A modified extraction technique for liberating occluded gases from ice cores.

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Abstract

We have developed a dry extraction technique to extract air from large pieces of glacial ice. The primary reason for developing this technique was to be able to perform a single extraction and measure a single sample of air from an ice core sample for as many atmospheric constituents as possible. The procedure is modeled after the dry extraction - “cheese grater” design of Etheridge et al., (1988). Extracted air samples are analyzed for the elemental and isotopic composition of O\textsubscript{2} and N\textsubscript{2} as well as the CH\textsubscript{4} concentration. Extensive experimental work to determine the integrity of the extraction procedure yielded blank values and external precision which are comparable with existing extraction procedures. Overall external precision for $\delta$\textsubscript{O\textsubscript{2}/N\textsubscript{2}}, $\delta^{18}$O of O\textsubscript{2}, and $\delta^{15}$N of N\textsubscript{2} analyses is $\pm 2.1‰$, $\pm 0.074‰$, and $\pm 0.045‰$ respectively. $\delta$\textsubscript{O\textsubscript{2}/N\textsubscript{2}} results from ice which is either completely bubbly or clathrated, are in good agreement with previous measurements. $\delta$\textsubscript{O\textsubscript{2}/N\textsubscript{2}} results from GISP II ice samples spanning the clathrate formation region (1,000-1,500m) are markedly different from previous results obtained with a “wet” extraction procedure. We attribute the differences to variable $O_2/N_2$ ratios in bubbles and clathrates in the clathrate formation region combined with a 21% difference in our extraction efficiency for bubbly vs. clathrated ice. The overall uncertainty and blank value for CH\textsubscript{4} measurements are $\pm 19$ ppb and 16 ppb, respectively. CH\textsubscript{4} concentrations for ice between 115 and 140mbs from the GISP II ice core appear to be 4.3% higher than the average value measured by five other laboratories. We attribute our elevated values to uncertainties in the actual concentration of our working standard and small differences in the CH\textsubscript{4} concentration of the liberated air.
relative to the total air trapped in ice. Our corrected CH$_4$ data spanning the last 25 kyr, are indistinguishable from the Brook et al., (1996) CH$_4$ record from the same period.

Introduction

Efforts to reconstruct the composition of the atmosphere over the last 400,000 years have relied, in a large part, on measurements of trapped gases in ice cores [Petit et al., 1999]. Such reconstructions have proven extremely valuable in our efforts to better understand the biogeochemical cycles that control the concentration of various trace gas species in the atmosphere. Of particular importance are those trace gases which absorb a portion of infrared radiation emitted by the earth. These gases (better known as greenhouse gases) play an important role in controlling the overall radiation balance of the earth. Because of their radiative properties, increasing concentrations of these greenhouse gases throughout the past century may be related to the small rise in global temperatures during the 20$^{th}$ century [Houghton et al., 1995]. Trace gas records spanning the last 25 kyr mimic polar temperature records though the precise timing of the trace gas concentration variations relative to the isotopic temperature records has yet to be established unequivocally [Fischer et al., 1999]. In order to better assess this potential, numerous studies have evaluated the relationship between changes in the composition of past atmospheres and proxy climate records spanning the last 400 kyr [Petit et al., 1999].

One problem in constructing the composition of past atmospheres from measurements of trapped gases in ice involves establishing the relationship between the measured ice core gas composition and the composition of the paleoatmosphere that was the original source of the occluded gas. Relating the trapped gas composition to the parent atmosphere has four separate components. The first involves the alteration of the air composition as the air parcels are incorporated into the ice matrix. Gases are initially trapped 50-130m below the surface where the firn reaches a density of 0.8-0.84 g/cm$^3$ [Martinerie et al., 1992]. Numerous studies of the composition of air in the interstitial spaces above the firm/ice transition region (firm air) have documented that gravitational settling of air within the
diffusive air column modifies the isotopic and elemental composition of firm air [Battle et al., 1996; Schwander et al., 1993]. Fortunately, measurements of the $\delta^{15}$N of trapped N$_2$ in ice provide an accurate means of correcting the composition of trapped gases in ice for gravitational fractionation [Sowers et al., 1992]. This correction is important for reconstructing the $^{18}$O/$^{16}$O of paleoatmospheric O$_2$ ($\delta^{18}$O$_{atm}$) but much smaller that the measurement uncertainty (which is generally greater than 1%) for all other gas species. A second issue is the potential in-situ alteration of occluded gases within the ice. For example, recent studies of CO$_2$ in Greenland ice have pointed to various in-situ chemical reactions which can either produce or consume CO$_2$ depending on the chemical make-up of the ice [Anklin et al., 1995; Delmas, 1993]. Most atmospheric constituents, on the other hand, do not appear to be measurably influenced during storage in polar ice sheets. Comparison of CH$_4$ records from Antarctica and Greenland are almost identical (Blunier et al., 1998). The integrity of these CH$_4$ records has recently been used for correlation purposes which in turn provide the means of establishing the interhemispheric CH$_4$ gradient (Brook et al., in press).

A third factor concerns the alteration of trapped air as the ice core relaxes after drilling. Small changes in the elemental composition of O$_2$, N$_2$ and Ar have been documented in response to air escaping from the core through microfractures during post core relaxation [Bender et al., 1995]. Finally, it is very important that the composition of gas extracted from an ice core sample is representative of the total trapped gas. This last issue (which is the focus of the present contribution) must be addressed by extensive laboratory tests and international calibration efforts [Sowers et al., 1997].

Presently, there are three types of extraction procedures that are routinely used to liberate trapped gases from ice [Sowers et al., 1997]. Sublimation and wet extraction techniques liberate trapped gases by subliming or melting the ice sample to remove the trapped gases[Gulluk et al., 1998; Wilson and Donahue, 1989]. Wet extraction techniques cannot, however, be used for studies of trace gas species (e.g. CO$_2$) which are either very soluble in water or are compromised by chemical reactions which occur in the presence of
liquid water. The concentration of these trace gas species in ice are generally determined after the ice core sample has been mechanically crushed into fine grains [Barnola et al., 1983; Etheridge et al., 1992; Etheridge et al., 1988; Etheridge et al., 1996; Fuchs et al., 1993; Zumbrunn et al., 1982].

