, and the low salinity water may have impeded deepwater formation in the North Atlantic [Hald and Hagen, 1998; Meissner and Clark, 2006]. The large fresh-water input into the North Atlantic may have driven the location of ocean ventilation toward the south, and may have reduced the strength of the meridional overturning circulation, leading to a reduced heat and salt transport, thus enabling winter sea ice cover and cooling of Greenland mean-annual temperature [Ganopolski and Rahmstorf, 2001].

As no external forcing can explain the large abrupt warming events, which are often observed in the last glacial period, the cause has to lie in the internal dynamics of the ocean itself. It has been suggested that the ocean circulation in the Atlantic has two stable modes [Ganopolski and Rahmstorf, 2001; Rahmstorf, 2002]. During the glacial period, the ocean is stable in the colder circulation mode, and only marginally stable in the warmer circulation mode. It has been shown that a switch from the colder to warmer mode can be easily triggered by a small forcing [Ganopolski and Rahmstorf, 2001], and the warming is greatly enhanced by a positive feedback in which low-latitude salty water is drawn into the sinking regions by the rejuvenated circulation, further enhancing the sinking (the so-called “advective feedback”) [Ganopolski and Rahmstorf, 2001]. This mechanism represents the leading hypothesis to explain the abrupt warmings [Ganopolski and Rahmstorf, 2001]. We speculate that the oceanic
condition after the termination of the Younger Dryas was still favorable to the colder circulation mode so that the ocean circulation gradually returned to the colder mode, possibly aided by fresh-water input. Then, a large abrupt warming was triggered by a small forcing such as changes in precipitation at 11,270 B.P. After the abrupt warming, the overall oceanic condition may have passed a threshold, and locked into the warm stable Holocene mode.

4.2.2. Similarities with Heinrich and Dansgaard-Oeschger events

The $\delta^{15}$N record (Fig. 1) shows that there are four detectable peaks (numbered 1-4), which start with the abrupt warming event at the Younger Dryas termination. These peaks become successively smaller with time. A broadly similar character is found during the last glacial period. A larger, longer-duration Dansgaard-Oeschger warm event seemingly follows a Heinrich event, and subsequent events become progressively smaller and shorter [Bond and Lotti, 1995]. The latest Heinrich-like event (H0) is found during the Younger Dryas [Bond and Lotti, 1995]. This may suggest that the large abrupt warming events at the terminations of the Younger Dryas and Preboreal Oscillation, and the two smaller abrupt warmings (Fig. 1) might be a smaller manifestation of similar underlying physics as the Dansgaard-Oeschger events, in the Holocene, as suggested by Bond et al. (1997) [Bond et al., 1997].

4.2.3. Comparison with the 8.2ka event

About three thousand years after the Preboreal Oscillation and the subsequent abrupt warming event, the Holocene was punctuated by another large climate change
at 8,200 years B.P. (the 8.2ka event) [Alley et al., 1997a]. The 8.2ka event had a
similar magnitude of cooling and geographical extent as the Preboreal Oscillation
[Kobashi et al., submitted-a]. The 8.2ka event is thought to have been caused by the
largest outburst of a proglacial lake in the last 100,000 years [Barber et al., 1999;
Clarke et al., 2003]. Temperature dropped by 3.3 ± 1.1 °C in less than 20 years, and
then temperature gradually rose to the condition prior to the event [Kobashi et al.,
submitted-a]. The difference in temperature evolution between the Preboreal
Oscillation and the 8.2ka event suggests that two events are likely caused by different
mechanisms. As discussed previously, the character of the Preboreal Oscillation is
more similar to the Dansgaard-Oeschger events in the last glacial. On the other hand,
at the time of the 8.2ka event the ocean circulation may have already established a
much more stable and warmer mode, which was only capable of being perturbed by a
huge proglacial-lake outburst. Then, the ocean circulation gradually returned to the
original state.

4.2.3. What can 14C tell us about the Preboreal Oscillation?

The 14C record from tree-rings has been extensively used to link the Preboreal
Oscillation with changes in ocean circulation or solar activity (Fig. 1) [Bjorck et al.,
1996; Bjorck et al., 1997; Bond et al., 2001; Van der Plicht et al., 2004; van Geel et al.,
2003]. Cosmogenic nuclide 14C concentrations in the atmosphere vary (with
modulation by the carbon cycle) with changes in ocean circulation, solar activity, and
the geomagnetic field [Muscheler et al., 2000; Reimer et al., 2004]. With the precise
chronology in our study, it is possible to compare the tree ring 14C record [Reimer et
al., 2004] with climate information in ice cores. Figure 1 shows that the $\Delta^{14}C$ decreases slightly until around 11,300 B.P, and then rapidly starts rising at 11,270 B.P. If weaker ocean ventilation during the Preboreal Oscillation had an impact on $\Delta^{14}C$, we would expect an increase of $\Delta^{14}C$. If solar activity decreased during the Preboreal Oscillation, we would also expect to see an increase of $\Delta^{14}C$. The observed $\Delta^{14}C$ data shows the opposite trends of what we would expect from postulated links between climate change and changes in either ocean circulation or solar insolation. Therefore, it is difficult to draw insights from the $^{14}C$ records about the cause of the Preboreal Oscillation and the subsequent abrupt warming from the currently available theories.

5. Conclusion

We have shown that the hemispheric-scale climatic event, “the Preboreal Oscillation”, was terminated with a rather abrupt warming of $4 \pm 1.5 ^\circ C$. Snow accumulation rate rose by 30% within a few years, suggesting a rapid reorganization of climate. The methane record shows a similar trend with the reconstructed surface temperature record, suggesting that the climatic trend in Greenland was synchronous with hemispheric-scale climate change, although a firm conclusion must await higher resolution methane data.

A new method is employed to reconstruct surface temperature changes, using argon and nitrogen isotopes in air trapped in the ice core and a heat transfer-firm densification model. The method calculates the surface temperatures by adding the model-derived firm bottom temperature to the isotope-derived temperature gradient in
the firn. The model reconstructs independent records well with the $\Delta T$ data corrected by a constant $+1 \, ^\circ\text{C}$, which may be due to artifacts.

The $\delta^{15}\text{N}$ record shows two large peaks over the interval 11,800 B.P. to 10,700 B.P. with two smaller subsequent peaks. We speculate that these oscillations may be a smaller manifestation of the Dansgaard–Oeschger events, which characterized the cold unstable glacial ocean. The last large abrupt warming at 11,270 B.P. likely marks the onset of a warm and stable oceanic condition in the Holocene.

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Figure 3.1. Measured $\delta^{15}$N and $\delta^{40}$Ar in air trapped in ice (GISP2), accumulation rate [Alley et al., 1997b; Cuffey and Clow, 1997], $\delta^{18}$Oice [Stuiver et al., 1995], and detrended $\Delta^{14}$C from tree rings [Reimer et al., 2004] over the interval 11,800-10,700 B.P. The $\delta^{18}$Oice and accumulation data were smoothed with a 5-year running mean after a 1-year resolution time series was generated by linear interpolation. $\delta^{15}$N and $\delta^{40}$Ar for the period 11,800-11,447 B.P are from Severinghaus et al. [1998] and for the later part are from Kobashi et al. [submitted-b]. The shaded areas numbered as 1 to 4 are cooler periods characterized by $\delta^{15}$N, as follows: (1) the Younger Dryas, (2) the Preboreal Oscillation, (3) the 11.0 ka event, (4) the 10.8 ka event. Note that the resolution of the $\delta^{18}$Oice record changes after ~11,300 B.P. in the original data [Stuiver et al., 1995].
Figure 3.2. $\delta^{15}$N records in the depth interval 1720 m to 1640 m. The triangles are means of replicate data from Severinghaus et al. [1998], and the diamonds are from Kobashi et al. [submitted].
Figure 3.3. Firn temperature gradient ($\Delta T$) records from 11,800 B.P. to 10,000 B.P. The black line from 11,800 B.P. to 11,417 B.P. is a model output with the $\delta^{18}O_{\text{ice}}$-based surface temperature. The observed $\Delta T$ records after 11,417 B.P. are used as inputs for three experiments. The blue line is $\Delta T$ shifted by 0.0 °C, the green line is $\Delta T$ shifted by 1.0 °C, and the red line is $\Delta T$ shifted by 2.0 °C. The shaded area shows the two centuries (11,400-11,200 B.P.) spanning the Preboreal Oscillation and the subsequent abrupt warming.
Figure 3.4. Surface temperature reconstructions with the $\Delta T$-based and $\delta^{18}O$-ice-based methods. The blue, green, and red lines are the surface temperature reconstructions with $\Delta T$ shifted by +0.0 °C, +1.0 °C, and +2.0 °C, respectively. The black and brown lines are the $\delta^{18}O$-ice-based surface temperature reconstruction [Cuffey and Clow, 1997]. The shaded area is as in Fig. 3.
Figure 3.5. Modeled and observed $\delta^{15}N$. The blue, green, and red lines are the modeled $\delta^{15}N$ with $\Delta T$ shifted by $+0.0 \, ^\circ C$, $+1.0 \, ^\circ C$, and $+2.0 \, ^\circ C$, respectively. The circles are the observed $\delta^{15}N$. The black line before 11,417 B.P. is the model result with the $\delta^{18}O_{ice}$-based surface temperature. The shaded area is as in Fig. 3.
Figure 3.6. Observed and modeled diffusive column height (DCH or firn thickness) from 11,800 B.P. to 10,000 B.P. The lines before 11,417 B.P. are model results with the $\delta^{18}$O ice-based surface temperature. The blue, green, and red lines are the modeled DCH with $\Delta T$ shifted by $+0.0 \degree C$, $+1.0 \degree C$, $+2.0 \degree C$, respectively. The diamonds are the DCHs computed from the observed $\delta^{15}$N grav computed from $\Delta T$ (+1.0 $\degree C$ correction). Note that the data are smoothed by a 5-point running mean (covering about 100 years for each point). The grey line is the model result with the $\delta^{18}$O ice-based surface temperature. The shaded area is as in Fig. 3.
Figure 3.7. Reconstructed surface temperature records (this study), accumulation rate [Alley et al., 1997b; Cuffey and Clow, 1997], and atmospheric CH$_4$ concentration [Brook et al., 2000] from GISP2 ice. (Top) The thick blue line is the $\Delta T$-based surface temperature reconstruction with the +1 °C shift, and the dashed blue lines are 1σ errors. The red line is the $\delta^{18}O_{\text{ice}}$-based surface temperature reconstruction [Cuffey and Clow, 1997]. The accumulation rate and the $\delta^{18}O_{\text{ice}}$-based temperature are smoothed with a 5-year running mean as for Figure 1. The shaded area includes the Preboreal Oscillation and subsequent abrupt warming at 11,270 B.P.

