

## An interlaboratory comparison of techniques for extracting and analyzing trapped gases in ice cores

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**Abstract.** We undertook an interlaboratory comparison of techniques used to extract and analyze trapped gases in ice cores. The intercomparison included analyses of standard reference gases and samples of ice from the Greenland Ice Sheet Project 2 (GISP2) site. Concentrations of CO<sub>2</sub>, CH<sub>4</sub>, the δ<sup>18</sup>O of O<sub>2</sub>, the δ<sup>15</sup>N of N<sub>2</sub>, and the O<sub>2</sub>/N<sub>2</sub>, and Ar/N<sub>2</sub> ratios were measured in air standards and ice core samples. The standard reference scales for CO<sub>2</sub> and CH<sub>4</sub> were consistent at the ±2% level. The δ<sup>18</sup>O of O<sub>2</sub> and δ<sup>15</sup>N of N<sub>2</sub> measurements showed substantial deviations between the two laboratories able to measure these ratios. The deviations are probably related to errors associated with calibration of the working standards. The δ<sup>Ar</sup>/N<sub>2</sub> and δ<sup>15</sup>N of N<sub>2</sub> measurements were consistent. Five laboratories analyzed the CH<sub>4</sub> concentration in a 4.2-m section of the GISP2 ice core. The average of 20 discrete CH<sub>4</sub> measurements was 748±10 parts per billion by volume (ppbv). The standard deviation of these measurements was close to the total analytical uncertainty associated with the measurements. In all cases, those laboratories employing a dry extraction technique determined higher CH<sub>4</sub> values than laboratories using a wet extraction technique. The origin of this difference is unclear but may involve uncertainties associated with blank corrections. Analyses of the CO<sub>2</sub> concentration of trapped gases showed extreme variations which cannot be explained by analytical uncertainties alone. Three laboratories measured the [CO<sub>2</sub>] on 21 discrete depths yielding an average value of 283±13 parts per million by volume (ppmv). In this case, the standard deviation was roughly a factor of 2 greater than the analytical uncertainties. We believe the variability in the measured [CO<sub>2</sub>] results from impurities in the ice which may have compromised the [CO<sub>2</sub>] of trapped gases in Greenland ice.

### Introduction

The first studies of the composition of trapped gases in polar ice were performed in the 1950s [Scholander *et al.*, 1956]. Since that time, numerous studies have focused on reconstructing the composition of the atmosphere from polar ice cores (see Raynaud *et al.*, 1993 for a recent review of the greenhouse gas records). Results of these studies suggest that atmospheric CO<sub>2</sub> and CH<sub>4</sub> levels were substantially lower

during glacial periods than during interglacial periods [Neftel *et al.*, 1985; Stauffer *et al.*, 1985; Barnola *et al.*, 1987; Neftel *et al.*, 1988; Stauffer *et al.*, 1988; Barnola *et al.*, 1991; Blunier *et al.*, 1993; Chappellaz *et al.*, 1993; Chappellaz *et al.*, 1993; Anklin *et al.*, 1995; Barnola *et al.*, 1995; Blunier *et al.*, 1995]. Such results have led to a number of biogeochemical studies designed to understand the nature of the concentration variations and their climatic significance. Given the importance of these records, we believe it is important to continually strive to increase the integrity of the paleoatmospheric records derived from data on the trapped gases in ice cores.

There are a number of factors to consider when reconstructing the composition of the paleoatmosphere from trapped gases in ice cores. After a core has been retrieved from the field and transported to the laboratory, the fossil air must be separated from the ice matrix for analysis. The composition of the air must be determined relative to a standard that has previously been calibrated on an acceptable concentration scale. The measured composition must be corrected for the effect of air enclosure in order to determine the composition of the atmosphere at the time the gases were occluded in the firn-ice region of the glacier. These corrections include gravitational and isotopic fractionation resulting from the diffusion of air in the firn layer above the

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**Table 1.** Listing of Laboratory Techniques Used to Extract Gases From Ice Cores, the Analytical Instrumentation Applied to the Extracted Fossil Air Samples, the Resulting Procedural Blank, and the External Precision

	Elemental Analyses			Isotopic Analyses
	CO <sub>2</sub>	CH <sub>4</sub>	$\delta\text{Ar}/\text{N}_2$ $\delta\text{O}_2/\text{N}_2$	$\delta^{15}\text{N}$ of N <sub>2</sub> $\delta^{18}\text{O}$ of O <sub>2</sub>
		<i>CSIRO</i>		
Method	cheese grater <sup>a</sup> + GC (as CH <sub>4</sub> )	cheese grater + GC	N/A	N/A
Blank	0.8 ppm <sup>b</sup>	5 ppb <sup>c</sup>		
External precision <sup>d</sup>	±1.2 ppm	±5 ppb		
Size of ice sample	0.5-1.5 kg	0.5-1.5 kg		
		<i>Bern</i>		
Method	N/A	small mill device <sup>c</sup> + GC	milling device <sup>f</sup> mass spectrometry	milling device mass spectrometry
Blank		19±4 ppb <sup>g</sup>	blank <1‰	blank <0.1‰
External precision <sup>d</sup>		±10 ppb	$\delta\text{Ar}/\text{N}_2$ ±0.3‰	$\delta^{15}\text{N}$ ±0.05‰
Size of ice sample		12-20 g	$\delta\text{O}_2/\text{N}_2$ ±0.1‰	$\delta^{18}\text{O}$ ±0.08‰
		<i>LGGE</i>		
Method	small crusher +GC (CO <sub>2</sub> )	wet extraction + GC	N/A	N/A
Blank	< 1 ppm	20±6 ppb <sup>g</sup>		
External precision <sup>d</sup>	±3 ppm	±10 ppb <sup>g</sup>		
Size of ice sample	40 g	50 g		
		<i>SIO</i>		
Method	microcrusher <sup>h</sup> + IR	wet extraction + GC	N/A	N/A
Blank	negligible	negligible		
External precision <sup>d</sup>	±3 ppm	±20 ppb		
Size of ice sample	4 g	100 g		
		<i>URI</i>		
Method	N/A	wet extraction + GC	wet extraction mass spectrometry	wet extraction mass spectrometry
Blank		15±6 ppb	Blank <1‰ <sup>i</sup>	Blank <0.03‰ <sup>i</sup>
External precision <sup>d</sup>		±15 ppb	±1‰	±0.03‰
Size of ice sample		35±3 g	10 g	10 g

GC is gas chromatography.

<sup>a</sup> [Etheridge *et al.*, 1988].

<sup>b</sup> [Etheridge *et al.*, 1996].

<sup>c</sup> [Etheridge *et al.*, 1992; Pearman *et al.*, 1986].