One important aspect of any extraction procedure is the degree to which the trapped air in the sample is quantitatively removed for analyses. The extraction efficiency (defined here as the fraction of the total air within an ice sample which is removed from the core) varies considerably from one extraction technique to another. Those techniques employing a milling device tend to liberate between 90 and 98% of the trapped gases from bubbly ice [Moor and Stauffer, 1984; Nakazawa et al., 1993]. Other types of dry extraction techniques involve crushing the ice samples using beds of tapered rods [Wahlen et al., 1991; Zumbrunn et al., 1982], stainless steel balls [Barnola et al., 1983], or grating the ice sample by sliding or shaking it in a perforated cylinder [Etheridge et al., 1988]. In general the extraction efficiencies of these later techniques tend to be less than 80%. There are two issues which need to be addressed in this context. First, extensive tests need to be performed in order to establish the degree to which the composition of trapped gases in ice are altered during the extraction process. Secondly, for those techniques which do not quantitatively remove all the trapped air from an ice sample, care must be taken to insure that the composition of the liberated air is representative of the total trapped air in the sample. If the composition of the extracted gas is not representative of the original trapped gas, then the measurements of the extracted air may not provide an accurate measure of the composition of the paleoatmosphere unless the magnitude of the extraction artifact is properly quantified.

In the following sections we describe our extraction technique and the various tests we performed to determine the integrity of the procedure. We compare results from various sections of the GISP II ice core which were extracted using our technique with results obtained on adjoining ice samples using other extraction techniques which have been previously tested (Sowers et al., 1997).
Dry Extraction Technique

Our dry extraction technique is modeled after the “cheese grater” design of Etheridge et al., (1988). Our apparatus consists of a 6 liter stainless steel cylinder which houses the inverted "cheese grater” assembly (Figure 1a). Ice samples are grated by oscillating the cylinder in a horizontal sense inside a commercial chest freezer at -20°C. The largest modification we have made to the Australian design is the incorporation of a flexible metal hose which connects the cylinder to the vacuum manifold allowing the liberated gas to be immediately removed from the extraction cylinder (Figure 1b). The air sample is passed through a water trap (-120°C) and cryogenically trapped in a sample tube within a liquid helium Dewar.

The extraction cylinder was made out of 304L stainless steel tubing (diameter = 15cm) with conflat flanges welded to both ends (Figure 1a). A smaller stainless steel cylinder (diameter = 7 cm) was perforated and welded to one mating conflat flange which was then attached to the bottom of the cylinder. A Nupro series bellows valve was welded to the top mating flange which was removed for each sample introduction. Ice core samples were prepared by initially removing 0.01m of ice from the outside of a 0.3 – 0.4 kg piece of core (0.05m x 0.07m x 0.10m) with a band-saw. The ice sample was then inserted into the extraction cylinder and evacuated with a rotary vacuum pump for 15 minutes. The cylinder was then isolated before being lowered into an alcohol bath and evacuated with a turbomolecular pump for one hour to insure no residual laboratory air remained in the cylinder. The pressure in the cylinder after one hour of pumping was between 0.02 and 0.03 torr depending on the temperature of the alcohol bath. The extraction cylinder was then closed and transferred to the cradle assembly inside a commercial chest freezer (253K) and reconnected to the vacuum manifold with a piece of braided flexible vacuum hose (Figure 1b). A previously evacuated $1.3 \times 10^{-5} \text{ m}^3 (13\text{cm}^3)$ stainless steel sample tube (0.003m O.D. x 1m with Nupro valve attached to top) was inserted into a liquid helium Dewar and attached to the vacuum manifold. As soon as the system was evacuated to a pressure of
1x10^{-3} torr, the extraction was initiated. The occluded gas was liberated by oscillating the
cylinder back and forth in a horizontal sense using an eccentric crankshaft assembly located
on the exterior of the chest freezer. The frequency and throw of the device are \sim 1 \text{ Hz} \text{ and}
0.12m respectively. The valves on the extraction cylinder and the sample tube were both
open so the liberated air was immediately removed from the extraction cylinder and
transferred to the sample tube in the liquid helium. After 15 minutes of shaking, the device
was turned off. After an additional 5 minutes the final pressure in the system was then
checked before the sample tube was finally closed off and removed from the helium Dewar.
The gas in the tube was allowed to equilibrate at room temperature for 12 hours before
analysis.

Mass spectrometric analyses were performed to determine the $\delta^{15}$N of N$_2$, $\delta^{18}$O of
O$_2$, $\delta^{18}$O$_2$/N$_2$ and $\delta$Ar/N$_2$ using a previously developed technique [Sowers et al., 1989]. Aliquots
from each sample are introduced into the bellows of a Finnigan™ MAT 252 isotope ratio
mass spectrometer and analyzed against a working air standard which had been previously
calibrated to present day air. Results have been corrected for isobaric interference from CO$_2$
ionization in the source, zero enrichments, and the measured $^{18}$O/$^{16}$O dependence on the
O$_2$/N$_2$ ratio as specified in Sowers et. al., 1989. Final results are reported relative to the
present day atmospheric composition.

The air in the sample tube was analyzed for [CH$_4$]. Aliquots of liberated air were
expanded into pre-evacuated $1 \times 10^{-5} \text{ m}^3$ (10cm$^3$) sample loop mounted on a six port Valco ™
valves attached to the HP 5890 Series II gas chromatograph equipped with a flame ionization
detector (FID). The pressure in the sample loops (10-90 torr) was measured with a pressure
transducer before each sample was injected onto the head of a 3.3 $\times 10^{-3}$ m x 2.4m
Porapak™ Q chromatographic column (313K) which separated the CH$_4$ from air for final
detection. The area under each CH$_4$ peak was integrated and compared to our working CH$_4$
standards to determine the concentration of CH$_4$ in each air sample. The CH$_4$ data are
reported on the NOAA/CMDL CH$_4$ calibration scale [Steele et. al., 1991].
Wet Extraction Techniques

*Methane analyses:* To compare our dry extraction technique with a previously developed technique for measuring [CH$_4$], we fabricated stainless steel extraction vessels for performing wet extractions following Brook et al., (1996). The extraction vessels were fabricated to hold 0.035 kg ice samples which are 0.03m x 0.03m x 0.06m. After placing the ice sample in the vessel, the vessel was sealed with a copper gasket and evacuated for 30 minutes. The vessel was then isolated and immersed in a 313K water bath to melt the samples. After 20 minutes, the hot water bath was replaced with a 233K alcohol bath to freeze the meltwater. After an additional 20 minutes of freezing, the air in the headspace of the extraction vessel was expanded into the sample loop on the gas chromatograph and analyzed for [CH$_4$] using the same procedure which was previously described for the dry extraction [CH$_4$] measurements.