To estimate 1σ error, 100 realizations of synthetic $\Delta T$ records were generated by Monte Carlo simulation by adding white noise to the $\Delta T$ data with a standard deviation of 1 °C, which was obtained from the error estimate (0.8 °C) for the last millennium dataset plus 20 % [Kobashi et al., submitted-b]. Then, the 100 realizations of surface temperatures were used to calculate mean surface temperature and the error (1σ).
Figure 3.8. Model outputs of the temperature profile of the firn and ice sheet before and after the abrupt warming at 11,270 B.P in the $\Delta T$-based surface temperature reconstruction (0.0 °C -shift). Firn depth is estimated to be ~82 m from the model.
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Chapter IV

Persistent multi-decadal Greenland temperature fluctuation through the last millennium
Abstract

Greenland temperature change in the future will affect melting of the ice sheet and associated sea-level change, so it is critical to understand Greenland temperature variability and its relation to global trends. Here, we reconstructed the last 1000 years of central Greenland surface temperature from air-bubbles in an ice core. This technique uses isotopes of N₂ and Ar, and has several advantages over previous methods. We found that Greenland temperature followed Northern Hemispheric temperature closely, with a possible 20-30 year lag and an amplification of the signal by 1.3-2.4 times. A quasi-periodic multidecadal temperature fluctuation persisted throughout the last millennium.

1. Introduction

One major concern for future global warming associated with increasing greenhouse gas is sea level rise by melting of polar ice sheets [Alley et al., 2005; IPCC, 2001]. By the year 2100, sea-level is expected to rise by 0.5 ± 0.4 m induced by global warming [IPCC, 2001]. However, recent studies suggest that future melting of polar ice may be underestimated, so greater sea level rise might become a reality [Alley et al., 2005; Rahmstorf, 2007]. Moreover, the Arctic polar region is expected to warm more rapidly than the global average owing to ice albedo feedback [IPCC, 2001], although the past few decades of Greenland warming are less pronounced than the global average warming [Alley and Koci, 1990; Chylek et al., 2004; DahlJensen et al., 1998]. Therefore, understanding past Greenland temperature and its relation to global temperature changes is important.
Most instrumental temperature records extend back only for 150 years [National Research Council (U.S.). Committee on Surface Temperature Reconstructions for the Last 2000 Years, 2006], limiting our understanding of climate dynamics on this time scale. Therefore, many proxies for temperature have been developed to extend the temperature history [Hegerl et al., 2006; Jones and Mann, 2004; Moberg et al., 2005; National Research Council (U.S.). Committee on Surface Temperature Reconstructions for the Last 2000 Years, 2006]. However, many of the proxies are qualitative and seasonally biased, and often the assumption of stationary relationships between the proxy and the short instrumental record cannot be verified [National Research Council (U.S.). Committee on Surface Temperature Reconstructions for the Last 2000 Years, 2006]. In Greenland, oxygen isotopes of ice [Stuiver et al., 1995] have been extensively used as a temperature proxy, but the data are noisy and do not clearly show multi-centennial trends for the last 1000 years, in contrast to borehole temperature records showing a clear “Little Ice Age” and “Medieval Warm Period” [DahlJensen et al., 1998]. Oxygen isotopes are known to be affected by numerous factors other than temperature, such as the frequency of storm precipitation and the seasonality of precipitation [Stuiver et al., 1995]. On the other hand, the resolution of the borehole surface temperature reconstruction is rapidly lost as time goes back, due to diffusion of heat [Alley and Koci, 1990; DahlJensen et al., 1998].

2. Obtaining temperature history from air trapped in ice
We used an ice core (GISP2) from central Greenland (72º 36’N 38º 30’W; 3203 masl), and analyzed nitrogen ($^{15}\text{N}/^{14}\text{N}$) and argon ($^{40}\text{Ar}/^{36}\text{Ar}$) isotopic ratios [Kobashi et al., submitted-b] (Fig. 1). Because these isotopic compositions are constant in the atmosphere for $>10^5$ years [Allegre et al., 1987; Mariotti, 1983], deviations of these isotopic compositions in an ice core can be attributed solely to processes in the firn layer (unconsolidated snow layer on the top of glacial ice; 60-70m thick in central Greenland) [Severinghaus et al., 1998]. The thickness of the firn layer and the temperature gradient between the top and bottom of the firn layer causes known amounts of isotopic separation by gravitational and thermal fractionation, respectively [Severinghaus et al., 1998]. Measurements of two isotopic ratios with differing sensitivity ($\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$) allow us to separate the two effects, providing the past firn thickness and temperature gradient $\Delta T$ (Fig. 1) [Severinghaus and Brook, 1999]. Surface temperature can be calculated from the $\Delta T$ and accumulation rate data combined with a firn-densification/heat diffusion model [Goujon et al., 2003; Kobashi et al., submitted-a]. The reconstructed temperature is a decadal average owing to smoothing of the record by the general gas diffusion and bubble close-off process. Notably, the record is not seasonally biased, does not require any calibration to instrumental records, and resolves decadal to multi-centennial temperature fluctuations with an uncertainty of 0.5 ºC [Kobashi et al., submitted-b]. Therefore, it provides an important independent temperature estimate for the last 1000 years.

We employed visual stratigraphy for the ice age chronology [Alley et al., 1997b]. The uncertainty of the ice age is estimated to be 1% [Alley et al., 1997b]. The gas age is calculated by the Goujon model [Goujon et al., 2003] with inputs of surface
temperature from calibrated oxygen isotopes of ice [Cuffey and Clow, 1997] and accumulation rate [Alley et al., 1997b; Cuffey and Clow, 1997]. The additional gas age uncertainty is estimated to be 10% of the gas-ice age difference or 20 years (the gas-ice age difference is 200 ± 4 years for the last 1000 years, varying with changes in the firn condition).

Observed isotopic values can be decomposed into two components:

\[ \delta^{40}\text{Ar}_{\text{observed}} = \delta^{40}\text{Ar}_{\text{grav}} + \delta^{40}\text{Ar}_{\text{therm}} \]

and

\[ \delta^{15}\text{N}_{\text{observed}} = \delta^{15}\text{N}_{\text{grav}} + \delta^{15}\text{N}_{\text{therm}} \]

where grav and therm represent gravitational and thermal components [Kobashi et al., submitted-b]. The magnitude of gravitational fractionation linearly scales with mass difference [Kobashi et al., submitted-b]. Therefore, we can write \( \delta^{40}\text{Ar}_{\text{grav}}/4 = \delta^{15}\text{N}_{\text{grav}}. \) For simplicity, we will use \( \delta^{40}\text{Ar}_{\text{grav}}/4 \) for later discussion so that argon and nitrogen isotopes are on the same scale in terms of mass. Thermal components linearly relate to the temperature difference \( \Delta T \) between top and bottom of the firn layer. Therefore,

\[ \delta^{15}\text{N}_{\text{therm}} = \Delta T \cdot \Omega^{15} \]

and

\[ \delta^{40}\text{Ar}_{\text{therm}} = \Delta T \cdot \Omega^{40} \]

where \( \Omega^{15} \) and \( \Omega^{40} \) are laboratory-derived thermal coefficients [Grachev and Severinghaus, 2003a; Grachev and Severinghaus, 2003b]. From these relationships, past temperature gradient \( \Delta T \) can be readily calculated from observed nitrogen and argon isotopic ratios as

\[ \Delta T = \left( \delta^{15}\text{N} - \delta^{40}\text{Ar}/4 \right) / \left( \Omega^{15} - \Omega^{40}/4 \right) \] (Fig. 1). Recent studies have shown that there may be a third isotopic fractionation associated with gas loss, especially for those gases with smaller molecular sizes (< 3.6 Å) [Huber et al., 2006; Severinghaus and Battle, 2006; Severinghaus et al., 2003]. We found strong evidence that argon isotopes are affected by gas loss. Therefore, we corrected \( \delta^{40}\text{Ar} \) using measured \( \delta\text{Ar}/\text{N}_2 \) following a previously established method [Severinghaus et al., 2003].
Firn conditions such as densification rate and heat transport are controlled by snow accumulation and surface temperature change [Goujon et al., 2003; Schwander et al., 1997]. Therefore, it is possible to numerically calculate the past firn condition with empirical glaciological models if surface temperature and accumulation rate are known [Goujon et al., 2003; Schwander et al., 1997]. Goujon et al. [Goujon et al., 2003] developed such a model to calculate the past firn condition based on a $\delta^{18}$O$_{ice}$-derived surface temperature calibrated with the borehole temperature record [Alley et al., 1997a; Cuffey and Clow, 1997] and accumulation rate [Cuffey and Clow, 1997]. The model also calculates the resultant isotopic fractionation of $\delta^{15}$N and $\delta^{40}$Ar in the firn. Goujon et al. found that the observed $\delta^{15}$N and $\delta^{40}$Ar are reproduced reasonably well with the $\delta^{18}$O-based temperature for the transition from the last glacial period to the Holocene in Greenland [Goujon et al., 2003; Kobashi et al., submitted-b]. The model is also found to reproduce current firn conditions well over a range of environmental conditions [Landais et al., 2006]. One exception is that the model fails to generate the observed isotopic signals ($\delta^{15}$N and $\delta^{40}$Ar) at very cold Antarctic sites such as Vostok with low accumulation during the last glacial [Goujon et al., 2003; Landais et al., 2006].

The temperature gradient ($\Delta T$) in the firn is constantly modified by changes in surface temperature and heat transport in firn and ice. As heat transport in the firn is much slower than gas diffusion, temperature gradient data ($\Delta T$) derived from observed $\delta^{15}$N and $\delta^{40}$Ar can be used to calculate the heat transport in the firn if combined with accumulation rate data. Therefore, a surface temperature history can be calculated from the $\Delta T$ history if the initial temperature profile of the firn and ice sheet is known.
We used a borehole calibrated $\delta^{18}O_{\text{ice}}$-based surface temperature record [Cuffey and Clow, 1997; Stuiver et al., 1995] to create an initial temperature profile. Actual calculation in the model is conducted as follows. In a model year, the firn condition is forced by a new surface temperature and accumulation rate. In the second model year, a new surface temperature ($T_s$) is obtained by adding $\Delta T$ from observed isotopic records to the temperature ($T_b$) at the bottom of the firn layer in the previous year model run [Kobashi et al., submitted-a]. Or simply,

$$T_s = T_b \text{ (model output from the previous model year)} + \Delta T \text{ (observation)}.$$

This calculation effectively takes the heat transport into account, and calculates a surface temperature from observed $\Delta T$ and accumulation rate [Kobashi et al., submitted-a]. A detailed description of this calculation can be found in the appendix.