<sup>d</sup> External precision is defined as the total uncertainty associated with the extraction and analytical procedure. In general, external precision is determined by introducing aliquots of working standard into an extraction vessel with degassed ice and then processing the standard/ice mixture as if it were a sample and recorded as ± 1 sigma. Abbreviations for the various laboratories are CSIRO, CSIRO Division of Atmospheric Research; Bern, Physics Institute, University of Bern; LGGE, CNRS Laboratoire de Glaciologie et Geophysique de l'Environnement; SIO, Scripps Institute of Oceanography; URI, University of Rhode Island.

<sup>e</sup> [Fuchs *et al.*, 1993].

<sup>f</sup> [Moor and Stauffer, 1984].

<sup>g</sup> Chappellaz *et al.* (manuscript in preparation, 1997).

<sup>h</sup> The microcrusher device involves a small extraction vessel fitted with a bed of tapered rods which lightly crush the ice samples, thereby avoiding pressure melting at the surface [Wahlen *et al.*, 1991].

<sup>i</sup> [Sowers *et al.*, 1989].

bubble close-off region [Craig *et al.*, 1988; Schwander 1989; Sowers *et al.*, 1989], and any in situ chemical reactions. Finally, although not discussed here, the age of the air in the ice must be determined [Schwander and Stauffer 1984; Schwander *et al.*, 1988].

We undertook an intercalibration study among five laboratories currently analyzing trapped gases in ice cores (Table 1). The study consisted of two separate components. The first part was the analysis of reference air samples by each laboratory in order to compare their working standards. The second part of the study included analyses of ice from a

4.2-m section of the GISP2 "F" ice core which was drilled in July 1991. The species that were measured in this study were CO<sub>2</sub>, CH<sub>4</sub>, the <sup>18</sup>O/<sup>16</sup>O ratio of trapped O<sub>2</sub>, the <sup>15</sup>N/<sup>14</sup>N ratio of trapped N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, and Ar/N<sub>2</sub>. Each laboratory analyzed the occluded air in ice samples relative to their working standard. Analytical capabilities, blanks, and the external precision associated with each extraction procedure (defined below Table 1) are listed in Table 1. One specific objective of this intercalibration study was to investigate the apparent disagreement between the average glacial CH<sub>4</sub> values measured by different laboratories on the GISP2 and the

**Table 2.** Results of NOAA Analyses of Primary High Pressure Cylinders Used to Fill the 2-L Glass Flasks Which Were Distributed to All Labs for Analyses

Cylinder No.	[CO <sub>2</sub> ], ppmv	[CH <sub>4</sub> ], ppbv
109923	356.1±0.06	1488.2 ± 3
114771	375.4±0.06	1824.4 ± 3
111836		463.5 ± 3

Greenland Ice Core Project (GRIP) ice cores from Summit, Greenland.

## Experimental Techniques

### Calibrating the Working Standards in Each Laboratory

For the first part of the study, samples of reference air were sent to each laboratory for analysis in 2-L glass flasks. Each glass flask was filled from one of three high-pressure cylinders that had been previously calibrated for CO<sub>2</sub> and CH<sub>4</sub> by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory group (NOAA/CMDL) (Table 2). Note that the elemental and isotopic composition of O<sub>2</sub>, Ar, and N<sub>2</sub> were not determined in these cylinders by NOAA. At least one, but generally two, glass flasks (equipped with two Louwers-Hapert™ 0 to 9mm, viton O-ring valves), were filled to 1 atm. at the University of Rhode Island (URI) laboratory and sent to each laboratory where they were analyzed for as many constituents as possible. To insure the integrity of the flask samples, the CH<sub>4</sub> concentration was measured at URI immediately after being filled, as well as after the flasks had been analyzed and returned to the URI laboratory. Results suggest that the CH<sub>4</sub> concentrations in the returned flasks were within 0.5% of those of the parent cylinder. We conclude from these results that the filling and subsequent analyses of the flasks did not compromise the CH<sub>4</sub> composition to a measurable extent. While it may be possible that other constituents (i.e., CO<sub>2</sub>, O<sub>2</sub>, or N<sub>2</sub>) were compromised during the filling and subsequent analyses, our previous experience with these flasks suggests this is rather unlikely.

Analysis of a common air standard by each laboratory was necessary to calibrate working standards for the second part of the study, the ice-core analyses. As part of this comparison, 10 samples from the GISP2 short "F" core (10 cm diameter) were selected between 116.18 and 120.33 m. below surface (mbs). Each sample was carefully inspected to insure there were no visible fractures in the ice that would have compromised the integrity of the trapped air. The age of the occluded air in this interval corresponds to 1817-1832 A.D. [Wahlen *et al.*, 1991; Alley *et al.*, 1993]. Fossil air from this period was chosen for the intercalibration because the CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O content of the atmosphere was fairly stable before, during, and after the study period [Wahlen *et al.*, 1991; Etheridge *et al.*, 1992; Blunier *et al.*, 1993; Etheridge

*et al.*, 1996]. Each ~30-cm piece of ice was split lengthwise, providing two sections of core from the same depth interval. The ice was divided among the laboratories such that two laboratories analyzed samples from the same 30-cm interval.

### Extraction Methods

Three methods have been developed to extract gases from ice: the wet, dry, and the sublimation techniques. The wet technique involves inserting an ice sample into an extraction vessel, evacuating the vessel, and then allowing the ice to melt in vacuo to liberate the trapped gases. This technique has been used to analyze constituents that are relatively insoluble and chemically stable in water (CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, and Ar). During a dry extraction, the trapped gases are liberated without melting the ice. This is accomplished by placing an ice sample into a stainless steel extraction vessel where the ice is mechanically crushed, grated, or milled into very small pieces to release the occluded air parcels. Finally, a sublimation method has been used to separate large quantities of air from ice for gas analyses. This technique employs a glass extraction vessel through which infrared light is applied to heat the ice in vacuo to a temperature just below the melting point. The water vapor and liberated air is cryogenically removed from the sublimation vessel by cold traps [Wilson and Donahue 1989; Wilson and Donahue 1990; Wilson and Long this issue]

One major difference in these techniques is the extraction efficiency. The wet and sublimation extraction techniques liberate all air occluded in the bubbles, as well as any air dissolved in the ice matrix, resulting in extraction efficiencies which are generally higher than 99%. Dry extraction methods do not release air from all trapped bubbles and probably do not liberate any air which may be dissolved in the ice matrix [Wilson and Long, this issue]. Extraction efficiencies for the crushing techniques are generally below 80% [Zimbrunn *et al.*, 1982; Barnola *et al.*, 1983; Neftel *et al.*, 1983]. The details of the extraction protocols used by the laboratories for various gases follow. The descriptions are general and intended to relay the pertinent aspects of the different techniques for comparative purposes. Further details can be found in the cited publications.