*Measuring the elemental and isotopic composition of O$_2$, N$_2$ and Ar:* An additional procedure was developed to measure the elemental and isotopic composition of O$_2$, N$_2$ and Ar in ice using a standard "wet" extraction technique (Sowers et al., 1989). Ice samples weighing 0.015-0.025 kg were initially placed into a pre-cooled 2.5 x 10$^{-4}$ m$^3$ glass vessel, attached to a vacuum line and evacuated before the trapped gases were liberated by melting the ice sample. The meltwater was then refrozen by slowly raising an alcohol bath around the vessel. The bath was cooled to 173K before the liberated air was transferred to a 5.5 x 10$^{-6}$ m$^3$ (5cm$^3$) stainless steel sample tube immersed in liquid helium. The tube containing the fossil air was then removed from the helium, allowed to equilibrate at room temperature for 1 hour, and analyzed using the Finnigan™ MAT 252.

**Procedure Verification**

As is the case with any new procedure, establishing the procedural blanks and the existence of any analytical artifacts is of paramount importance in deciphering the integrity of the resulting data. This task is especially difficult for experiments involving extraction of trapped gases from ice due to the absence of a standard ice core sample with known gas
composition [Sowers et al., 1997]. In light of this complication, sensitivity tests with standard gases and bubble-free ice must be performed to mimic, as closely as possible, the actual extraction procedure.

**Dry Extraction**

We deduced the integrity of the “dry” procedure by performing a number of “simulated blank transfers”. The objective of this test was to process an aliquot of air with know composition through the complete extraction procedure in order to deduce the degree to which our procedure altered the composition of the air. We started with ~0.250 kg of bubble-free ice in the cylinder which was evacuated following our normal protocol (1 hr in a 213K alcohol bath). The cylinder was then transferred to the chest freezer (253K) and the bubble-free ice was “grated” into snow to liberate any residual trapped gas in the “bubble-free” ice. The small amount of air that remained in the “bubble-free ice” was liberated with subsequent oscillation/evacuation cycles which were repeated until all the air in the cylinder was evacuated. Next we attached a $1.3 \times 10^{-5} \text{m}^3$ (13cm$^3$) stainless steel tube with a high vacuum bellows valve containing $0.5-1x10^{-3}$ moles of standard gas to a tee between the cylinder and the flexible vacuum hose (Figure 1). The pressure of air standard in the transfer tube was measured with a pressure gauge attached to the vacuum manifold and adjusted to provide a quantity of air which was comparable to the amount of air liberated from a typical 0.25kg ice sample ($0.5-1x10^{-3}$ moles). After the connecting lines were properly evacuated, the air standard was introduced into the cylinder where it was allowed to equilibrate for five minutes before being processed using the same protocol we use for our ice core samples. Finally, we analyzed the processed standard against fresh aliquots of the parent standard to quantify the compositional alterations associated with the dry extraction technique.

**Wet Extraction Techniques**

Analytical artifacts associated with both “wet” extraction techniques were determined by degassing an ice sample by repeated melt/refreeze cycles followed by headspace evacuation. After the ice was properly degassed, aliquots of standard air were introduced
over the refrozen meltwater and processed as if it were a sample. The recovered standard was analyzed against fresh aliquots of parent air standard to determine the degree to which the processed air standard had been altered relative to the parent standard. In all cases, the amount and composition of the working standards were chosen to match the quantity and composition of trapped gas in recent ice from the GISP II ice core.

One of the largest sources of uncertainty in using this approach to estimate the procedural blank is the fact that we have not liberated aliquots of working standard from the ice matrix. Rather, by introducing air over degassed ice/water, we are effectively measuring the alteration of gas after it has been liberated from an ice sample. Until such time as an internationally recognized ice core standard is developed (with know gas composition), we are forced to rely on simulated transfers of this type to deduce the procedural blank.

**Results and Discussion**

**Extraction efficiency for the dry extraction technique.**

The extraction efficiency of our dry extraction technique was determined by isolating the cylinder after a GISP II ice core sample had been completed and allowed the snow/ice mixture to melt. The cylinder was then cooled in a 173K alcohol bath for an hour to insure the temperature of the ice in the cylinder was close to 173K. The cylinder was attached to a vacuum manifold and the pressure in the cylinder was measured. The calculated amount of air in the cylinder (at 173K) was then compared with the total gas content of the ice for the depth interval based on total gas content measurements performed on the GRIP ice core [Raynaud et al., 1997]. Our extraction efficiency in the upper 1,000m of bubbly ice was 75±3\% (Table 2). In the lower portion of the core (where air is clathrated), our extraction efficiency dropped to 54±3\%.

**The elemental and isotopic composition of O\textsubscript{2} and N\textsubscript{2}**

Results from the simulated blank transfers for all three extraction procedures are listed in Table 1. We analyzed three simulated blank transfers for the elemental and isotopic
composition of O₂ and N₂ using both the dry and wet extraction protocols. Results for both procedures indicate the δ¹⁸O of O₂, and δ¹⁵N of N₂ of the processed standards were within one standard deviation of zero indicating no measurable systematic alteration of the isotopic composition of O₂ or N₂ associated with either extraction technique. The δ₁⁸O₂/₁⁵N₂ ratios for the simulated wet extractions were –2.9± 0.56‰ reflecting a small O₂ loss during the simulated transfer. The missing O₂ is probably trapped in the refrozen ice. We speculate that after the working standard was equilibrated over the degassed ice and the ice was allowed to melt, the air in the headspace slowly diffuses into the meltwater. Because O₂ is much more soluble in water than N₂, the O₂/N₂ ratio of air dissolved in the meltwater is much higher than the original working standard. Then, as the meltwater is slowly refrozen, the dissolved air is largely excluded from the reformed ice back into the headspace. However, the dissolved gas is not quantitatively removed from the meltwater during the refreezing process. Because the small amount of residual air trapped in the refrozen ice is highly enriched in O₂, the air in the headspace must be depleted in O₂ yielding the negative δ₁⁸O₂/₁⁵N₂ values. Similar results were observed by Sowers et al., 1989.