3. Instrumental Greenland temperature records

Instrumental temperature measurements are available from multiple automatic weather stations (AWS) near the GISP2/Summit site in central Greenland starting from May 1987 [Shuman et al., 2001]. From these data, and ancillary satellite observations, a composite temperature record can be generated, which provides a record of Greenland temperature for nearly two decades (Fig. 2). The record shows average surface air temperature of this period to be -29.2 °C with about 40 °C of seasonal range [Shuman et al., 2001] (Fig. 2). The range of interannual temperature
variation is about 5 °C during this period with no distinct warming or cooling trends (Fig. 2, lower panel), which contrasts to the rapid warming observed at Greenland coastal sites during the same period [Chylek et al., 2006] and globally [Hansen et al., 2006]. The direct comparison of ice core data with the instrumental data is complicated by the fact that near surface air temperature is slightly warmer than firn [Alley and Koci, 1990]. A heat transfer model study [Li et al., 2002] shows that firn temperature at 15 m forced by the instrumental surface air temperature (1987-1999) is ~1 °C warmer than observed firn temperature at 30 m. Although part of difference may arise from natural temperature change, the reason for this difference may be that the snow radiates to space more effectively than air and so is cooler.

Several instrumental temperature records at Greenland coastal sites from 1873 show near-stable temperature from the late 19th century to 1920, a warming from 1920-1940, a cooling toward 1980 and a recent warming from 1990 to present [Box, 2002; Chylek et al., 2004; Chylek et al., 2006]. The earlier warming is also found in the surface temperature reconstruction from borehole temperature records from Greenland summit [Alley and Koci, 1990; DahlJensen et al., 1998]. Our gas-based temperature records also show that temperature slightly cooled from 1873 to 1910, and a rapid warming occurred during 1920-1930 [Box, 2002; Chylek et al., 2006].

4. Greenland gas-isotope temperature for the last 1000 years

Reconstructed gas-based temperature shows a warmer period in the earlier part of the millennium and cooling toward the 18th century, and a temperature increases from the late 19th century to the 20th century (Fig. 3). This pattern is consistent with
the well-known “Medieval Warm Period” and “Little Ice Age”, and is remarkably similar to reconstructions of Northern Hemispheric temperature (Fig. 4; see later discussion) [Esper et al., 2002; Hegerl et al., 2006; Moberg et al., 2005]. The average Greenland temperature for the last 1000 years is -31.4 °C with a minimum temperature of -33.4 °C in the early and late 18th century and a maximum temperature of -29.5 °C in the mid 12th century and the early 20th century (Fig. 3). The general trend is similar to previous Greenland temperature reconstructions, based on borehole temperature records [Alley and Koci, 1990; Cuffey and Clow, 1997; DahlJensen et al., 1998] (Fig. 5). The temperature history obtained from borehole inversion alone shows the least variation, as expected from the nature of the method [DahlJensen et al., 1998]. A temperature history using borehole-calibrated δ18Oice, with two different oxygen isotope-temperature-sensitivities before (0.25 ‰/°C) and after (0.47 ‰/°C) after 1500 CE [Cuffey and Clow, 1997], shows the largest variation (Fig. 5).

At the beginning of the last millennium, Greenland climate started with a cooler period, then the temperature warmed toward the middle of the 12th century (which was the warmest century in the last 1000 years). Then, temperature decreased toward 1300 CE. This early phase of the Little Ice Age coincides with an initial culmination of alpine glacier advances in the Northern Hemisphere [Grove, 2001]. Then, temperature increased again toward the early 15th century. From the middle 15th century onward, Greenland temperature began a 400-year long cooling trend with a clear multidecadal oscillation (Fig. 3). Around this time, storminess and/or sea ice cover substantially increased as indicated by an increase in Na concentration in the ice [Mayewski et al., 1997] (Fig. 4). Temperature reached its minimum in the 18th century.
The lengths of alpine glaciers around the globe also reached a maximum around 1800 [Oerlemans, 2005]. Thereafter, temperature started to increase toward the present. Cooler decades in the warm early millennium are similar to temperatures of warmer decades of the 17th-19th centuries, reflecting the severity of the late Little Ice Age.

The reconstructed temperature record shows a quasi-periodic multi-decadal temperature fluctuation (Fig. 3). The spectrum shows three significant peaks with periods of 330, 70, and 40 years (Fig. 6). The 70-year periodicity may relate to the multidecadal temperature fluctuations in the Atlantic Basin (Atlantic Multidecadal Oscillation: AMO), which is a leading large-scale pattern of multidecadal variability in instrumental records of global temperature [Knight et al., 2005; Schlesinger and Ramankutty, 1994]. The coldest decades of the last millennium around 1700 (Fig. 4) are known as the climax of the Little Ice Age or “Late Maunder Minimum (1675-1715LMM)” in Europe [Grove, 2004; Luterbacher et al., 2001]. The peak-to-peak agreement between our temperature record and the composite $\delta^{18}O_{\text{ice}}$ record from GRIP, DYE-3, and NGRIP [Andersen et al., 2006] suggests that the $\delta^{18}O_{\text{ice}}$ proxy records temperature change at a multidecadal scale, although the multi-centennial $\delta^{18}O_{\text{ice}}$ trends are clearly subdued, likely by factors other than local temperature. The GISP2 $\delta^{18}O_{\text{ice}}$ record also shows a good agreement but to a lesser degree than the composite record. The GISP2 accumulation rate history also seems to be mostly in phase with the multi-decadal temperature fluctuations (Fig. 4).

5. Iceland and Greenland climate and impacts on humans
The people who lived in climatically marginal Greenland and Iceland received the hardest hits from climatic changes during the last millennium, and they left much climatically relevant documentation [Ogilvie, 1984; Ogilvie and Jonsson, 2001]. These records provide critical insights on the relationship between climate and people. In addition, Grove [2004] noted that weather in four periods (the 14th, late 16th, late 17th, and 18th centuries) during the last millennium was so severe in Europe that it created crop failures sometimes leading to famines. These periods also appear to be the most variable and coldest in our data (Fig. 3).

Historical documents suggest that Iceland climate in the first few centuries of the millennium seems to have been similar to the early 20th century [Ogilvie and Jonsson, 2001], in agreement with our record. A cold period started as early as 1180 C.E., and occurred again in the last 13th century [Ogilvie, 1984; Ogilvie and Jonsson, 2001]. The 14th century was characterized by highly variable climate [Ogilvie and Jonsson, 2001]. Some evidence suggest that climate from 1430 to 1560 was mild. The end of the 16th century was relatively harsh, continuing toward the 1630s in which climate was very severe until ~1640 [Ogilvie and Jonsson, 2001]. Then, it was relatively mild until 1680 [Ogilvie and Jonsson, 2001]. The late 17th century was very cold. The early 1700s were relatively mild, but the 1740s-1750s were cold. The 1760s to 1770s returned to a milder climate [Ogilvie and Jonsson, 2001]. The 1780s were likely the coldest decade in the 1700s [Ogilvie and Jonsson, 2001]. The 1810s, 1830s, 1860s, and 1880s were comparatively cold, but the middle 19th century was relatively mild [Ogilvie and Jonsson, 2001]. Icelandic glaciers reached their Little Ice Age maxima in the mid 18th century [Grove, 2004]. Although some of the descriptions
suggest temperature anomalies beyond our uncertainty limits, the general trends from historical documents agree with our data quite well (Fig. 3).

Inuit are known to have inhabited Greenland intermittently for several millennia, and the Norse initiated their first large colony in Greenland in 985 C.E. during the Medieval Warm Period [Ogilvie, 1984]. Progressive cooling after their settlement, as illustrated in our data, made their pastoral life with cattle, sheep, and goats more and more difficult [Ogilvie, 1984]. By ~1350 the West settlement was abandoned, and the larger Eastern settlement vanished by 1450, possibly linked with the rapid cooling around 1450 in our record (Fig. 3) [Grove, 2004]. It is interesting to note that the Inuit, who depended on sea ice hunting, flourished in Greenland as the colder climate intensified [Grove, 2004].

6. Causes of Greenland temperature fluctuation

As the reconstructed Greenland temperature strongly correlates with Northern Hemispheric temperature (Fig. 4), it can be inferred that similar mechanisms caused part of the variation in the Greenland temperature for the last 1000 years. The correlation between Greenland temperature and Northern Hemispheric temperature is $r = 0.5$ for the Moberg et al. [2005] and Hegerl et al. [2006] reconstructions. The highest correlations with the Moberg et al. reconstruction ($r = 0.7$) and with the Hegerl et al. reconstruction ($r = 0.62$) are obtained as Greenland temperature is shifted by 30 years and 20 years toward older age, respectively. One possible interpretation is that Greenland temperature may have lagged Northern Hemispheric temperature (Fig. 4). However, as the $\delta^{18}O_{ic}$-based surface temperature reconstruction shows only a 6-year
lag with the North Hemispheric temperature (Moberg reconstruction), with a correlation of \( r = 0.3 \), we cannot eliminate the possibility of a small systematic error in the gas-ice age difference calculation. On the other hand, our Greenland temperature and the \( \delta^{18}O_{\text{ice}} \)-based surface temperature reconstruction has a high correlation of \( r = 0.6 \) with a 6-year lag, here suggesting the gas-ice age difference calculation has negligible error.

A similar lag (~30 yr) has been found in the response of North Atlantic meridional overturning circulation to forcing by changes in solar irradiance [Cubasch and Voss, 2000]. Also, our Greenland temperature is anti-correlated with the Northern Hemispheric temperature on a multidecadal time scale. We hypothesize that an oscillatory mode of atmospheric circulation such as the Arctic Oscillation (AO) or (NAO) with an anti-phase relation between Greenland and Europe [Hurrell, 1995], may have caused the observed anti-phase relationship between Greenland temperature and Northern Hemispheric temperature through the last millennium.

The polar climate is known to amplify a global or hemispheric temperature signal by ice albedo feedback [IPCC, 2001]. General Circulation Models (GCMs) find that warming of polar regions will progress at a rate 1.2 to 3 times faster than the global average [IPCC, 2001]. Using our data, the ratio of Greenland to Northern Hemisphere temperature change for the last 1000 years is 2.3 with the Hegerl reconstruction, and 1.4 with the Moberg reconstruction (Fig. 7 with Mann et al. (1999), reconstruction). These ratios are similar to the GCM results [IPCC, 2001] and the ratio 2.2 found from instrumental records [Chylek and Lohmann, 2005]. This confirms that despite slightly different recent Northern Hemisphere and Greenland
temperature trends, the future Greenland temperature will likely follow the global
temperature trend with an amplified magnitude.

Changes in solar irradiance and volcanism can explain as much as 41 to 64% of variation of Northern Hemispheric temperature (Fig. 4) [Crowley, 2000]. The strong correlation between Greenland and Northern Hemisphere temperature suggests a common causation. Energy balance model results with solar and volcanic forcing produce the general trend we see in the Greenland temperature record, including the cool 11th, 13th, and 14th centuries, the warm 12th, 14th, and 20th centuries, and the cold 17th and 19th centuries (Fig. 4). Therefore, it is clear that current and future climate change in Greenland is going to be affected by these natural variations in addition to increasing human-made greenhouse gases [Crowley, 2000; IPCC, 2001]. Projections of future Greenland temperature and sea level contribution thus must take these natural variations into account.