**CO<sub>2</sub> analyses.** Of the five laboratories listed in Table 1, four measure the CO<sub>2</sub> concentration of trapped gases on a routine basis. Unfortunately the Bern laboratory (Physics Institute, University of Bern, (Bern)) was unable to participate in the CO<sub>2</sub> intercalibration because they were in the process of rebuilding their extraction device at the time of this study. There are two reasons why a wet extraction technique cannot be used for CO<sub>2</sub> analyses. First, CO<sub>2</sub> is extremely soluble in water, making quantitative extraction via a melt/refreeze technique almost impossible. Second, CO<sub>2</sub> may be produced in an extraction vessel if acidic aerosol species can attack carbonate dust particles. The probability of carbonate dust particles interacting with acidic aerosols is much higher when both species are suspended in a liquid medium.

The Commonwealth Scientific and Industrial Research Organization (CSIRO) employs a "cheese grater" extraction device in which large ice samples (500-1500 g of ice at -80°C) are inserted into a cylinder of perforated stainless steel

(perforations toward the inside of a cylinder suspended inside a vacuum container). The container is then evacuated before loading horizontally into a shaker device which oscillates back and forth, sliding the ice sample along the perforations. The ice-core sample is grated into very fine pieces (snow) which liberate the trapped gases. As soon as the ice has been grated, the air in the container is cryogenically transferred through a water trap ( $-100^{\circ}\text{C}$ ) to a cold finger ( $\sim 18\text{K}$ ). The air sample is warmed before the  $\text{CO}_2$  is separated from other constituents on a packed chromatography column, catalytically converted to  $\text{CH}_4$ , and detected with a flame ionization detector [Etheridge *et al.*, 1996].

The Scripps Institute of Oceanography (SIO) laboratory uses a microcrusher to liberate the gases trapped in small ice samples. The crusher (cooled to  $-60^{\circ}\text{C}$  (213K)) contains a bed of tapered rods to crush the sample lightly to avoid pressure melting during extraction. The released air is rapidly condensed into a minisample tube cooled to  $-243^{\circ}\text{C}$  (30K). Standard air samples are introduced over the crushed ice and analyzed in an identical fashion. After transfer, the trap is warmed to  $-60^{\circ}\text{C}$  (213K) and the gas is mixed into an IR cell with a bellows assembly before the  $\text{CO}_2$  is measured with a diode laser tuned to  $4.3\mu\text{m}$  (R-12) [Wahlen *et al.*, 1991].

At the Centre National de la Recherche Scientifique Laboratoire de Glaciologie et Geophysique de l'Environnement (CNRS LGGE), a  $\sim 40\text{-g}$  ice sample is placed inside a stainless steel container with stainless steel ball bearings. After evacuation, the container is shaken vigorously to crush the ice into a very fine powder. The released gas is then expanded into a sample loop and injected into a gas chromatograph equipped with a thermal conductivity detector [Barnola *et al.*, 1983].

The overall analytical precision of these dry extraction techniques for  $\text{CO}_2$  analyses is generally better than  $\pm 3$  parts per million by volume. Uncertainties derive from difficulties in separating  $\text{CO}_2$  from  $\text{H}_2\text{O}$  during the extraction, and from adsorption of  $\text{CO}_2$  to the walls of the extraction apparatus [Zumbrunn *et al.*, 1982; Barnola *et al.*, 1983; Wahlen *et al.*, 1991]. The overall experimental  $\text{CO}_2$  blank is negligible.

**$\text{CH}_4$  analyses.** All five laboratories measure the  $\text{CH}_4$  concentration of trapped gases in ice. Two laboratories use a dry extraction technique similar to that used for  $\text{CO}_2$  and the other three use a wet extraction technique (Table 1). At LGGE and URI, an ice sample is inserted into an extraction vessel, which is then sealed and evacuated to pressures below 1 mbar (the approximate water vapor pressure over ice at  $-20^{\circ}\text{C}$ ). The vessel is then isolated and the ice melted, thereby liberating the trapped gases into the headspace above the water. Next, the water sample is refrozen from the bottom of the vessel to the top. This process forces the dissolved air into the head space. The ice is then cooled to temperatures between  $-80$  and  $-110^{\circ}\text{C}$  (URI) or  $-50^{\circ}\text{C}$  (LGGE) to reduce the water vapor pressure in the head space.

The SIO procedure begins with the introduction of 100 g of ice into a 200-mL glass vessel sealed with a teflon O-ring before evacuation. The sample is allowed to melt before 50 mL of distilled/degassed water is introduced into the vessel in order to increase the total gas pressure in the headspace. The sample is then refrozen to  $-10^{\circ}\text{C}$  to force the dissolved air into the headspace. All three wet extraction techniques then allow the fossil air in the headspace to expand into a previously evacuated sample loop; the air is then injected into a gas chromatograph where the  $\text{CH}_4$  is detected by a flame ionization detector.

The remaining two laboratories use a dry extraction procedure to liberate the trapped gases. The CSIRO laboratory uses the same aliquot of air from the large crusher for analyses of both  $\text{CH}_4$  and  $\text{CO}_2$ . In Bern, a small milling device is used to shave a 12 to 20g ice sample to liberate the trapped gases. The gases are then trapped in a cryofocusing device (Porapak-Q™ column, cooled to  $-170^{\circ}\text{C}$ ) and analyzed with a gas chromatograph equipped with a flame ionization detector [Blunier *et al.*, 1993; Fuchs *et al.*, 1993].

The experimental precision of the  $\text{CH}_4$  analyses is generally better than 2% of preindustrial atmospheric values (700 ppbv). Part of the uncertainty can be attributed to variables associated with the chromatography. The other source of uncertainty comes from the extraction procedure itself. Those procedures involving a "melt-refreeze" cycle to liberate  $\text{CH}_4$  tend to develop  $\text{CH}_4$  contamination that is proportional to the amount of time the ice sample remains in the liquid state, although the exact nature of this contamination is unclear. Multiple blank determinations at LGGE and URI infer a small and reproducible blank of  $20\pm 6$  ppbv and  $15\pm 6$  ppbv, respectively, indicating that the blank corrections can be made precisely. For those systems utilizing stainless steel bellows valves, a small  $\text{CH}_4$  contamination may result from  $\text{CH}_4$  outgassing from the bellows when the valve is opened or closed. Depending on the configuration and the tendency for  $\text{CH}_4$  to outgas from a specific valve, varying amounts of  $\text{CH}_4$  can be added to the sample [Chappellaz 1990].