Methane (CH₄)

Simulated transfer experiments to determine the CH₄ blank for the two techniques yielded values of 16±18 ppb and 17±11 ppb for the dry and wet extraction techniques respectively. The origin of the CH₄ blank is believed to be related to CH₄ out-gassing from the stainless steel vessels and vacuum bellows valves when they are opened and closed. Our blank results are very similar to the blank determinations which were made by five different laboratories as part of a recent intercalibration effort (Sowers et al., 1997) suggesting our wet and dry extraction techniques are indeed comparable with other techniques which are currently being used to analyze CH₄ in ice cores.

Another way to assess the integrity of an extraction technique is to compare measurements of the composition of trapped gases from an ice core that has previously been measured. We analyzed sections of the GISP II F core (117-123m) which was used in the
recent intercalibration effort (Sowers et al., 1997) for the elemental and isotopic composition of O$_2$ and N$_2$ as well as the CH$_4$ concentration using our wet and dry extraction techniques. This six meter interval corresponds to gas ages ranging from 1807 AD to 1832 AD [Alley et al., 1993; Wahlen et al., 1991] when the composition of the atmosphere was relatively stable. This section of ice was chosen to minimize the possibility that heterogeneous bubble composition might alias our results. However, we cannot completely exclude this possibility but note that the good agreement between the measurements from five different labs strongly suggests that any heterogeneities are probably smaller than our measurement uncertainty.

The CH$_4$ results (Table 1) for the wet and dry extraction procedures were 761±8 (N=6) and 780±20 (N=14) ppb respectively. The average CH$_4$ concentration of the intercalibration ice core (from the same depth interval of the same core) was 748±10 (N=20) ppb. Results from the wet and dry extraction procedures applied here at Penn State were 13ppb (1.7%) and 32 ppb (4.3%) respectively higher than those obtained during the intercalibration study [Sowers et al., 1997]. Applying a student t test to determine whether our measured values are significantly different from the intercalibration results indicates that both our wet and dry results are statistically different from the intercalibration study at the 98% and 99% confidence level respectively.

We can think of two possible reasons why our results differ from the intercalibration estimates. First, our working standard (C#5) was not actually calibrated at NOAA/CMDL. We determined the CH$_4$ concentration in C#5 by calibrating it with a NOAA calibrated air cylinder (C#4, [CH$_4$] = 1441 ppb) approximately every six months. The average CH$_4$ concentration for our working standard (C#5) was 689±6 ppb (N=9). Given this level of uncertainty, we can account for almost 50% of the measured difference between our wet extraction results and those produced during the intercalibration study by considering uncertainties in the absolute concentration of our working standard. Another possible explanation for our elevated CH$_4$ values may be related to an underestimate of our procedural blank. For the wet extraction procedure, an underestimated blank value may be related to the
fact that we did not process the degassed ice sample exactly the same way we processed our ice samples. In the future, the degassed ice samples should be removed from the extraction vessel and shaved with the bandsaw before the ice cube was transferred to another vessel for the simulated transfer (Brook et al., in press). Another factor which may have provided a low procedural blank involves the preferential trapping of CH$_4$ in the refrozen meltwater during the simulated transfers. Given that the diffusivity of CH$_4$ in water is greater than either O$_2$ or N$_2$, an incomplete equilibration between the headspace gas and the initially degassed water would cause the CH$_4$ concentration in the water/ice to be higher than the starting value. This would reduce the CH$_4$ concentration in the headspace which is subsequently measured with the GC. Because the air in a normal glacial ice sample is initially distributed throughout the meltwater, the high CH$_4$ diffusivity tends to produce elevated [CH$_4$] in the headspace relative to the actual [CH$_4$] in the ice (opposite to the effect postulated for the simulated transfer). The net result of this would be an underestimation of the blank associated with the wet extraction technique and a corresponding overestimate of the CH$_4$ concentration in glacial ice samples.

The dry extraction results on the intercalibration ice (117-123mbs) were 19 ppb higher than the wet extraction results and 32 ppb higher than the average CH$_4$ concentration measured during the intercalibration study. Interestingly enough, both laboratories which used a dry extraction technique to measure the CH$_4$ during the intercalibration study also produced CH$_4$ values which were 15±1 ppb higher than those laboratories utilizing wet extraction techniques [Sowers et al., 1997]. We can think of two possible explanations for the elevated CH$_4$ results associated with our dry extraction technique. One explanation involves a blank value which varies over time. While it is difficult to completely rule out this possibility, we performed blank determinations and measurements of intercalibration ice over the same period to minimize any uncertainty associated with a time dependent drift in the blank. We have not observed a measurable drift in our blank values over the last year. There is, however, a slight chance that the actual CH$_4$ blank during the period when we
measured the intercalibration ice was slightly higher than the average value we measured throughout the two year period surrounding the intercalibration ice measurements.

Another possible explanation for the elevated dry extraction results may involve differences in the composition of gas extracted from the ice and the composition of the total gas in the ice core. Because dry extraction techniques do not quantitatively liberate all the gas in the ice, it is possible that the liberated gas has an elevated CH\textsubscript{4} concentration with respect to the [CH\textsubscript{4}] of total trapped gas. Given our extraction efficiency is 75% on the intercalibration ice (Table 2) and assuming the real [CH\textsubscript{4}] is 748ppb (from Sowers et al., 1997), we calculate that the [CH\textsubscript{4}] of residual gas left in the extraction cylinder (25%) would have to be 652ppb in order to account for the elevated [CH\textsubscript{4}] measurements associated with our dry extraction technique. At this point we cannot measure the [CH\textsubscript{4}] of gas remaining in the cylinder after an extraction. However, efforts are currently underway to measure the concentration of this air in order to assess the elevated CH\textsubscript{4} results.