7. Conclusions

We present a new Greenland temperature record for the past 1000 years based upon argon and nitrogen isotopes in trapped air in ice. The data show clear evidence of the Medieval Warm Period and Little Ice Age in agreement with documentary evidence. The overall trends are remarkably similar to Northern Hemispheric temperature records, with a 20-30 year lag. A multidecadal temperature fluctuation with a period of 70 and 40 years, which seems to be anti-phased with the North Atlantic Oscillation (or Arctic Oscillation), persisted for the last millennium, and so will likely continue into the future.
Acknowledgements

We thank C. Shuman for helping us to obtain the last 18 years of central Greenland instrumental temperature. We thank R. Alley, K. Cuffey, G. Clow, T. Crowley, and J. Ahn for helpful information. We appreciate the support of R. Beaudette and the staff of the National Ice Core Laboratory (NICL). This work was supported by NSF grants OPP 05-38657 and ATM 99-05241 (to J.P.S.).
Figure 4.1. Gas-isotope data including $\delta^{15}\text{N}$, $\delta^{40}\text{Ar}$, and deduced temperature gradient ($\Delta T$) in the firn. Circles are means of replicate data, and error bars are 1σ standard errors calculated from pooled standard deviation and number of replicates. $\delta^{40}\text{Ar}$ is raw data, but $\Delta T$ uses corrected values. Spline fits [Enting, 1987] are applied for each data with a 30-year cutoff period. Error bands are 1σ.
Figure 4.2. Instrumental record of central Greenland temperature from May 1987 to May 2005 [Shuman et al., 2001]. Blue line is mean daily temperature [Shuman et al., 2001]. Red line is interannual temperature variation (365-day running mean).
Figure 4.3. The last 1000 years of Greenland temperature derived from nitrogen and argon isotopes in air bubbles in ice. Thick blue line is mean of results of Monte Carlo simulation, and thin blue lines are error bands (1σ). Red line is a smoothed temperature history (50-year running mean).
Figure 4. Last-millennium records of comprehensive climate indicators. Temperature record on the top panel is the same as figure 3 with a green line for the bottom temperature of the firn. Second panel shows δ\textsuperscript{15}N as in figure 1. Third panel shows GISP2 ice accumulation rate (green) [Alley et al., 1997b; Cuffey and Clow, 1997] and stacked record (red) for Greenland accumulation rate from the DYE-3, GRIP, and NGRIP ice cores [Andersen et al., 2006]. Data are smoothed with a 20-year running mean. Fourth panel shows GISP2 δ\textsuperscript{18}O\textsubscript{ice} (green) [Stuiver et al., 1995] and stacked record (red) for Greenland δ\textsuperscript{18}O\textsubscript{ice} from the DYE-3, GRIP, and NGRIP ice cores [Andersen et al., 2006]. Fifth panel shows Na concentration from GISP2 [Mayewski et al., 1997]. Sixth and seventh panels are solar and volcanic forcing, respectively [Crowley, 2000]. Last panel shows Northern Hemispheric temperature from Moberg et al. [Moberg et al., 2005] and Hegerl et al. [Hegerl et al., 2006], and a model result by Crowley [Crowley, 2000]. Red or black dashed lines embedded in all panels are the Greenland temperature from the top panel with a 50-year running mean. Note that the temperature scale varies. Shaded areas are cooler periods as shown in the temperature records.
Figure 4.4.
Figure 4.5. Greenland temperature reconstructions for the last 1000 years. Blue line is a reconstruction from borehole temperature using an inverse model for the GRIP site [DahlJensen et al., 1998]. Black dots are a δ¹⁸O ice-based reconstruction for the GISP2 site [Cuffey and Clow, 1997; Cuffey et al., 1995]. Green line is an heuristic reconstruction using a forward model [Alley and Koci, 1990]. Red line is the reconstruction from this study.
Figure 4.6. Power spectrum of Greenland temperature for the last 1000 years plotted with red-noise 95 % (dotted) and 99 % (solid) significance levels.
Figure 4.7. Greenland temperature (this study) compared with one early estimate of Northern Hemispheric temperature (Mann et al., 1999). Scales are the same. The latter estimate is given as one example, and is not necessarily accurate.
References


Grachev, A.M., and J.P. Severinghaus, Laboratory determination of thermal diffusion constants for N-29(2)/N-28(2) in air at temperatures from-60 to 0 degrees C for reconstruction of magnitudes of abrupt climate changes using the ice core fossil-air paleothermometer, *Geochimica Et Cosmochimica Acta, 67* (3), 345-360, 2003b.


Appendices

1. Data description

Argon and nitrogen isotopes (δ\(^{15}\)N and δ\(^{40}\)Ar), and argon/nitrogen ratio (δAr/N\(_2\)) in air trapped in the GISP2 ice core have been analyzed for the last 11,600 years [Kobashi et al., submitted]. The detailed methodologies for the isotopic analyses and comprehensive description of data quality are presented elsewhere [Kobashi et al., submitted]. Special efforts were made for the last 1000 years with higher-resolution (10-year) and precision analyses (Fig. S1). The climatic interpretation for the last 1000 years is described in the main text. A total of 275 samples from 97 depths were analyzed for the period 1000-1950 C.E. (Fig. S1). Pooled standard deviation of both δ\(^{15}\)N and δ\(^{40}\)Ar/4 are 0.004 ‰. Therefore, the standard errors of means are 0.0023 ‰, 0.0028 ‰, and 0.004 ‰ for the depths with triple, double, and single analyses, respectively (Fig. S1). The pooled standard deviation of δAr/N\(_2\) is 0.65 ‰ [Kobashi et al., submitted].

2. Surface temperature of the last 50 years

Our latest data for gas isotopes is 1950 C.E. as the air occlusion process is not completed for recent decades. For the period 1950-1993, the surface temperature is estimated heuristically by a forward model [Goujon et al., 2003] running various surface temperature scenarios to find the best fit with the borehole temperature record. The method is principally the same as that used by Alley et al. (1990) [Alley and Koci, 1990] (Fig. S2). The reconstructed temperature is similar to the instrumental
temperature trend and temperature reconstruction by Alley et al. [Alley and Koci, 1990], showing a gradual cooling toward 1970 and slight warming toward 1990. The use of the Alley et al. temperature reconstruction from 1950 onward creates a slight deviation from observed borehole temperature in the upper 80m by $<0.3 \, ^\circ C$. As the main focus of the current paper is the $\Delta T$-based surface reconstruction for the period 1000-1950 C.E., we will not discuss this post-1950 period further.

3. $\Delta T$-based temperature calculation

To apply the $\Delta T$-based surface temperature calculation, a prerequisite is to know the initial temperature profile of the firn and ice sheet. To accomplish this, we run the model from 24,300 B.P. (Before Present, present is defined as 1950 C.E.) until 2957 B.P. with the $\delta^{18}O_{ice}$-based borehole-calibrated surface temperature [Cuffey and Clow, 1997; Stuiver et al., 1995]. This surface temperature is quite robust for the long term temperature trend [Goujon et al., 2003; Kobashi et al., submitted]. We employ the $\Delta T$-based surface temperature calculation from 2957 B.P. onward. The $\Delta T$-based surface temperature calculation produces $\delta^{15}N$ results more consistent with observed $\delta^{15}N$ for the period from 2957-1000 B.P. than the $\delta^{18}O_{ice}$-based calculation (Fig. S3). However, note that different temperature histories ($\delta^{18}O$- or $\Delta T$-based) before 1000 C.E. only slightly affect the first century of calculated surface temperature for the last 1000 years. As the Goujon model runs with a 1-year time step, an annual resolution $\Delta T$ time series is generated by linear interpolation. The data density (1 sample/20 years) from 2957 B.P. to 990 B.P. is about six times lower than that (~3 samples / 10 years) for the last 1000 years [Kobashi et al., submitted] so that data is noisier.
At the end of the calculation, the temperature profile of the firn and ice sheet is compared with observed borehole temperature at GISP2 (Fig. S4) [Alley and Koci, 1990; Clow et al., 1996]. We combined two borehole records for the firn section, from Alley et al. [Alley and Koci, 1990] measured in summer 1989, and for the ice sheet section by Clow et al. [Clow et al., 1996] measured in summer 1994. As the two temperature records show a slight offset in the overlapping depth, we shifted the Alley measurement by +0.035 °C to fit with the Clow data as the Clow thermometer has better accuracy. Also we adjusted the Alley temperature profile by lowering 9 m to align it with the Clow measurements, based on our expectation that the temperature profile moved downward during the 5 intervening years by new snow accumulation and temperature diffusion (Fig. S4). The two data sets are combined at the depth of 230 m.

To estimate the error of the surface temperature calculation, we employed a Monte Carlo simulation from 960 to 1950 C.E. 800 synthetic ΔT time series were produced by adding white noise according to its analytical errors. Then, 800 surface temperature histories were generated from these ΔT time series. After each calculation of surface temperature, the temperature profile of the firn and ice sheet in the last model year is compared with the observed borehole temperature. Only those surface temperature histories (n = 102) with average root mean square temperature difference (<0.05 °C) in the upper 600 m of the ice sheet were used to calculate mean surface temperature and error for the last 1000 years. The resultant surface temperature and its error are little changed by this selective process, but it substantially reduced errors
in the reconstructed firn thickness. This reflects the fact that the surface temperature calculation is relatively insensitive to firn thickness variation in the model.

Modeled borehole temperature below ~600m is slightly colder than the observation by < 0.2 °C (Fig. S4). This is likely due to the fact that the δ¹⁸O-based surface temperature reconstruction used before 2957 B.P. is too cold, as can be seen in the modeled δ¹⁵N being generally higher than observed δ¹⁵N before 2957 B.P. owing to colder firn temperature (Fig. S5). This offset has negligible impact on the temperature reconstruction for the last 1000 years.

The absolute temperature in the ΔT-based surface temperature calculation is sensitive to the initial absolute temperature of the firn, as the input ΔT has only relative temperature information. On the other hand, the ΔT-based surface temperature “change” is less sensitive to the initial absolute temperature. Therefore, the δ¹⁸O-based surface temperature in the period 4000-2957 B.P. is lowered by 0.14 °C to decrease the ΔT-based temperature history such that the final temperature profile fits with the observed borehole temperature record.