**The  $\delta\text{O}_2/\text{N}_2$ ,  $\delta\text{Ar}/\text{N}_2$ ,  $\delta^{18}\text{O}$ , and  $\delta^{15}\text{N}$  analyses.** Both wet and dry extraction procedures were used to separate the trapped gases from the ice for  $\text{O}_2$ , Ar, and  $\text{N}_2$  analyses [Sowers *et al.*, 1989; Leuenberger, 1992]. After the gases are separated from the ice, the fossil air sample is allowed to expand into a sample reservoir on a mass spectrometer. The sample is then analyzed against a reference air standard and the results are reported using the standard delta notation. The elemental and isotopic results are reported as deviations from a standard. The  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$ , and  $\text{Ar}/\text{N}_2$  atmospheric ratios are extremely homogeneous and constant on millennial timescales. Therefore the atmosphere has been used as the primary standard for reporting the elemental and isotopic composition of  $\text{O}_2$ , Ar, and  $\text{N}_2$  in ice.

The  $\text{O}_2/\text{N}_2$  ratio of the atmosphere fluctuates by as much as 0.16‰ on a seasonal basis due to photosynthesis and respiration [Keeling *et al.*, 1996]. In addition, the atmospheric  $\text{O}_2/\text{N}_2$  ratio has been decreasing throughout the last century because of  $\text{O}_2$  consumption associated with fossil fuel combustion and land use changes. The measured  $\delta\text{O}_2/\text{N}_2$  decline is approximately 0.014 ‰/yr, while seasonal fluctuations in mid-high latitudes can be as large as 0.16‰ [Keeling and Shertz 1992]. Therefore, depending on when a working standard was calibrated for  $\text{O}_2/\text{N}_2$ , the resulting  $\delta\text{O}_2/\text{N}_2$  values on fossil air could vary by as much as 0.2‰. However, because the analytical uncertainty associated with the  $\text{O}_2/\text{N}_2$  analyses in this study is greater than 1‰, seasonal or interannual  $\text{O}_2/\text{N}_2$  variations do not measurably affect the results in this study. The  $\text{O}_2/\text{N}_2$  ratio of trapped air in ice is not influenced by seasonal changes in the atmosphere because of mixing via molecular diffusion in the firn above the bubble close-off region.

The overall analytical precision of the elemental and isotopic analyses is generally better than 2‰ and  $\pm 0.04\%$ , respectively. Part of the uncertainty derives from the mass spectrometric analyses ( $\pm 0.8\%$  for the elemental and  $\pm 0.03\%$

**Table 3.** Results of Analyses of 2-L Glass Flasks Which Were Filled From High Pressure Cylinders of Commercial Air and Distributed to All Laboratories

Cylinder ID/Lab	Elemental Analyses <sup>a</sup>				Isotopic Analyses <sup>a</sup>	
	CO <sub>2</sub> ppmv	CH <sub>4</sub> ppbv	δO <sub>2</sub> /N <sub>2</sub> ‰ w.r.t. air	δAr/N <sub>2</sub> ‰ w.r.t. air	δ <sup>18</sup> O of O <sub>2</sub> ‰ w.r.t. air	δ <sup>15</sup> N of N <sub>2</sub> ‰ w.r.t. air
NOAA/CMDL Calib.	375.4	1824.4				
114771/CSIRO	375.5	1825.3				
114771/URI	N/A	N/A	0.1 ± 0.1	0.2 ± 0.15	-0.13 ± 0.02	-0.06 ± 0.02
114771/SIO	375.9±1.7 (2)	1825±9 (5)				
114771/LGGE	376.9±0.8	1858±7				
114771/BERN		1844±5 (14)	-0.16 ± 0.06	0.29 ± 0.4	0.01 ± 0.01	-0.04 ± 0.01
NOAA/CMDL Calib.	356.1	1488.2				
109923/CSIRO	356	1484.5				
109923/URI	N/A	N/A	0.0 ± 0.1	0.35 ± 0.15	-0.09 ± 0.03	-0.02 ± 0.02
109923/SIO	357.5±0.9 (8)	1495±9 (5)				
109923/LGGE	357.3±0.4	1521±3				
109923/BERN	N/A	1502±3 (15)	-0.47 ± 0.14	0.23 ± 0.18	0.02 ± 0.01	-0.03 ± 0.01
NOAA/CMDL Calib.		463.5				
111836/CSIRO		463.8±1 (6)				
111836/SIO		475.5 ± 7 (10)				
111836/LGGE		463.5±2 (11) <sup>b</sup>				
111836/BERN		468.3±9 (8)				
111836/URI		464.6±8 (15) <sup>c</sup>				

<sup>a</sup> The values reported are the average values of all analyses. Uncertainties are ± 1 sigma and the number of analyses are reported in parentheses. Values without parentheses are the average values obtained on a single flask or cylinder.

<sup>b</sup> The two glass flasks with air from the 111836 cylinder (CH<sub>4</sub>~464 ppb) analyzed at LGGE were analyzed using a separate working standard which was previously calibrated to the NOAA scale.

<sup>c</sup> URI used the calibrated standards as their working standards. Analyses of the 114771 and 109923 cylinders are, by definition, equivalent to the NOAA values and therefore are not included in the table. The 111836 cylinder was analyzed against the 114771 and 109923 cylinder before the 111836 cylinder was calibrated at NOAA. The URI results on this cylinder are therefore reported.

Also included are the CO<sub>2</sub> and CH<sub>4</sub> values assigned to each high pressure cylinder by NOAA/CMDL. The δO<sub>2</sub>/N<sub>2</sub>, δAr/N<sub>2</sub>, δ<sup>18</sup>O of O<sub>2</sub>, and δ<sup>15</sup>N of N<sub>2</sub> values are given in permil with respect to (w.r.t.) air.

for the isotopic analyses). The elemental analyses also appear to be influenced by heterogeneities in the trapped gas composition, possibly related to small amounts of gas loss through small fractures in the ice that develop as the core relaxes after recovery from the ice sheet [Craig *et al.*, 1988; Sowers *et al.*, 1989; Bender *et al.*, 1995].

## Intercalibration Results

### Standard gases

The results of the standard gas intercalibration are listed in Table 3. The CO<sub>2</sub> analyses indicate that the concentrations of the working standards in all three laboratories are between 0.0 and 0.38% higher than the NOAA calibrated standards. The difference between the measured CO<sub>2</sub> values on each air flask and the CO<sub>2</sub> values assigned by NOAA/CMDL is negligible after considering the overall analytical uncertainty associated with the measurements themselves. This suggests that the working CO<sub>2</sub> standards in all three laboratories are consistent with one another.

Analyses of the various CH<sub>4</sub> working standards also agreed reasonably well (Table 4). CSIRO measured CH<sub>4</sub>

values which were indistinguishable from the NOAA values. The other three laboratories (LGGE, Bern, and SIO) analyzed CH<sub>4</sub> levels which were 2.0%, 1.0%, and 1.0%, respectively, higher than the NOAA values. Because the URI laboratory uses the two cylinders as their working standards, their results are not reported.