In summary, we have measured the methane blank associated with both the wet and dry extraction techniques developed here at Penn State and found them to be consistent with previous estimates from other laboratories employing similar techniques. We have analyzed ice from the GISP II ice core and found our results to be 1.7% and 4.3% higher than previous measurements for the wet and dry techniques respectively. We attribute the difference to: 1) uncertainties in actual CH\textsubscript{4} concentration or our working standard relative to the NOAA CH\textsubscript{4} calibration scale, 2) uncertainties in our day to day CH\textsubscript{4} blanks, and 3) potential differences between the CH\textsubscript{4} concentration in the liberated gas and the total trapped gas. It is likely that the elevated values we measured are related to a combination of these three factors. In order to compare our CH\textsubscript{4} results with previous CH\textsubscript{4} measurements reported on the NOAA/CMDL CH\textsubscript{4} scale, we reduce all our blank corrected CH\textsubscript{4} values from the dry extraction technique by 4.3%.
Overall precision of our dry extraction procedure

We calculate the overall precision of our dry extraction technique by propagating errors from each part of the technique. For the elemental and isotopic composition of $O_2$ and $N_2$, we include uncertainties associated with, 1) zero enrichment on the mass spectrometer, 2) the calibration of our working standard with respect to air, and 3) the simulated blank extractions. A zero enrichment is routinely measured by admitting the same gas to both sides of the mass spectrometer and measuring them relative to one another. Because the gas in both reservoirs is identical, the mass spectrometric analyses should provide delta values which are 0.00‰. In practice, the two sides of the mass spectrometer are not identical causing the measured delta values to deviate from zero. Because all samples are subjected to the same analytical conditions, the measured delta values must all be corrected for the measured zero enrichment. The total uncertainty is calculated by taking the square root of the sum of the squares of each of the three uncertainties (calculated as the standard deviation of each set of measurements). For the $\delta^{18}O_{/N_2}$, $\delta^{18}O$ of $O_2$, and $\delta^{15}N$ of $N_2$ the resulting procedural uncertainties are $\pm 2.1‰$, $\pm 0.074‰$, and $\pm 0.045‰$ respectively (Table 1). For our CH$_4$ analyses, the overall uncertainty is calculated based on the standard deviation about the mean of all simulated blank transfers ($\pm 18$ ppb) and the uncertainty in the absolute concentration of our working standard (C#5) ($\pm 6$ ppb). Taking the square root of the sum of the squares of these two sources of uncertainty, we calculate an overall precision for our CH$_4$ measurements of $\pm 19$ ppb.

Comparing extraction procedures on ice covering the past 25,000 years

Another way of checking the integrity of our new extraction technique is to compare results with previous measurements all along a deep ice core. This is especially important for analyses of clathrated ice and air from the last glacial period, where the atmospheric composition differed most dramatically from recent air located just below the firn/ice transition region. We measured 56 samples from the GISP II ice core using our dry extraction technique. Samples were chosen between 116 and 2031 mbs with corresponding
gas ages of 0.13 and 25.4 ka. Results are plotted in Figure 2 along with previous results (employing wet extraction techniques) from Bender et al., 1994, 1995 and Brook et al., 1996. In each of the next four sections which we compare our results using the dry extraction procedure with these previous results.

δ¹⁵N data

In the top panel of Figure 2, δ¹⁵N of trapped N₂ data for the GISP II core from Bender et al., 1994 are plotted as discrete points along with our results (line between points). For the uppermost portion of the core (Z< 1,000m) our δ¹⁵N data are indistinguishable from the wet extraction results (mean value of 0.30‰ compared to 0.29‰ for the wet and dry extraction results respectively). Between 1,000 and 1,500m, bubbles in both the GISP II and GRIP ice cores are slowly transformed into air hydrates due to increasing hydrostatic pressure [Gow et al., 1997; Pauer et al., 1999]. We have denoted this region with a shaded area in Figure 2. Within this bubble/hydrate transition region, δ¹⁵N data from our dry extraction technique are 0.03‰ higher on average than the δ¹⁵N data from Bender et al., 1994. This difference is smaller than our overall precision for δ¹⁵N measurements (0.045‰) indicating we cannot deduce a statistically significant difference between the two techniques without additional dry extraction data. Below 1500m, we note a strong degree of covariance between the two δ¹⁵N data sets. Of particular significance are the two regions which exhibit high δ¹⁵N values in response to the thermally induced fractionation of firn air associated with the abrupt warming episodes at 11.7 and 14.8ka [Severinghaus et al., 1998]. In both cases, the δ¹⁵N data from our dry extraction technique fall within 0.03‰ of the δ¹⁵N data from Bender et al., 1994 and Severinghaus et al., 1998.

δ¹⁷/¹⁵N₂ data

Measurements of the δ¹⁷/¹⁵N₂ ratio of trapped air in ice cores provide fundamental information about numerous processes which impact the elemental and isotopic composition of trapped gases in ice. Before we discuss the δ¹⁷/¹⁵N₂ data, we recall that the atmospheric δ¹⁷/¹⁵N₂ ratio has remained within 2‰ of the present day value for the last 100 kyr
Thus, any $\delta^{18}O_2/N_2$ data which fall outside the $0 \pm 2\%$ envelope are likely to be the result of one or more of the following processes: 1) fractionation during the trapping of air in the firm ice transition region, 2) fractionation during diffusion of $O_2$ and $N_2$ within the ice sheet especially near the clathrate formation region, or 3) fractionation during post coring loss of trapped gases from the core as it undergoes volume relaxation.

$\delta^{18}O_2/N_2$ data from the GISP II ice core are plotted in an analogous fashion as the $\delta^{15}N$ data in Figure 2. Data from the upper 1,000m of core were similar for the two extraction procedures (wet vs. dry). However, within the clathrate formation region (1,000 to 1,500m) the $\delta^{18}O_2/N_2$ data from the wet extraction procedure was generally much higher than data obtained using a dry extraction procedure. We attribute the elevated wet extraction $\delta^{18}O_2/N_2$ data to preferential inclusion of $O_2$ in clathrates during clathrate formation and subsequent loss of bubble $N_2$ through microfractures in the ice [Bender et al., 1995].