4. Correction for gas loss impacts on isotopes

The observed δ⁴⁰Ar/⁴ data for the last 10,000 years show generally higher values than δ¹⁵N by 0.01 ‰ to 0.005 ‰, implying a negative temperature gradient (ΔT) in the firn of -1 °C to -2 °C for the past 10,000 years. However, a model study [Goujon et al., 2003] showed that the long term average temperature gradient in the firn layer should have been near zero in central Greenland for the last 8,000 years owing to high accumulation rate and relatively stable climate. This may be explained
by the observation that the relatively small argon molecules leak out of the ice
during/after coring, leaving heavier isotopes behind in the bubbles [Huber et al., 2006;
Severinghaus and Battle, 2006; Severinghaus et al., 2003].

Measured $\delta$Ar/N$_2$ (mass 40/29 ratio) provides information on preferential
argon loss, as nitrogen (with larger molecular size) is fairly conservative with regard
to potential artifacts [Severinghaus and Battle, 2006; Severinghaus et al., 2003].
$\delta$Ar/N$_2$ in the atmosphere should have been nearly constant (<0.03 ‰; M. Headly,
personal communication) for the last 1000 years as ocean temperature (or heat
content) only varied by < 0.1 °C (or $\sim$5.0 $\times$ 10$^{23}$ Joules [Crowley et al., 2003]).
Therefore, the observed variation of $\delta$Ar/N$_2$ by as much as 3 ‰ in the ice core (Fig.
S1) must have originated after the air was removed from the atmosphere.

$\delta$Ar/N$_2$ in ice cores is also affected by gravitational and thermal fractionation
in the firn layer. Therefore, $\delta$Ar/N$_2$ is corrected for these processes using measured
$\delta^{15}$N: $\delta$Ar/N$_2$ corrected = $\delta$Ar/N$_2$ observed $- 11 \times \delta^{15}$N. The slight difference in thermal
coefficients of $\delta^{15}$N and $\delta$Ar/N$_2$ is negligible for the purpose of this correction. The
corrected $\delta$Ar/N$_2$ is used as an indicator of argon loss.

It has been suggested that an argon leak through microcracks in the ice may be
associated with isotopic fractionation with an enrichment of $\delta^{40}$Ar by $\sim$0.007 ‰ per
1 ‰ increase in $\delta$Kr/Ar [Severinghaus et al., 2003]. $\delta$Kr/Ar and $\delta$N$_2$/Ar are thought to
be very similar after gravitational correction [Severinghaus et al., 2003]. Therefore,
the corrected $\delta$Ar/N$_2$ values of -6 ‰ to -1 ‰ in the interval from 3000 B.P. to 0 B.P.
(Fig S6), implying potential impacts on $\delta^{40}$Ar/4 of as much as 0.01 ‰ (Fig. S7). In
addition, the corrected $\delta$Ar/N$_2$ shows a gradual decrease from 1000 B.P. to 500 B.P.
(Fig. S6), implying that more pronounced argon leak occurred in the shallower ice. We corrected $\delta^{40}$Ar for gas-loss effects using the corrected $\delta$Ar/N$_2$: $\delta^{40}$Ar$_{\text{corrected}} = \delta^{40}$Ar$_{\text{observed}} + 0.0075 \times \delta$Ar/N$_2$$_{\text{corrected}}$. The coefficient 0.0075 is obtained by running the $\Delta T$-based surface temperature calculation with various coefficients and comparing the outputs with the borehole temperature record and observed $\delta^{15}$N. The coefficient is close to the value of 0.007 found for the Siple Dome ice core [Severinghaus et al., 2003]. The correction lowers $\delta^{40}$Ar and raises $\Delta T$, but the decadal to centennial fluctuations are mostly preserved (Fig. S7). The fact that the $\Delta T$ surface temperature calculation runs without drift for 3000 years (small errors in $\Delta T$ create large drifts in calculated surface temperature during the integration), and the fact that the modeled borehole temperature and $\delta^{15}$N agree with observations, supports the validity of the $\delta^{40}$Ar correction.

Evidence for impacts of argon loss on $\delta^{40}$Ar can also be inferred from the following experiments. We ran the model by shifting $\Delta T$ by a constant 1.8-1.9 °C. to produce a surface temperature history for the last 1000 years consistent with observed borehole records. We also performed a $\Delta T$-based surface temperature calculation for the period 3000-1000 B.P. with the same $\Delta T$ shift of 1.8-1.9 °C, and found that this creates a large drift (increasing temperature through this period) and a resultant $\delta^{15}$N inconsistent with observed $\delta^{15}$N. However, a constant $\Delta T$ shift by 1 °C for the period 3000-1000 B.P. produced a consistent picture. Therefore, it is clear that the magnitude of artifacts on $\delta^{40}$Ar changed around 1000 B.P., which is consistent with the $\delta$Ar/N$_2$ data. We plot the two alternative surface temperature histories (Fig. S8) using $\Delta T$.
corrected by a constant shift and $\delta^{40}$Ar corrected by $\delta$Ar/N$_2$. Both histories show similar multi-decadal to centennial trends, except for a slightly higher temperature in the Medieval Warm Period by $\sim$0.5 °C with the $\Delta T$ constant shift. Therefore, the centennial to multidecadal trends in the reconstructed temperature appear to be a robust feature.

5. Firn thickness change from gas isotopes: model vs. observation

The model (driven by $\delta$Ar/N$_2$ corrected $\delta^{40}$Ar) shows a gradual increase of firn thickness by $\sim$3m through the last millennium (Fig. S9), reflecting the reduced densification rate due to the cooling from the Medieval Warm Period to the Little Ice Age. The last 150 years of warming are not significantly reflected in the firn thickness owing to slow heat diffusion in the firn. The past firn thickness change should be reflected as an increase in the gravitational component of observed $\delta^{15}$N (Fig. S10). Observed $\delta^{15}$N$_{grav}$ shows the expected magnitude of increase toward the late millennium, but in the last 200 years observed $\delta^{15}$N$_{grav}$ shows a significant reduction, in contrast to the model result (Fig. S10). Discrepancies are also found around 1300-1500 C.E. Observed $\delta^{15}$N$_{grav}$ shows more variation than the model $\delta^{15}$N$_{grav}$, although the variations are near the limit of analytical error. Observed and modeled $\delta^{15}$N records also show overall agreement but with the same noticeable discrepancies (Fig. S11). As the thermal component of $\delta^{15}$N is an input in the model as $\Delta T$, all discrepancies between the model and observed $\delta^{15}$N$_{grav}$ (Fig. S10) are also reflected in the model and observed $\delta^{15}$N comparison (Fig. S11).
Accumulation rate data, which are also inputs in the model, may provide some insights on this discrepancy. We compared accumulation rate data between GISP2 [Alley et al., 1997; Cuffey and Clow, 1997] and composite data from three Greenland cores (DYE-3, GRIP, NGRIP) [Andersen et al., 2006] (Fig. 4). The GISP2 accumulation rate and composite data show little correlation ($r^2 = 0.04$). It is known that accumulation rate can be considerably different even from two adjacent ice cores owing to snow drifting [Fisher et al., 1985], suggesting that long term averaging or compilation of accumulation rate from various cores are required to obtain real accumulation signals. Notably, $\delta^{15}$N shows more correlation ($r = 0.36$) with the composite accumulation history than with GISP2 accumulation data ($r = 0.1$).

The largest peak in $\delta^{15}$N in the early 15th century is also the time of the highest snow accumulation in Greenland [Andersen et al., 2006]. Some of the disagreements between model and observed $\delta^{15}$N occur in times of disagreements between GISP2 accumulation and composite data. For example, the model overestimates observed $\delta^{15}$N for 1100-1150, 1300-1400, and 1600-1750 (Fig. S11), when the GISP2 accumulation rate data is higher than composite estimates (Fig. 4). This may suggest that to reconstruct the firn thickness change more precisely it may be better to use the composite accumulation rate data. However, as the model firn thickness variation during the last millennium is small (<5%), the use of the slightly different accumulation rate histories have little effects on the surface temperature calculation.

The observed $\delta^{15}$N$_{grav}$ shows a significant decrease from ~1800 onward, but model $\delta^{15}$N$_{grav}$ stayed relatively constant. This significant deviation may relate to the observed decrease in air content of shallow ice owing to incomplete bubble closure
(Fig. S12), which may alter the gas isotopes [Severinghaus and Battle, 2006]. However, this isotopic fractionation should be similar to gravitational fractionation [Severinghaus and Battle, 2006] so that the effects on isotopes should be canceled during the calculation of $\Delta T$. Firn thickness obtained from $\delta^{15}$N$_{grav}$ would be biased by this effect, so $\delta^{15}$N$_{grav}$ should be interpreted with caution in this interval.

Observed $\delta^{15}$N$_{grav}$ shows more decadal variation than model results. This may relate to inadequacies in the model representation of shallow firn. Recent shallow firn thickness studies show that conventional firn densification models may underestimate higher frequency variation [Li et al., 2003; Zwally and Jun, 2002]. Therefore, further research on shallow firn modes is warranted.
Figure 4.S1. Observed $\delta^{15}$N, $\delta^{38}$Ar, $\delta$Ar/N$_2$, and number of samples per depth. The circles are means and error bars are 1σ standard deviation of replicate samples. Three depths with a single analysis are shown only circles.
Figure 4.S2. Temperature reconstructions after 1950 by Alley et al. (blue) [Alley and Koci, 1990] and this study (green). Dotted lines are the ending years of the calculations (1989 for Alley et al. and 1993 for this study).
Figure 4.S3. Modeled (green) and observed (blue) $\delta^{15}N$ for the last 3000 years. Note that the high resolution and precision data start after 990 B.P.
Figure 4.S4. Observed (red) [Clow et al., 1996] and modeled (blue) borehole temperature histories. Broken blue lines are 1σ error bands.
Figure 4.S5. Modeled (green) and observed (blue) $\delta^{15}$N for the past 10,000 years. Note that the model result overestimates observed $\delta^{15}$N before 3000 B.P., suggesting that the $\delta^{18}$Oice-based surface temperature (firn thickness) in the model is too cold (thick) before 3000 B.P. The model calculation switches from the $\delta^{18}$Oice-based to the $\Delta T$-based calculation at ~3000 B.P.
Figure 4.S6. Corrected $\delta$Ar/N$_2$. Note the decrease in mean value around 1000 C.E. from -3 ‰ to -5 ‰, suggesting that argon loss was more extensive for shallower ice.
Figure 4.S7. Raw (green) and corrected (blue) $\delta^{18}$Ar and $\Delta T$. Note that the multi-decadal to centennial fluctuations are little affected by the correction.
Figure 4.S8. Surface temperature reconstruction with the $\Delta T$ corrected by a constant shift (red) and by the $\delta^{40}\text{Ar}$ corrected by $\delta\text{Ar}/N_2$ (main result).
Figure 4.S9. Model result of firm depth for the last 1000 years. The model firm depth increased ~3m (5%) since the beginning of the millennium.
Figure 4.S10. Model and observed gravitational component of $\delta^{15}\text{N}$ (or $\delta^{15}\text{N}_{\text{grav}}$) for the last 1000 years.
Figure 4.S11. Model (green) and observed (blue) $\delta^{15}N$ for the last 1000 years.
Figure 4.S12. Air content in ice for the last 1000 years. The values are normalized to the mean value for the last 1000 years.