Two laboratories (Bern and URI) were able to analyze the elemental and isotopic composition of O<sub>2</sub>, N<sub>2</sub>, and Ar in the standard gas. The δ<sup>15</sup>N of N<sub>2</sub> results from the two laboratories

**Table 4.** Normalization Factors for Comparing Working Standards From Each Laboratory With the NOAA/CMDL Scale

Laboratory	[CO <sub>2</sub> ], %	[CH <sub>4</sub> ], %
CSIRO	0.00	0.0
SIO	0.38	1.0
LGGE	0.37	2.0
BERN	N/A	1.0

Values reported are the deviations (in percent) with respect to the NOAA/CMDL values given in Table 1. The normalized values in Table 5 are calculated by dividing the measured value by the corresponding normalization factor listed above.

**Table 5.** Results of CO<sub>2</sub> and CH<sub>4</sub> Analyses on GISP 2 Ice Between 116 and 121 Meters Below the Surface (mbs)

Depth,mbs/ lab ID	Normalized to NOAA/CMDL		Uncorrected	
	[CO <sub>2</sub> ], ppmv	[CH <sub>4</sub> ], ppbv	[CO <sub>2</sub> ], ppmv	[CH <sub>4</sub> ], ppbv
116.30-116.35/ URI		739(1)		739(1)
116.63-116.9/ CSIRO	289.6(1)	770.6(1)	289.6(1)	770.6(1)
116.7-116.75/ URI		737 ± 6(2)		737 ± 6(2)
117.02-117.04/ SIO	290.5 ± 11(3)		291.6 ± 11(3)	
117.09-117.11/ SIO	303.6 ± 11(3)		304.7 ± 11(3)	
117.115-117.135/ SIO	292.0 ± 22(3)		293.1 ± 22(3)	
117.28-117.33/ SIO		751 ± 15(1)		759 ± 15(1)
117.3-117.33/ URI		753 ± 14(2)		753 ± 14(2)
117.48-117.52/ LGGE		740 ± 11(2)		755 ± 11(2)
117.53-117.57/ LGGE		741 ± 10(1)		756 ± 10(1)
117.6-117.65/ URI		754 ± 10(2)		754 ± 10(2)
118.00-118.33/ CSIRO	291.5(1)	763.4(1)	291.5(1)	763.4(1)
118.3-118.32/ BERN		762 ± 1(3)		769 ± 1(3)
118.407-118.453/ LGGE		734 ± 7(2)		749.5 ± 7(2)
118.42-118.444/ SIO	273.7 ± 15(2)		274.7 ± 15(2)	
118.45-118.48/ SIO	266.6 ± 15(3)		267.6 ± 15(3)	
118.453-118.483/ LGGE	281.8 ± 2(1)		282.8 ± 2(1)	
118.483-118.513/ LGGE	291.5 ± 2(1)		292.6 ± 2(1)	
118.57-118.63/ SIO		745 ± 19(1)		753 ± 19(1)
118.70-119.01/ CSIRO	291.9(1)	758.4(1)	291.9(1)	758.4(1)
118.72-118.74/ SIO	256.1 ± 23(2)		257.1 ± 23(2)	
118.74-118.76/ SIO	249.3 ± 3(3)		250.2 ± 3(3)	
119.045-119.065/ SIO	281.4 ± 2(3)		282.4 ± 2(3)	
119.17-119.23/ SIO		753 ± 20(1)		761 ± 20(1)
119.185-119.205/ SIO	275.2 ± 10(2)		276.2 ± 10(2)	
119.22-119.27/ SIO		747 ± 20(1)		755 ± 20(1)
119.27-119.33/ SIO		745 ± 17(1)		753 ± 17(1)
119.74-119.78/ LGGE		736 ± 7(2)		751 ± 7(2)
119.76-119.80/ LGGE		737 ± 7(2)		752 ± 7(2)
119.80-119.83/ LGGE	289.0 ± 2(1)		290.1 ± 2(1)	
119.83-119.86/ LGGE	288.9 ± 3(1)		290.0 ± 3(1)	
119.86-119.89/ LGGE	289.9 ± 4(1)		291 ± 4(1)	
119.89-119.92/ LGGE	294.4 ± 3(1)		295.5 ± 3(1)	
120.02-120.04/ SIO	279.4 ± 1(2)		280.4 ± 1(2)	
120.04-120.06/ SIO	281.6 ± 10(3)		282.6 ± 10(3)	
120.07-120.09/ SIO	288.6 ± 0.1(2)		289.7 ± 0.1(2)	
120.17-120.23/ SIO		747 ± 15(1)		755 ± 15(1)
120.22-120.27/ SIO		744 ± 21(1)		754 ± 21(1)
Average normalized values	283 ± 13(21)	748 ± 10(20)		

The CO<sub>2</sub> and CH<sub>4</sub> values listed have been corrected for procedural blanks listed in Table 1. Results in the second and third columns have been further corrected by normalizing to the NOAA/CMDL standard scale using the correction factors in Table 4. None of the data have been corrected for gravitational fractionation. The magnitude of the correction is -1.5 ppm and +2.7 ppb for CO<sub>2</sub> and CH<sub>4</sub> respectively, based on an average δ<sup>15</sup>N of N<sub>2</sub> = 0.32‰ (Table 6 and equation (11) from *Sowers et al.*, [1989]). Stated uncertainties are ± 1 sigma.

were identical within the overall analytical uncertainty (Table 3). The δ<sup>18</sup>O results from URI were lower than Bern by 0.13±0.02‰. One possible explanation for this δ<sup>18</sup>O discrepancy involves the presence of substantial amounts of water vapor in some of the glass flasks which were used to transport aliquots of the URI working standards. Adsorption and/or isotopic exchange of water vapor with O<sub>2</sub> may have compromised the isotopic composition of the standard air in the source of the mass spectrometer. The origin and concentration of the water vapor are unclear. The δ<sup>18</sup>O/N<sub>2</sub> and δ<sup>15</sup>N/N<sub>2</sub> data from the two laboratories were consistent, although there does appear to be a slight (0.4‰) discrepancy

in the δ<sup>18</sup>O/N<sub>2</sub> data with the URI values being higher than the Bern values. This latter difference could be due to previously mentioned difficulties in calibrating the δ<sup>18</sup>O/N<sub>2</sub> of the working standard against present-day air.