The lower $\delta^{18}O_2/N_2$ values between 1,000m and 1,500m (5-9ka) obtained with the dry extraction technique are probably related to the preferential liberation of bubble air relative to clathrated air. Spectroscopic studies of the $O_2/N_2$ ratio of air clathrates and bubbles in the Vostok ice cores show progressively lower $O_2/N_2$ ratios for the bubble air with a corresponding enrichment of $O_2$ in the clathrates as one progresses down through the bubble/clathrate transition region [Ikeda et al., 1999]. Assuming that clathrates are more stable than bubbles in the clathrate formation region, post-core microfracture formation associated with volume relaxation is liable to be concentrated around bubbles thereby allowing more bubble air to escape relative to the clathrated air. Because the bubble air has a low $O_2/N_2$ ratio relative to clathrate air in the clathrate formation region, the net effect of gas loss from this portion of the core would be an increase in the $O_2/N_2$ ratio of the total occluded air in the core. This explanation is consistent with the elevated $\delta^{18}O_2/N_2$ data obtained using the wet extraction technique [Bender et al., 1995].

Our extraction efficiency (dry extraction procedure) in bubbly ice is about 21% greater than clathrated ice (Table 2) indicating air in bubbles is easier to liberate than
clathrated air with our technique. Thus, when processing samples with bubbles and clathrates, the liberated air will have slightly more bubble air (~21%) with respect to the clathrated air. Because the $O_2/N_2$ ratio of the bubbles is lower than the clathrates [Ikeda et al, 1999], the liberated air (via dry extraction) will tend to have lower $\delta^{18}O_2/N_2$ values compared with the total trapped air in the core (as measured by the wet extraction technique). We can quantify the net effect of these variables on the $O_2/N_2$ ratio of liberated air ($\left(\frac{O_2}{N_2}\right)_{lib}$) from our dry extraction using the following equation:

$$\left(\frac{O_2}{N_2}\right)_{lib} = \frac{\beta_{\text{clathrate}} \left( \Gamma_{\text{clathrate}} \times \left(\frac{O_2}{N_2}\right)_{\text{clathrate}} \right) + \beta_{\text{bubbles}} \left(1 - \Gamma_{\text{clathrate}}\right) \left(\frac{O_2}{N_2}\right)_{\text{bubbles}}}{\beta_{\text{clathrate}} (\Gamma_{\text{clathrate}}) + \beta_{\text{bubbles}} (1 - \Gamma_{\text{clathrate}})}$$

(1)

Where:

$\left(\frac{O_2}{N_2}\right)_{\text{clathrate}}$ = the $O_2/N_2$ ratio in the clathrates

$\left(\frac{O_2}{N_2}\right)_{\text{bubbles}}$ = the $O_2/N_2$ ratio in the bubbles

$\beta_{\text{clathrate}}$ = the extraction efficiency for clathrated ice (54%)

$\beta_{\text{bubbles}}$ = the extraction efficiency for bubbly ice (75%)

$\Gamma_{\text{clathrate}}$ = % of total trapped air in clathrate form

The $O_2/N_2$ ratio of bubbles and clathrates were measured in clathrate formation region of the Vostok core by Ikeda et al, 1999. They showed that the $O_2/N_2$ ratio of air in bubbles above the bubble/clathrate transition region was similar to air (0.27). Measurements within the transition interval showed a progressive decline in the $O_2/N_2$ ratio in the bubbles with a minimum value (0.085) measured near the base of the bubble/clathrate transition region. $O_2/N_2$ measurements on the clathrates showed a similar trend with elevated values near the top of the transition region (~0.56) decreasing to atmospheric levels near the bottom of the transition region. $O_2/N_2$ measurements on clathrates below the bottom of the clathrate formation region were very close to atmospheric values. Assuming similar $O_2/N_2$...
characteristics apply to clathrate formation in the GISP II core, we calculated the $\delta^{18}O/\delta^{15}N_2$ values of gas liberated with our dry extraction technique as a function of the % of total gas in clathrate form ($\Gamma_{(\text{clathrate})}$) in Figure 3. As shown, the maximum deviation (-185‰) in the $\delta^{18}O/\delta^{15}N_2$ value of liberated gas occurs when 50% of the trapped air has been converted to clathrates. Therefore, if the $O_2/N_2$ ratio of trapped air in the GISP II ice core had not been altered by gas loss through microfractures during post-core relaxation, we predict our measured $\delta^{18}O/\delta^{15}N_2$ values would have been close to $-185‰$ near the middle of the transition zone. Assuming the positive $\delta^{18}O/\delta^{15}N_2$ values between 1,000 and 1,500 mbs measured by Bender et al., 1995 are the result of preferential N$_2$ loss through microfractures, then the corresponding $\delta^{18}O/\delta^{15}N_2$ values obtained with the dry extraction procedure should be between 0 and 185‰ lower than the Bender et al. 1995 $\delta^{18}O/\delta^{15}N_2$ data depending on the fraction of air in bubbles. Our $\delta^{18}O/\delta^{15}N_2$ data are 40-100‰ lower than the Bender et al., 1995 data though the scatter in both data sets is large. The net result implies that measurements of the $\delta^{18}O/\delta^{15}N_2$ of air extracted from ice containing both clathrates and air bubbles via our dry extraction technique are not representative of the $\delta^{18}O/\delta^{15}N_2$ of the air in the sample.

Below the clathrate formation region $\delta^{18}O/\delta^{15}N_2$ values for the dry extraction technique gradually increase while $\delta^{18}O/\delta^{15}N_2$ data from the wet extraction technique remain stable at $\sim10‰$. We speculate that this trend may involve the preferential liberation of clathrates formed near the top of the bubble/clathrate transition region which have high $O_2/N_2$ ratios relative to the total trapped air. At this point, we do not have an explanation as to why these clathrates might be preferentially liberated relative to clathrates formed deeper in the transition region.