CHAPTER V

Greenland temperature, climate change, and human society
during the last 11,600 years
1. General trend of climate and human evolution before the Holocene (>11,600 B.P.)

The earth has been undergoing a progressive cooling since the early Eocene (~50 Million years ago) when polar regions had no glaciers and tropical areas expanded 10-15° of latitude poleward [Crowley and North, 1991; Kobashi and Grossman, 2003; Kobashi et al., 2004; Kobashi et al., 2001; Zachos et al., 2001] (Fig. 1). This time also coincided with the expansion of mammals [Zachos et al., 2001]. It has been suggested that tectonic events such as the opening of the passage between South America and the Antarctic continent, and the collision of the Indian subcontinent to the Eurasian continent were the underlying causes of the cooling through the Cenozoic [Crowley and North, 1991; Zachos et al., 2001]. The uplift of the Himalayas changed aspects of silicate rock weathering and reduced the atmospheric CO$_2$ concentration [Crowley and North, 1991; Zachos et al., 2001]. The effect of these tectonic events was to radically reorganize the climatic configuration during this period [Crowley and North, 1991; Zachos et al., 2001]. By ~35 million years ago, the Antarctic was partially glaciated [Zachos et al., 2001] (Fig. 1). Ice sheets in the Arctic began around 6 million years ago, although a recent study suggests much earlier glaciation in the Arctic [Eldrett et al., 2007]. An important evolutionary change in the human lineage from apes happened around this period in Africa coinciding with cooling and drying [Fagan, 2004]. By ~2 million years ago, the more human-like Homo erectus appeared in Africa, and rapidly radiated out of Africa with a more climatically adapted physical nature [Fagan, 2004]. In addition, early humans started using fire around this time [Fagan, 2004].
The increasingly colder and drier climate with distinctive glacial cycles during the last 2 million years further promoted human evolution, notably with an increase of brain size. Full scale glaciation cycles with a 100,000-year period set in ~700,000 years ago [Tiedemann et al., 1994], where warmer interglacial periods occurred only 10% of the time [Crowley and North, 1991]. *H. erectus* evolved to *H. sapiens* around 500,000 years ago, and the two species coexisted for several 100,000s of years [Fagan, 2004]. Anatomically modern human *H. sapiens sapiens* appeared around 100,000 years ago [Fagan, 2004].

The oxygen isotope records of ice from Greenland and other paleo proxy records show that the climate during the last glacial period (70,000 B.P.-15,000 B.P.) was characterized by large abrupt climate changes (Fig. 2), which were centered on the North Atlantic region and at least hemispheric in extent [Alley et al., 2003]. The abrupt climate events occurred in a short time, as quickly as a few years [Alley et al., 1993], and the temperature changes in central Greenland often exceeded 10 °C [Huber et al., 2006; Severinghaus and Brook, 1999]. The climatic events occurred roughly with an interval of 1,470 years or multiples thereof [Rahmstorf, 2003]. During the glacial period, human culture was advancing steadily as can be seen in the gradual advance of blade technology in Southwest Asia by 50,000 years ago, and appearance of art objects in Europe by 40,000 years ago [Fagan, 2004]. It is most likely that the abrupt climate changes provided important ingredients for human evolution through vigorous competition for survival, combined with frequent changes in food supplies that selected for mental flexibility [Calvin, 2002].
2. Climate change for the last 11,600 years

2.1. Stable Greenland temperature during the last 11,600 years

After an abrupt warming of 10 °C at the end of the Younger Dryas cold interval [Grachev and Severinghaus, 2005; Severinghaus et al., 1998], Greenland temperature gradually rose 5 °C over several millennia (Fig. 2) [Cuffey and Clow, 1997; Cuffey et al., 1995; Stuiver et al., 1995]. Then, Greenland temperature showed remarkable stability until today as compared with the abrupt climate changes throughout the glacial period (Fig. 2) [Cuffey and Clow, 1997; Cuffey et al., 1995; Stuiver et al., 1995]. The nitrogen and argon data completed in this work show that temperature was even more stable than the δ¹⁸O ice-based temperature reconstruction indicates [Kobashi et al., submitted-b]. During this stable climate, only two modest temperature fluctuations occurred, which were comparable but still smaller than those in the glacial period, as shown in previous chapters [Kobashi et al., in press; Kobashi et al., submitted-a].

2.2. Millennial-scale climate change during the Holocene

It has been suggested that a millennial-scale climate oscillation with a period of ~1,500 years persisted through the Holocene and the last glacial period [Bond et al., 2001; Bond et al., 1997; Obrien et al., 1995]. Bond et al. (2001) suggested that this millennium-scale climate variation may be caused by changes in solar activity. The ∆T record produced in this work from gas isotopes also shows a millennium-scale variation with a period of 1055-1450 years (Fig. 3 and 4). However, the observation should be considered provisional at this point owing to the fact that gas isotopes
record progressively smaller signals in $\Delta T$ for longer time-scale variations and the potential gas loss impacts on argon isotopes. It is noted that a power spectrum of nitrogen isotopes shows a broad peak at a period of ~1550 years (Fig. 4).

2.3. The $\Delta T$-based temperature reconstruction for the last 4000 years

In the previous chapters, the $\Delta T$ method is developed and applied to the Preboreal Oscillation and the last 1000 years [Kobashi et al., submitted-a; Kobashi et al., In preparation]. The gas leak and potential artifactual imprints on argon isotopes hinder the application of the $\Delta T$ method to the entire 11,600 years because the $\delta$Ar/N$_2$ used for the argon correction is heavily enriched in the gas-clathrate transition [Kobashi et al., submitted-b]. However, the high $\delta$Ar/N$_2$ anomaly is limited to a period from 5000 B.P. (1000m) to ~9000 B.P. [Kobashi et al., submitted-b]. Therefore, it is possible to apply the $\Delta T$-based surface temperature reconstruction method to the last 4,000 years. Figure 5 shows the reconstructed surface temperature for the last 4,000 years with the same procedure as for the last 1000 years [Kobashi et al., in prep.]. The precision and resolution (~20 years) before 1000 AD are lower than those for the last 1000 years [Kobashi et al., submitted-b]. The $\Delta T$-based temperature record shows some general agreement with the reconstruction from borehole temperature by an inverse model [DahlJensen et al., 1998], although the latter is highly smoothed. Comparison of calculated ($\Delta T$-based) and observed borehole temperature records shows a good agreement above 800m with a difference of less than 0.2 °C (Fig. 6), but it deviates below 800m suggesting that actual surface
temperature may have been warmer than the $\delta^{18}$O_{ice}-based temperature before 4000 B.P. However, this issue requires further investigation.

The last 4000 years marks the rise of civilization in many parts of the globe. The Greenland temperature history, which may represent a global to hemispheric temperature trend [Kobashi et al., in prep.], provides valuable information to study relationships between climate changes and human society. The data indicate that 1600-1800 C.E. were the coldest centuries in the last 4000 years. Around 700 C.E. there was a period of warm temperature, and in the centuries around 500 B.C. temperatures were colder than the surrounding millennia. These temperature fluctuations may have contributed to the rise and fall of civilization (see later discussion).

2.4. Isotope records and $\Delta T$ for the last 11,600 years.

Changes in $\delta^{15}$N and $\delta^{40}$Ar in ice cores should reflect either changes in firn thickness or the temperature gradient between the top and bottom of the firn layer during the Holocene. Another possible variable, convective zone thickness, can be considered to be a minimal effect for this period [Goujon et al., 2003]. Therefore, a close examination of the gas-isotope data with the $\delta^{18}$O_{ice} and accumulation rate may enhance understanding of firn processes and climate change. Figures 7-10 are plots for different intervals (0-3000 B.P., 3000-6000 B.P., 6000-9000 B.P. and 9000-12000 B.P.) with the gas-isotope records, $\Delta T$, $\delta^{18}$O_{ice}, accumulation rate, and $\Delta^{14}$C. The $\Delta^{14}$C is added to examine a possible link between Greenland climate and changes in solar
activity [Reimer et al., 2004]. Note that $\delta^{40}$Ar and $\Delta T$ data are plotted for entire periods without gas-loss corrections.

Figure 7 shows the interval of 0-3000 B.P. The general increase in the isotopic value toward present reflects the increasing accumulation rate and cooling, thus a thickening of the firn layer. The multi-centennial fluctuations of isotopes are clear, and mostly coincide with temperature fluctuations ($\Delta T$). The relationship between temperature and solar activity is not clear except for the past 1000 years. Figure 8 shows the interval of 3000-6000 B.P. This interval seems to be the most stable period during the last 11,600 years. The $\Delta T$ around 5000 B.P. suggests one of the most pronounced warming periods in the last 11,600 years (Fig. 3). Figure 9 shows the interval of 6000-9000 B.P. This interval contains one of two large climatic events during the Holocene, “the 8.2ka event” [Kobashi et al., in press]. It is noted that the warming after the 8.2ka event is quite large although it is not a rapid warming. This may reflect an overshooting of the meridional overturning circulation during its recovery after the 8.2ka event. Finally, Figure 10 shows a long decrease in $\delta^{15}$N and $\delta^{40}$Ar over 6000-9000 B.P. This reflects a gradual surface temperature rise for a few thousand years after the Younger Dryas, and a rather slow warming of the ice sheet after the last glacial because of the large heat sink of the ice sheet [Kobashi et al., submitted-a]. The Preboreal Oscillation (a few centuries of cooling) occurred a few centuries after the abrupt warming at the end of the Younger Dryas, and it ended with an abrupt warming by $\sim$4 °C [Kobashi et al., submitted-a]. Smaller multicentennial climate fluctuations persisted through this period.
3. Climatic impacts on human society for the last 11,600 years

3.1. Beginning of agriculture

The variations of climate during the past 11,600 years influenced the development of early human societies. In some cases it resulted in the collapse of civilizations and in other cases it stimulated new technologies [Diamond, 2005]. Agriculture, the basis of civilization, started around 11,000 years ago after a rapid improvement of the environment for human habitation in many parts of the globe [Fagan, 2004]. The earliest documented evidence for an agriculture-based society (Pre-pottery Neolithic A: PPNA) occurred in the Near East at the beginning of the Holocene [Byrd, 2005]. The rapidly improving environment after the Younger Dryas may have provided opportunities for the expansion of agriculture and technological advances [Byrd, 2005]. Figure 11 shows plots of the timing of PPNA sites with the ice core \( \delta^{18}O_{\text{ice}} \) record from Greenland. It is clear that most of the PPNA sites came after the end of the Younger Dryas around 11,590 B.P. and the peak of the PPNA-site occurrences coincides with the period after an abrupt warming at the end of the Preboreal Oscillation around 11,270 B.P. [Kobashi et al., submitted-a].