#### Analyses of the Trapped Gases in the GISP2 Ice Core

CO<sub>2</sub> and CH<sub>4</sub> results on the fossil air extracted from the GISP2 ice core are included in Table 5 and illustrated in Figures 1 and 2, respectively. In addition to the raw data, we have calculated and included the results from each laboratory on the NOAA calibration scale, using the normalization

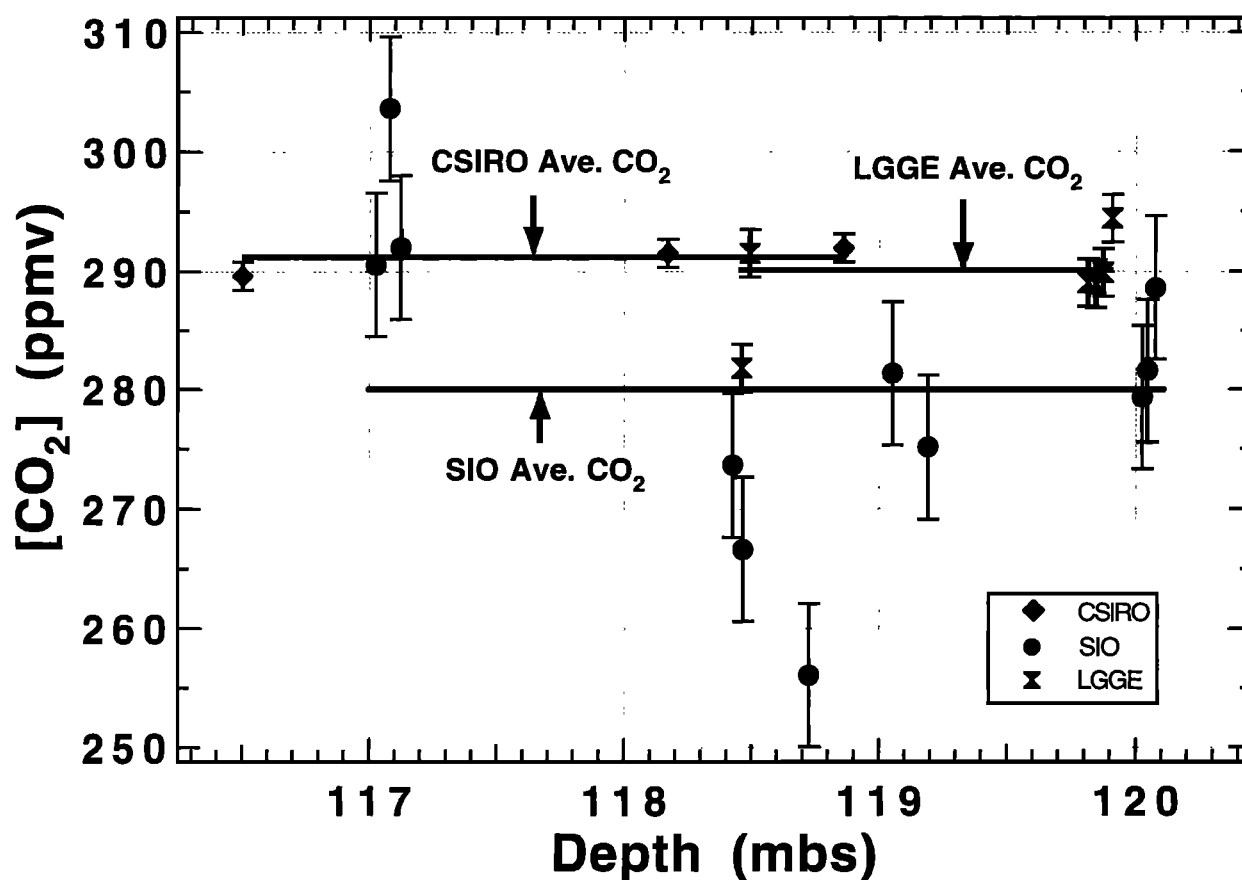


Figure 1. CO<sub>2</sub> results for the intercalibration ice. All data have been corrected for procedural blanks and normalized to the NOAA concentration scale using the normalization factors in Table 4. All data are plotted with  $\pm 1$ -sigma error bars. A horizontal line corresponding to the average value for each laboratory was drawn across the depth interval where the analyses were made.

factors in Table 4. All data in Table 5 have been corrected for blank values in Table 1. In the case of CO<sub>2</sub>, the average concentration was  $283 \pm 13$  ppmv for twenty one discrete depths. Note that the standard deviation about the mean of all 21 analyses ( $\pm 13$  ppmv) is considerably higher than the averaged external reproducibility of CO<sub>2</sub> measured in ice by each laboratory ( $\pm 6$  ppmv). Normalized CO<sub>2</sub> values measured at LGGE ( $N=6$ ) and CSIRO ( $N=3$ ) differed by 1.7 ppmv. The average CO<sub>2</sub> value measured at SIO ( $N=12$ ) was 11 ppmv lower than either LGGE or CSIRO. These results suggest that the CO<sub>2</sub> concentration along the 4.2-m section of intercalibration ice is not homogeneous.

In contrast, the normalized CH<sub>4</sub> results from the intercalibration ice were mostly consistent. The average of 20 discrete samples was  $748 \pm 10$  ppbv. This range of values is comparable to the external precision associated with the CH<sub>4</sub> measurements, suggesting that the CH<sub>4</sub> concentration in all intercalibration ice was constant. In all cases, LGGE provided the lowest average CH<sub>4</sub> value ( $738 \pm 3$  ppbv,  $N=5$ ) (Figure 2). The Bern and CSIRO data (762 and 764 ppbv, respectively) agreed within their uncertainties and were both higher than the SIO and URI data (747 and 746 ppbv, respectively). It is noteworthy that the two laboratories using dry extraction techniques both generated mean CH<sub>4</sub> values that were slightly higher ( $\sim 20$  ppbv) than those laboratories using a wet extraction technique. This difference is larger than the external precision of the measurements and may be

related to differences in the extraction efficiencies and/or errors in blank estimates during the period when the intercalibration ice was analyzed.

Analyses of the isotopic and elemental composition of O<sub>2</sub>, N<sub>2</sub>, and Ar in trapped air from the intercomparison ice were performed at two laboratories, URI and Bern (Table 6). The average  $\delta^{15}\text{N}$  values were  $0.32 \pm 0.01\text{‰}$  and  $0.39 \pm 0.05\text{‰}$  for URI and Bern, respectively. The difference between the mean values determined by the two laboratories ( $0.07\text{‰}$ ) is outside the 95% confidence limits for the two sets of analyses. The average  $\delta^{18}\text{O}$  values from URI were  $0.12\text{‰}$  lower than Bern and slightly larger than the analytical uncertainties of the two laboratories. As the average  $\delta^{18}\text{O}$  values from the two laboratories were approximately twice the  $\delta^{15}\text{N}$  values, the artifact appears to be mass dependent. We suspect that this artifact is related to the sample extraction protocol or analytical procedures in one or both of the laboratories, although the precise origin is not clear. Because the artifact appears to be mass-dependent, the calculated  $^{18}\text{O}/^{16}\text{O}$  ratio of paleoatmospheric O<sub>2</sub> ( $\delta^{18}\text{O}_{\text{atm}} = \delta^{18}\text{O}_{\text{measured}} - 2 * \delta^{15}\text{N}_{\text{measured}}$ ) [Sowers *et al.*, 1989] from the two sets of analyses are in complete agreement ( $\delta^{18}\text{O}_{\text{atm}} = 0.03 \pm 0.01\text{‰}$ ).