$\delta^{18}O_{\text{atm}}$ data

The $^{18}O/^{16}O$ ratio of atmospheric O$_2$ ($\delta^{18}O_{\text{atm}}$) has been shown to vary by $\sim1.4‰$ over glacial/interglacial timescales in response to changes in the isotopic composition of O$_2$ introduced and removed from the atmosphere [Sowers et al., 1993]. $\delta^{18}O_{\text{atm}}$ is calculated using the following equation:
\[ \delta^{18}O_{\text{atm}} = \delta^{18}O_{\text{measured}} - 2\delta^{15}N_{\text{measured}} \]  

Where \( \delta^{18}O_{\text{measured}} \) and \( \delta^{15}N_{\text{measured}} \) are the \( \delta^{18}O \) of \( O_2 \), and \( \delta^{15}N \) of \( N_2 \) measured on each sample. As illustrated in Figure 2c, there is a very close agreement between our results employing a dry extraction and previous results that are based on a wet extraction procedure (Bender et al., 1994). There is however, one region of the record where the two sets of results disagree. Within the bubble/clathrate transition region (between 5 and 9ka) our \( \delta^{18}O_{\text{atm}} \) data are 0.2 – 0.3‰ lower than the Bender et al., 1994 data. Part of the reason for these low values stems from the elevated \( \delta^{15}N \) data in this region discussed earlier. However, the largest discrepancy between our data and the Bender et al., (1994) data occurs at 8.7ka where the \( \delta^{15}N \) values agree with one another. A speculative explanation for this trend involves a small isotope effect associated with the formation of \( O_2 \) clathrates where the \( ^{18}O \) isotope tends to form clathrates slightly faster than the \( ^{16}O \) isotope. The end result is a decrease in the \( ^{18}O/^{16}O \) ratio in the bubbles as one progresses down through the clathrate region. As our extraction technique favors bubble air, the net result of this isotope discrimination is to progressively reduce the \( \delta^{18}O_{\text{atm}} \) measurements until all the air has been converted into clathrates. Below the clathrate formation zone, \( \delta^{18}O_{\text{atm}} \) data from our extractions agree with the Bender et al., 1994 data within 0.1‰.

**Methane (CH\(_4\)) data**

Methane data from this study and the Brook et al., (1996) study are plotted in the lower portion of Figure 2. The blank corrected data from our (Penn State) dry extraction procedure have been reduced by 4.3% to account for the difference between our results and those from the intercalibration study discussed earlier. The two curves are effectively indistinguishable from one another throughout the whole 25 kyr record. Even within the clathrate formation region, the two data sets agree with one another with the exception of a single wet extraction data point at 8.2ka which was ~50ppb lower than samples from either side of it. This extremely low CH\(_4\) data point was not observed in the GRIP record, which is of similar resolution, suggesting the Brook et al., (1996) value may be suspect.
Overall, the degree to which our CH$_4$ record covaries with the CH$_4$ record from the Brook et al., 1996 study reinforces our previous conclusion that we must reduce our blank corrected CH$_4$ data by 4.3% in order to compare our data with other records which are also presented on the NOAA/CMDL CH$_4$ scale. If one considers the ±19 ppb uncertainty in the dry extraction CH$_4$ data, only 7 out of the 56 data using our dry extraction technique (Figure 2) fall more than one standard deviation away from the contemporaneous CH$_4$ value inferred from the Brook et al., (1996) data. However, due to the relatively coarse resolution of the two data sets during the last glacial period, it is not possible to directly compare the two records because of potential complications arising from rapid changes (<500 years) in atmospheric CH$_4$ which are not resolved in both records.

Conclusions

We have developed a new dry extraction technique to extract air from large pieces of glacial ice. The primary reason for developing this technique was to be able to perform a single extraction and measure a single sample of fossil air for as many atmospheric constituents as possible. This technique has three main advantages. First we can directly compare compositional variations on each sample to deduce rapid changes in the paleoatmospheric composition. A prime example of this can be seen by comparing the $\delta^{15}$N and CH$_4$ records at 11.8 and 14.8 ka in Figure 2. Here, the abrupt increase in the $\delta^{15}$N values associated with thermal fractionation of the firn air during periods of abrupt warming coincide with abrupt CH$_4$ increases which have previously been shown to lag the temperature signal by less than 30 years (Severinghaus et al., 1998). Subsequent analyses within these intervals utilizing our extraction technique may help to refine the temporal relationship between warming events over Greenland and increases in atmospheric CH$_4$. Secondly, we can now correct each sample for gravitational fractionation which previously had to be done by interpolating the $\delta^{15}$N record. Thirdly, we only have to extract fossil air from a single piece of ice to obtain data on multiple atmospheric components.
We have performed numerous tests to determine the integrity of our new extraction procedure. We estimate our overall external precision for $\delta^{18}O_{/N_2}$, $\delta^{18}O$ of $O_2$, and $\delta^{15}N$ of $N_2$ analyses as $\pm 2.1‰$, $\pm 0.074‰$, and $\pm 0.045‰$ respectively. We have determined the CH$_4$ blank value as 16±18ppb. We have also analyzed CH$_4$ in ice which is adjacent to ice used in a recent intercalibration experiment for comparison. Our CH$_4$ results were 4.3% higher than the average value measured by five other laboratories. We attribute our elevated values to uncertainties in the actual concentration of our working standard and small differences in the CH$_4$ concentration of the liberated air relative to the total air trapped in the ice. We estimate our overall uncertainty for the CH$_4$ measurements as ±19 ppb.

We have compared our new results from the upper 2,400m of the GISP II core with previous measurements. With the exception of the $\delta^{18}O_{/N_2}$ data and some isotope measurements within the clathrate formation region, our data were indistinguishable from previous measurements. Within the clathrate formation region, we observed $\delta^{18}O_{/N_2}$ values which were ~100‰ lower than the corresponding results obtained with a wet extraction procedure. We attribute these results to variable $O_2/N_2$ ratios within the bubbles and clathrates in this region in conjunction with preferential gas loss from bubbles through microfractures and slight differences in our extraction efficiency for bubbly vs. clathrated ice. Below this region, our $\delta^{18}O_{/N_2}$ values gradually increased to ~+30‰. At present we have no explanation for this trend.

In conclusion, we have demonstrated that our new extraction procedure provides a reliable means of extracting gases from ice cores. Data on the isotopic composition of $O_2$ and $N_2$ as well and the CH$_4$ concentration are consistent with previous measurements above or below the clathrate formation region. Our results highlight the need for careful consideration of occluded gas analyses within the clathrate formation region as the composition can be influenced by a number of factors.
Acknowledgments: This research was supported by two grants from the national science foundation (OPP-9526556 and ATM 9618067). Special thanks to Amy Rodebaugh who oversaw the mass spectrometry.

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Figure 1. Schematic diagram of the extraction apparatus. A detailed drawing of the stainless steel extraction cylinder is presented in (A). The complete apparatus is shown in the bottom portion of figure with the cylinder and cradle assembly located within the chest freezer. The cradle is attached to the vacuum manifold with a reinforced piece of flexible metal hose so liberated air can be immediately transferred to the sample tube during the extraction.