3.2. Abrupt climate changes and past civilizations

Recent advances in paleoclimate proxies such as ice cores and sediment cores have shown that climate changes during the last 11,600 years had major impacts on the development of past societies [deMenocal, 2001; Staubwasser and Weiss, 2006; Weiss, 2000]. For example, an abrupt climate change 8,200 years ago [Alley et al., 1997; Kobashi et al., in press] caused a major disturbance for the northern
Mesopotamian society. A rain-fed agriculture based society (the Pre-pottery Neolithic B; PPNB), which was established for several millennia, collapsed due to a century-long cold and dry climate during the 8.2ka event [Weiss, 2003]. This may have led people to invent the first irrigation as an adaptation measure [Weiss, 2003]. Around 5,200 B.P. a cooler and drier climate was present, possibly on a global scale [Staubwasser and Weiss, 2006; Weiss, 2000]. This climatic event has been associated with the collapse of the Late Uruk colony and the termination of the Uruk urbanization in southern Mesopotamia [Weiss, 2000]. However, our data does not show a particularly large event around this time (Fig. 8).

Asia and Africa experienced a severe drought around 4,200 B.P. [Arz et al., 2006; Cullen et al., 2000; Weiss, 2000]. A sediment core from the Gulf of Oman shows a rapid increase in aeolian dust at 4025 ± 125 B.P., suggesting increased aridity. This coincides with the collapse of the world’s first empire, the Akkadian empire, at 4170 ± 150 B.P. [Cullen et al., 2000]. In Greece and Crete, a large population decrease is found around this time likely due to a drought [Weiss, 2000]. In Egypt, the Old Kingdom dynasties developed political instability and economic disaster as a ramification of reduced Nile flow and agricultural production [Weiss, 2000]. Weiss (2000) summarizes overall impacts of this climatic event to civilizations. When imperialized dry-farming became impossible, states collapsed (e.g., northern Mesopotamia) or people adopted a new measure, for instance moving from dry-farming to irrigated agriculture. As a result, large increases in population are found in irrigation lands (e.g., southern Mesopotamia, Margiana, and the Indus Valley). In
In some cases, people chose to abandon sedentary life, and adopted pastoralism (e.g., Greece, Anatolia, Egypt, Palestine, northern Mesopotamia).

The Preclassic Maya developed in low- to high-lands of Mesoamerica from the second millennium B.C. to ~250 C.E., and then the Classic Maya rapidly advanced until 850 C.E. with highly developed urban centers and increased trade networks [deMenocal, 2001]. Then, the civilization collapsed around 750-900 C.E., presumably due to a prolonged drought [deMenocal, 2001; Hodell et al., 1995]. A sediment core taken from Lake Chichancanab in Yucatan, Mexico documents these events [Hodell et al., 1995]. The sediment compositions and oxygen isotopes of gastropods show that the driest period of the last 8000 years occurred during the period of 800-1000 C.E., coinciding with the timing of the Classic Maya collapse [Hodell et al., 1995]. The densely populated areas were already marginal for water supply at the peak of the civilization so that the prolonged drought had a major impact on the Classic Maya civilization [deMenocal, 2001].

The highland Peruvian civilization, Moche, developed from ~300 B.C. to ~500 C.E. in northern coastal Peru with large ceremonial centers and large irrigation works [deMenocal, 2001; Fagan, 2004]. However, it was abandoned abruptly at ~600 A.D [deMenocal, 2001]. The Quelccaya ice core record with annual resolution indicates ~30 years of reduced precipitation and ~60 years of increased wind-born particles preceding the collapse of the Moche [deMenocal, 2001; Shimada et al., 1991]. Archeological evidence shows loss of irrigation by encroaching sand dunes and migration of people to wetter locations around this time, which is consistent with an increased aridity inferred from ice core records [deMenocal, 2001]. Another instance
of increased aridity around 1,100 C.E. indicated in the Quelccaya ice core, likely caused the collapse of the Tiwanaku culture, which developed around Lake Titicaca in the southern Bolivian-Peruvian altiplano [deMenocal, 2001].

3.3. Japanese Islands

Located along the east coast of the Eurasian continent, the islands of Japan provide insights on the relationship between climate and people in the past. During the last glacial maximum, the islands were connected with the Eurasian continent allowing free migration of animals and vegetation including humans [Habu, 2004]. The sea level rise during the deglaciation eventually isolated the islands from the continent [Habu, 2004]. The earliest documented pottery was found around 16,500 B.P. in the islands [Habu, 2004]. With bountiful resources due to increasing temperature, precipitation and humidity, population rapidly increased after the last glacial [Diamond, 1998]. During the middle Holocene warmth around 5000 B.P. sea level was higher than present by <6m [Habu, 2004], and the population reached its highest level of 260,000 in the Jomon period [Habu, 2004]. Since then, temperature decreased and subsequently land productivity decreased [Habu, 2004]. It is estimated that population decreased to less than a third of its peak by 2000 B.P. owing to reduced productivity of the land [Habu, 2004]. With the introduction of agricultural practices from the continent during the Yayoi period around 300 B.C., population started increasing rapidly again [Habu, 2004].

3.4. World system and climate change
Over the last 11,600 years, increasing population and networks gradually connected all parts of human society leading some authors to describe a “world system” [Frank and Gills, 1993]. By 5000 B.C., a core of the world system was established in the Mesopotamia region [Frank and Gills, 1993]. At a similar time, several cores of the world system including North Africa, East Asia, Europe, South Asia, and Mesoamerica were also developing. Subsequently, these cores and peripheral regions progressively converged into a world system. In this view, the current globalization is part of an on-going process of development of the world system [Frank and Gills, 1993].

It has been noticed that the world system exhibited repeated contraction and expansion in a quasi-periodic way for the past 5000 years, with a general increasing trend [Chase-Dunn and Manning, 2002; Frank and Gills, 1993; Frank and Thompson, 2005]. The rise and fall of civilizations changed the relative importance of regions in the world system through time. As the world system became more and more integrated into a larger system, the rise and fall became more synchronous over a broader area [Chase-Dunn and Manning, 2002; Frank and Gills, 1993; Frank and Thompson, 2005]. The apparent synchronous change may have been caused by change in long distant trade, by interactions with third parties in Central Asia, by epidemic diseases, or by climate changes [Chase-Dunn and Manning, 2002].

The Greenland temperature record for the last 4000 years can provide a test for a hypothesis of the climate-driven falls and rises of the world system. As the last 1000 years of Greenland temperature shows a high correlation with the Northern Hemispheric temperature records, Greenland temperature may be a good proxy for
hemispheric temperature change or moisture status [Kobashi et al., in prep.]. Figure 12 shows the last 4000 years of Greenland temperature record with archaeological observations of the rise (A phase) and fall (B phase) of civilization compiled by Frank et al. [Frank and Gills, 1993; Frank and Thompson, 2005]. Both the temperature change and the rise-fall of civilization show a multi-centennial fluctuation (Fig. 12). Although a relation between the temperature change and the rise-fall of the world system is not obvious, a closer visual examination may indicate that in cooling periods the world system tends to expand, and in warming phases it tends to contract (Fig. 12). The rather weak correlation likely suggests that in some cases climate change had a major control, and in some other cases endogenous causes had larger importance on contraction-expansion of the world system.

Chase-Dunn et al. [Chase-Dunn et al., 2006; Chase-Dunn and Manning, 2002] suggest that cities and empires in East Asia and the West Asia/Mediterranean region were expanding and contracting at the same time from 500 BC to 1500 BC. Their data show that the periods of 200BC – 100AD, 700-1100 AD, and ~1300 AD were the times when both East and West Asia had large population in the largest cities. On the contrary, the periods of 1000 BC - 800 BC, 300 AD - 500 AD, and 1100-1200 AD were the times of smaller cities. Comparison with the Greenland temperature record does not show any particular relationship with the changes in city size (Fig. 12).

4. Societal development during the last 11,600 years

Since the advent of agriculture around 11,000 years ago, human society found a new path for its development. The complexity of the human societal system
increased substantially, and human society increasingly found ways to manipulate the natural system. These changes can be understood as an adaptive response of human society. Severe environmental conditions of the glacial period refined the physical and mental abilities of humans, and the subsequent, more habitable Holocene climate unleashed these abilities toward ongoing development. Human societies in various parts of the world took similar paths more or less independently for the last 11,600 years, suggesting that the timing of human societal evolution was not merely by chance, but rather it was a fully conditioned event. Although it is not clear that the relatively warm and stable Holocene was a necessary condition, it is clear that the rapid rate of development of human society during the past 11,600 years could not have been achieved without the more habitable and productive environment of the Holocene.

Various parts of the world experienced slightly different rates of societal evolution, which were likely consequences of various geographical conditions [Diamond, 1997]. West Asia connected four different regions (North Africa, Europe, South Asia, and East Asia) and acted as an information hub, showing the earliest development. However, the increasingly arid environments of this region provided a challenge for later development. On a continental scale, Diamond [Diamond, 1997] argues that the longitudinally-long Eurasian continent provided human society with easier transmission of domesticated animal and plant species owing to similar climates, and it permitted faster development than societies in the latitudinally-long American continents. The eastern side of the Eurasian continent had more rainfall and productive land than the western side therefore fostering denser population in the eastern side.
Many lines of development in the various parts of the world expanded and converged with time, continually producing a planet-wide world system. Seen from this perspective, the current globalization is part of an on-going process of expansion and integration of human societies.