The average  $\delta^{18}\text{O}/^{16}\text{O}$  and  $\delta^{40}\text{Ar}/^{39}\text{Ar}$  data from the two laboratories were also consistent with one another as well as with previous measurements on the GISP2 core [Bender *et al.*, 1995]. There is a large amount of scatter in the elemental

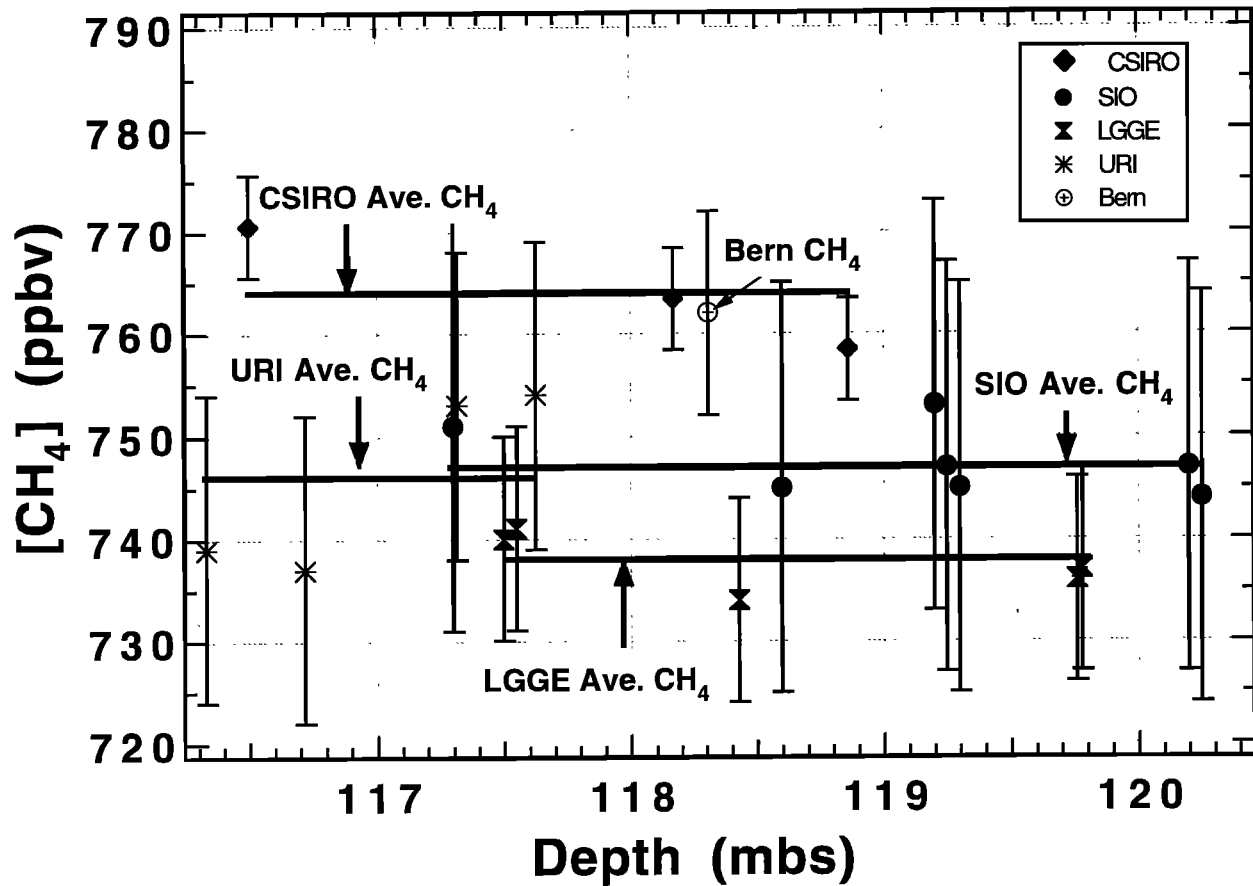


Figure 2,  $\text{CH}_4$  results for the intercalibration ice. All data have been corrected for procedural blanks and normalized to the NOAA concentration scale using the normalization factors in Table 4. All data are plotted with  $\pm 1$ -sigma error bars. A horizontal line corresponding to the average value was drawn across the depth interval where the analyses were made. As there was only one depth measured by the Bern laboratory, no horizontal line is displayed.

data which has previously been attributed to heterogeneities in the bubble composition resulting from differential gas loss through microfractures [Bender *et al.*, 1995].

## Discussion

### Heterogeneous Bubble Composition

One of the greatest uncertainties associated with this type of intercalibration is the degree to which the composition of

the trapped air in the 4.2-m section of GISP2 ice (used for this study) is homogeneous. There are at least three possible causes of heterogeneous gas composition over centimeter spatial scales: (1) neighboring bubbles may be closed off at different depths in the firn-ice transition region, thereby trapping air of slightly different age, (2) compositional alterations may occur along microfractures in the ice whereby occluded air can escape as the ice relaxes,

Table 6. Elemental and Isotopic Composition of  $\text{O}_2$ ,  $\text{N}_2$ , and Ar in the GISP 2 Ice Core

Depth Interval/ lab	Elemental Analyses		Isotopic Analyses	
	$\delta\text{O}_2/\text{N}_2$ , ‰ w.r.t. air	$\delta\text{Ar}/\text{N}_2$ , ‰ w.r.t. air	$\delta^{18}\text{O}$ of $\text{O}_2$ , ‰ w.r.t. air	$\delta^{15}\text{N}$ of $\text{N}_2$ , ‰ w.r.t. air
116.15-116.21/ BERN	-3.8	-2.5	0.75	0.34
116.25-116.27/ URI	-3.5	-9	0.65	0.31
116.80-116.82/ URI	$-5.8 \pm 9$ (2)	$9.5 \pm 0.9$ (2)	$0.66 \pm 0.02$ (2)	$0.32 \pm 0.006$ (2)
117.20-117.22/ URI	$-9.0 \pm 1.7$ (2)	$-9.0 \pm 1.7$ (2)	$0.73 \pm 0.05$ (2)	$0.33 \pm 0.01$ (2)
117.7-117.75/ URI	$-9.1 \pm 5.3$ (2)	$4.2 \pm 5.9$ (2)	$0.68 \pm 0.02$ (2)	$0.33 \pm 0.001$ (2)
119.73-119.83/ BERN	-2.5	-1.3	0.88	0.44
120.01-120.11/ BERN	-1.1	-0.7	0.78	0.39

Depth values are given in meters below surface. All other values are in permil with respect to (w.r.t.) present day air.



and (3) chemical reactions within the ice may alter the trapped gas composition [Sowers *et al.*, 1989; Anklin *et al.*, 1995; Bender *et al.*, 1995]. To address this potential heterogeneity, we split each core section into two equal halves. Each of the half-core sections was then shipped to a different laboratory for analyses so we could obtain two data sets from exactly the same depth interval. With the exception of  $\text{CO}_2$ ,  $\delta^{18}\text{O}/\text{N}_2$ , and  $\delta^{\text{A}}/\text{N}_2$ , our results suggest that the gases are essentially homogeneous (within analytical uncertainty) throughout the 4.2-m section. Variability in the  $\delta^{18}\text{O}/\text{N}_2$  and  $\delta^{\text{A}}/\text{N}_2$  ratios has previously been documented in closely spaced samples from numerous cores [Sowers *et al.*, 1989]. It is noteworthy that this artifact is probably not related to the  $\text{CO}_2$  variability in Greenland ice because the magnitude of the  $\delta^{18}\text{O}/\text{N}_2$  and  $\delta^{\text{A}}/\text{N}_2$  variations is much smaller than the measured  $\text{CO}_2$  variability [Sowers *et al.*, 1989].