Figure 2. Results of the elemental and isotopic composition of O\textsubscript{2}, N\textsubscript{2} and CH\textsubscript{4} from the GISP II ice core. For each panel, results from wet extractions are plotted with individual markers while the results obtained with a dry extraction (at Penn State) are plotted with lines connecting open markers. a) δ\textsuperscript{15}N of N\textsubscript{2} results from Bender et al., 1994 (wet extraction) are plotted as dark purple triangles (no line). δ\textsuperscript{15}N of N\textsubscript{2} results from our dry extraction procedure are shown with lines connecting open triangles. b) δO\textsubscript{2}/N\textsubscript{2} data plotted in the same fashion as the δ\textsuperscript{15}N data with asterisks. Note the large difference between the two data sets in the clathrate formation region (1,000-1,500m). c) δ\textsuperscript{18}O\textsubscript{atm} data plotted in the same format as a and b using open and closed circles. Note reversed scale on δ\textsuperscript{18}O\textsubscript{atm} axis. d) CH\textsubscript{4} measurements from Brook et al., 1996 (wet extraction) with a dashed line between crosses along with our dry extraction data as a solid line between dotted circles. New CH\textsubscript{4} data have been corrected for the 4.3% offset as discussed in text.

Figure 3. Calculated δO\textsubscript{2}/N\textsubscript{2} ratios of liberated air from the clathrate formation region employing our dry extraction procedure as described by equation 1. The δO\textsubscript{2}/N\textsubscript{2} data are presented relative to the original total trapped air assuming no alteration via gas loss through microfractures. Maximum deviation occurs when the 50% of the original trapped air has been converted to clathrates.
Table 1. Results of analyses to verify the integrity of the wet and dry extraction procedures.

<table>
<thead>
<tr>
<th>Description of test</th>
<th>#Analyses</th>
<th>$\delta^{18}$O of O$_2$ (‰ wrt air)</th>
<th>$\delta^{15}$N of N$_2$ (‰ wrt air)</th>
<th>Methane Cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero Enrichments</td>
<td>38</td>
<td>-0.029±0.061</td>
<td>+0.015±0.035</td>
<td></td>
</tr>
<tr>
<td>Simulated Dry Extractions</td>
<td>3</td>
<td>-0.045±0.20</td>
<td>-0.033±0.041</td>
<td>11</td>
</tr>
<tr>
<td>Simulated Wet Extractions</td>
<td>3</td>
<td>-2.9±0.56</td>
<td>+0.017±0.045</td>
<td>8</td>
</tr>
<tr>
<td>Calibration of AS#2 to air</td>
<td>9</td>
<td>-1.51±2.1</td>
<td>-0.06±0.05</td>
<td>N/A</td>
</tr>
<tr>
<td>Overall analytical precision for the dry extraction procedure$^c$</td>
<td></td>
<td>±2.1</td>
<td>±0.074</td>
<td>±0.045</td>
</tr>
</tbody>
</table>

**Analyses of GISP II ice from 117-123 mbs**

| Wet extraction                           | 5         | -6.2 ± 2.1                           | 0.52 ± 0.07                         | 6          |
| Dry extraction                            | 10        | 2.1 ± 1.7                            | 0.55 ± 0.03                         | 14         |

**Analyses of GISP II ice from 135-140 mbs**

| Wet extraction                           | 5         | -7.9 ± 5.0                           | 0.57 ± 0.04                         | 15         |
| Dry extraction                            | 6         | 4.1 ± 2.1                            | 0.60 ± 0.04                         | 7          |

---

$^a$ The values reported are the average values of all analyses. Uncertainties are ± one sigma.

$^b$ Results for the CH$_4$ blank are average values for the two cylinders which are used to extract gases.

$^c$ The overall analytical precision for the dry extraction technique was estimated by calculating the square root of the sum of the squares of the uncertainties in the zero enrichments, the simulated extractions and the calibration of AS#2 to air. The overall uncertainty for the CH$_4$ analyses was calculated by taking the square root of the sum of the uncertainty in the simulated dry extractions (±18 ppb) and the uncertainty in the calibration of the working standard (C#5, ±6 ppb).
Table 2: Extraction efficiency for samples of GISP II ice processed with a dry extraction procedure.

<table>
<thead>
<tr>
<th>Sample Depth (mbs)</th>
<th>Weight (kg)</th>
<th>Content (x10^{-6} m^3/kg) (^a)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.8</td>
<td>0.3547</td>
<td>8.7</td>
<td>84</td>
</tr>
<tr>
<td>523.2</td>
<td>0.3571</td>
<td>9.0</td>
<td>85</td>
</tr>
<tr>
<td>950.4</td>
<td>0.3847</td>
<td>8.9</td>
<td>88</td>
</tr>
<tr>
<td>1279.6</td>
<td>0.3067</td>
<td>8.8</td>
<td>84</td>
</tr>
<tr>
<td>1557.2</td>
<td>0.3625</td>
<td>8.4</td>
<td>77</td>
</tr>
<tr>
<td>2016.1</td>
<td>0.3366</td>
<td>9.3</td>
<td>69</td>
</tr>
<tr>
<td>2045.0</td>
<td>0.3488</td>
<td>9.3</td>
<td>72</td>
</tr>
<tr>
<td>2271.2</td>
<td>0.3545</td>
<td>9.0</td>
<td>68</td>
</tr>
<tr>
<td>2437.0</td>
<td>0.3385</td>
<td>9.0</td>
<td>72</td>
</tr>
</tbody>
</table>

\(^a\) Total gas content data are from Raynaud et al., 1997. Gas content measurements were made on the GRIP ice core. Estimated gas content for the GISP II samples were obtained by assuming gas content vs. depth relation was the same for the two cores.
Figure 1
GISP II Isotope and CH$_4$ Results

GISP II Depth (mbs)

- a) $\delta^{15}$N
- b) $\delta^{18}$O$_2$/N$_2$
- c) $\delta^{18}$O$_{atm}$
- d) CH$_4$ (Brook et al., 1996)

Clathrate Formation Region

Figure 2
Figure 3

\( \delta^{18}O_2/N_2 \) (permil) vs. % of total air as clathrates.