5. Conclusion

Climate during the last 11,600 years was substantially more favorable to human society than in the glacial periods. In this environment, human society developed a robust system within the natural system. No obvious correlation with Greenland temperature is observed for expansions and contractions of organized human societies over the past 4000 years. However, substantial uncertainties in the archaeological estimates preclude a firm conclusion regarding the influence of climate on emerging civilizations. Some events, such as the 8.2ka event, clearly had societal consequences, especially for rain-fed-agriculture-based societies in west Asia.
Figure 5.1. Last 65 million years of $\delta^{18}O$ of foraminifera (proxy for ocean temperature; top: Zachos et al., 2001; bottom: Tiedemann et al., 1994). Increasing $\delta^{18}O$ toward present reflects both cooling and increasing continental glaciers.
Figure 5.2. Oxygen isotopes of ice (GISP2) for the last 100,000 years (Stuiver et al., 1995). The record can be considered as a temperature proxy (Cuffey et al., 1995).
Figure 5.3. $\Delta T$ with spline fit with a 500-year cut-off period. Shaded areas represent cooler periods.
Figure 5.4. Power spectra of $\delta^{15}N$ (top) and $\Delta T$ (bottom) for the last 11,600 years
Figure 5.5. Last 4000 years of Greenland temperature. As the data resolution and precision are low before 1000 A.D., the record before 1000 A.D. should be considered provisional at this point. The reconstruction (green) is based on borehole temperature with an inverse model (Dahl-Jensen, 1998).
Figure 5.6. Borehole temperature records from observation and the model for last 4000 years of temperature reconstruction.
Figure 5.7. $\delta^{15}$N, $\delta^{40}$Ar, $\Delta T$, $\delta^{18}$Oice, accumulation rate, and $\Delta ^{14}$C for the period of 0-3000 B.P. Spline fits are applied for isotopes and $\Delta T$ (Enting, 1987), and error bands are 1$\sigma$. 
Figure 5.8. $\delta^{15}$N, $\delta^{40}$Ar, $\Delta T$, $\delta^{18}$Oice, accumulation rate, and $\Delta^{14}$C for the period of 3000-6000 B.P. Spline fits are applied for isotopes and $\Delta T$ (Enting, 1987), and error bands are $1\sigma$. 
Figure 5.9. δ^{15}N, δ^{38}Ar, ΔT, δ^{18}Oice, accumulation rate, and Δ^{14}C for the period of 6000-9000 B.P. Spline fits are applied for isotopes and ΔT (Enting, 1987), and error bands are 1σ.
Figure 5.10. $\delta^{15}$N, $\delta^{40}$Ar, $\Delta T$, $\delta^{18}$Oice, accumulation rate, and $\Delta^{14}$C for the period of 9000-12,000 B.P. Spline fits are applied for isotopes and $\Delta T$ (Enting, 1987), and error bands are 1σ.
Figure 5.11. Combined likelihood plot for 77 PPNA sites, and oxygen isotopes of ice from the Greenland ice core (GISP2). Note that the peak of the PPNA likelihood coincides with the end of the Preboreal Oscillation. The likelihoods based on ¹⁴C dating error for each site are combined to make a probability function.
Figure 5.12. Last 4000 years of Greenland temperature as for Figure 5. Shaded areas are contraction phases of the world system (B Phase; Frank and Gils, 1993).
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Conclusion
As an individual life is much shorter than the history of civilization or the human species, it is difficult to understand the true relationship of humans to their natural environment. Therefore, it is critical to ask for help from studies of the past environment and human species to frame the present into a larger entity. In this study, the last 11,600 years of Greenland temperature was reconstructed with nitrogen and argon isotopes in air trapped in ice. Although the gas loss problem hindered the temperature reconstruction of the entire period, several important findings are listed below. These results are compared with human history, and an attempt is made to untangle the current problems of human society from a perspective of the natural system.

1. A new method for simultaneous analysis of argon and nitrogen isotopes

A new method is developed to analyze argon and nitrogen isotopes from the same sample, which reduced the uncertainty of estimates of past temperature difference across the firn layer, and substantially reduced the time required for analyses. The method is applied to the Holocene section of the GISP2 ice core. High precision for δ¹⁵N and δ⁴⁰Ar is achieved, which are similar to conventional methods, but with improvement in δ¹⁵Nexcess due to cancellation of correlated errors. The δ¹⁵N and δ⁴⁰Ar data show a very similar trend of a gradual decrease from 1700m to 1400m due to the response of the firn to the warming at the start of the Holocene, followed by relatively constant values from 1400m to 80m. The general trends agree well with previous modeling studies [Goujon et al., 2003], although model fluctuations on
shorter time scales do not match with observed results, suggesting that borehole-calibrated $\delta^{18}$O$_{ice}$ is not a reliable temperature indicator on these time scales.

Available data suggests that two types of fractionation occur during/after coring, which affect the gas composition in ice cores. The smaller molecules such as oxygen and argon leak through the ice lattice with little isotopic fractionation as observed in firm air studies. Mass-dependent fractionation of $^{40}$Ar/$^{36}$Ar occurs during gas loss through cracks especially in brittle ice, affecting isotopic composition. Krypton isotopes show a very similar trend to argon and nitrogen isotopes, and due to the large atomic diameter may be insensitive to gas loss and provide a constraint on the gas-loss process in the future.

2. The 8.2ka event

A large number of paleoclimatic records over a near-global area show a large and abrupt climate change around 8,200 years B.P. However, the duration and general character of the event have been ambiguous. A precise general character and timing of the event is presented using methane and nitrogen isotopes in trapped air in a Greenland ice core. Climate change in Greenland and at a near-global scale were simultaneous (within ±4 years) as supported by the GCM model results. The event started around 8175±30 years B.P., and it took less than ~20 years to reach the coldest period, with a magnitude of cooling of 3.3±1.1 °C in central Greenland. After ~60 years of the coldest period, climate gradually recovered for ~70 years to a similar state as before the event. The duration of the event was roughly 150 years.
3. Abrupt warming at the end of Preboreal Oscillation

The hemispheric-scale climatic event, “the Preboreal Oscillation”, was terminated with a rather abrupt warming of $4 \pm 1.5 \, ^\circ C$. Snow accumulation rate rose by 30% within a few years, suggesting a rapid reorganization of climate. The methane record shows a similar trend with the reconstructed surface temperature record, suggesting that the climatic trend in Greenland was synchronous with hemispheric-scale climate change, although a firm conclusion must await higher resolution methane data. The character of this event was much more like the Dansgaard – Oeschger (D/O) events than the 8.2ka event, hinting that the mechanisms involved were similar to those of the D/O events.

4. A new method for surface temperature reconstruction

A new method is developed and employed to reconstruct surface temperature changes, using argon and nitrogen isotopes in air trapped in the ice core and a heat transfer-firn densification model. The method calculates the surface temperatures by adding the model-derived firn bottom temperature to the isotope-derived temperature gradient in the firn. The model reconstructs independent records well with the $\Delta T$ data corrected by a constant +1 °C, which may be due to artifacts. The $\delta^{15}N$ record shows two large peaks over the interval 11,800 B.P. to 10,700 B.P. with two smaller subsequent peaks. These oscillations may be a smaller manifestation of the Dansgaard–Oeschger events, which characterized the cold, unstable glacial ocean. The
last large abrupt warming at 11,270 B.P. likely marks the onset of a warm and stable oceanic condition in the Holocene.

5. The last 1000 years of Greenland temperature

The Greenland temperature record for the past 1000 years was reconstructed with the $\Delta T$ method derived from argon and nitrogen isotopes in trapped air in ice. The data show clear evidence of the Medieval Warm Period and Little Ice Age, agreeing with documented historical records. The overall trends are remarkably similar to Northern Hemispheric temperature records with a 20-30 years lag of Greenland temperature. A multidecadal temperature fluctuation with periods of 70 and 40 years, which seems to be related to the Atlantic Multidecadal Oscillation, persisted for the last millennium, suggesting that it might continue into the future.

6. Greenland temperature, climate change, and human society during the last 11,600 years

Climate during the last 11,600 years was substantially more favorable to human society than in the glacial periods. In this environment, human society developed a robust system within the natural system. No obvious correlation with Greenland temperature is observed for expansions and contractions of organized human societies over the past 4000 years. However, substantial uncertainties in the archaeological estimates preclude a firm conclusion regarding the influence of climate on emerging civilizations. Some events, such as the 8.2ka event, clearly had societal consequences, especially for rain-fed-agriculture-based societies in west Asia.
Epilogue

* This section contains opinions of the author regarding the future, rather than scientific findings about the past.
1. Natural and human societal systems for the last 11,600 year and the future

On this planet, the natural system consists of various forms of life, water, air etc, all of which are interdependent and play crucial roles for the entire system (Fig. 1). The human system among others is a subsystem of this entire natural system. As all the subsystems are compensating for each other, the entire system can stay in balance. A small imbalance in a subsystem may be covered by changes in another subsystem or by a buffer of the entire natural system. As the human system grew more and more for the past 11,600 years, it placed unprecedented pressure on other parts of the system. In some cases, this resulted in the extinctions of subsystems. Especially, after the human system gained access to a large reservoir of energy (fossil fuel), the influence became so large that the entire natural system is now becoming imbalanced. For example, the increasing greenhouses gases now trap more energy than the radiation of earth to space inducing global warming [Hansen et al., 2005].

For the last 11,600 years, the human system has expanded to occupy all habitable space on earth, and human population is expected to reach its peak later this century [Lutz et al., 2001]. Now for its survival human society is experiencing a major change in the course of development toward another dimension. The new direction is to adjust the current human system to fit more harmoniously into the natural system. In other words, we need to redirect the search for our happiness to that kind of happiness all the natural systems can enjoy together.

One of the prime drivers for human societal evolution is to seek happiness, and a source of happiness for life is to thrive. The manifestation of happiness has been widely different in space and time. Expansion and development of human society for
the past 11,600 years were a way of seeking happiness. The result was to build a climatically resilient society and a robust human system capable of controlling other parts of the natural system. As the development in this direction is coming to completion, now it is time to align our happiness with one that can satisfy a much large entity.

2. How can we start?

In recent years, global warming associated with increasing greenhouse gases has been identified as an important issue for human society. However, this is only a surficial problem among much deeper problems, as discussed previously. Our society now needs a new conceptual expansion from a humanocentric world to a world where we identify ourselves within the framework of the natural system. For the past few centuries, we established many human rights, and now we need to radically expand these concepts into the natural system.

The change in our conceptual thinking comes relatively slowly, but as we realize more and more realities of changes in subsystems and the main system of nature, it will create a basis for new realizations. Although each individual’s life is too short to capture long-term changes by experience, our bodies and minds are part of the natural system. Therefore, it is likely that the real truth (a human society consistent with the natural system) is readily going to be accepted in human society in the future once we find it. Probably, the process to find the path will require many tries and errors. It is important to keep in mind that many current norms and values we believe
to be true may not be true, and may need substantial revisions. The diversity of human societies will likely provide a basis of potential future norms.

In the future, human society will require a much less energy intensive lifestyle, as many issues relate to the huge energy consumption of current human society. For example, a continuation of the current level of carbon emissions may result in a dangerous climatic condition [Hansen et al., 2006]. Importantly, the use of energy itself reinforces the human belief in their dominance of the natural system. To build an entirely sustainable society, we need to identify an acceptable level of energy use, and change the societal system according to it. As a society consistent with the natural system may substantially differ from the current industrialized societies, societies in the peripheral regions with less energy intensive lifestyles may be able to explore a new dimension of human societal development.

As our current societies are so spiritually detached from the natural system, especially in the industrialized nations, we would need to conduct an intentional rehabilitation to connect our society back to the natural system. This may come from actions to incorporate the natural system into our society by increasing opportunities to connect ourselves with the natural system. Society is a sum of individuals. Therefore, a step by each individual will eventually lead to a change of the whole. Only through these exercises will our value system gradually transform, and eventually we will find a path to a happier human society.
Figure Epilogue 1. The natural system (green) with human society (one of the blue circles) as a subsystem. The red circle is sun. Arrows represent inputs and outputs.
References