### Extreme $\text{CO}_2$ Variations

Delmas [1993], Anklin *et al.* [1995], and Barnola *et al.* [1995] suggested that the high degree of variability associated with Greenland  $\text{CO}_2$  measurements may be related to  $\text{CO}_2$  liberation from carbonate dust due to dissolution by acid species in the ice or the in situ decomposition of organic acids. As the concentrations of carbonate dust, organic acids and hydrogen ions vary considerably over small spatial scales [Mayewski *et al.*, 1993], it is entirely possible that the large  $\text{CO}_2$  variations we observed in Greenland ice were caused by in situ carbonate dissolution. We conclude therefore that it is impossible to make a detailed  $\text{CO}_2$  intercomparison using Greenland ice. Future efforts in this regard will use ice from an Antarctic ice core which has much lower dust and  $\text{H}^+$  concentrations and thus has  $\text{CO}_2$  concentrations that are both representative of the past atmosphere and homogeneous over larger spatial scales [Etheridge *et al.*, 1996].

### Glacial $\text{CH}_4$ Data From GISP2 and GRIP

One important reason for performing a  $\text{CH}_4$  intercalibration was the apparent disagreement between the GISP2 and GRIP  $\text{CH}_4$  data during the last glacial period (17,000 to 22,000 years before present (yr B.P.)), Figure 3 [Chappellaz *et al.*, 1993a, Brook *et al.*, 1996]. We can think of three possible explanations for the apparent disagreement: (1) a calibration artifact between the two different  $\text{CH}_4$  working standards used in the two laboratories (LGGE and URI), (2) an unidentified  $\text{CH}_4$  blank associated with the analyses of glacial ice, or (3) nonlinearities in the flame ionization detector(s) used.

We present the  $\text{CH}_4$  data from the two ice cores covering the last 40,000 years along with the isotopic composition of the ice ( $\delta^{18}\text{O}_{\text{ice}}$ ) in Figure 3. GRIP  $\text{CH}_4$  data were generated by the LGGE and Bern laboratories [Blunier *et al.*, 1993; Chappellaz *et al.*, 1993; Blunier *et al.*, 1995] and the GISP2  $\text{CH}_4$  data were measured at URI [Brook *et al.*, 1996]. We have constructed a common timescale by mapping the GRIP  $\delta^{18}\text{O}_{\text{ice}}$  record [GRIP Members 1993] into the GISP2 record [Grootes *et al.*, 1993], which has been dated by counting annual layers throughout the GISP2 core [Alley *et al.*, 1993; Meese *et al.*, 1994]. The gas age-depth relation was derived by correcting for the ice age-gas age differences all along the cores using the protocol described by Brook *et al.* [1996]. After placing the two  $\text{CH}_4$  records on a common timescale,

the data from the various laboratories were normalized to the NOAA scale using the normalization factors listed in Table 4. The normalization tends to exaggerate the  $\text{CH}_4$  discrepancy between the GRIP and GISP2 cores during the glacial period by 2%. Note that the original GRIP data from Blunier *et al.* [1995] were lowered by 15 ppbv to account for a previously unidentified blank associated with the Bern milling device. The GRIP data from LGGE are directly from Chappellaz *et al.* [1993a].

Between 0 and 9ka, all  $\text{CH}_4$  records agree. Prior to 9ka, URI values are consistently higher than corresponding GRIP values. The discrepancy is clearest during the Younger Dryas (11.7-13ka) and the peak of the last glacial period (between 17 and 23ka) where URI values are 50 ppbv higher. Because the two cores are located 28 kilometers apart in very similar climatological settings, the  $\text{CH}_4$  records from the two cores should be identical.

One major difference between the URI and LGGE extraction protocols is the use of a stainless steel extraction vessel at URI versus a glass vessel at LGGE. Since the URI values are higher than LGGE during these periods (but not during the Holocene), it is conceivable that the elevated URI values before 9ka are the result of an unexplained  $\text{CH}_4$  contamination associated with the stainless steel vessel which is not apparent in the younger samples. Owing to increasing hydrostatic pressure with depth in the ice sheet, the pressure in the bubbles increases until a threshold pressure is reached and the bubbles are slowly transformed into air hydrates, also known as clathrates [Gow *et al.*, this issue]. The transformation in the GISP2 and GRIP cores occurs between 1300 and 1500 meters (7.4-9.3 ka), with all fossil air samples below this depth found in clathrate form. When samples of clathrated ice are allowed to melt, they tend to explode due to the rapid destabilization of the clathrates. One potential explanation for the elevated URI values in the clathrated ice involves enhanced  $\text{CH}_4$  outgassing from the stainless steel vessels as the ice shards from the exploding ice strike the walls. However, this explanation does not appear to hold during the Bolling and Older Dryas periods (13-17 ka) where URI and LGGE show good agreement in clathrated ice.

Because the discrepancy is largest when the measured values are below 550 ppbv, another explanation for the observed difference may involve nonlinear responses in one or both of the laboratories' flame ionization detectors. However, the analyses performed in all laboratories on the standard air with a nominal  $\text{CH}_4$  concentration of 463.5 ppbv (NOAA scale) (Table 2) do not support this explanation.

Finally, it is also possible that the magnitude of the blank may depend on the concentration of  $\text{CH}_4$  in the sample. Here again, however, blank determinations using different standards with varying  $\text{CH}_4$  concentrations do not support this explanation. Both URI and LGGE have performed blank determinations using standard gases with  $\text{CH}_4$  concentrations below 489 ppbv. Neither laboratory demonstrated any dependence of the blank on the  $\text{CH}_4$  concentration.

At present, we do not have an acceptable explanation for the different  $\text{CH}_4$  values measured by URI and LGGE during the Younger Dryas and last glacial periods. Future efforts to resolve this issue will focus on analyses of glacial ice from the Vostok and other Antarctic ice cores. At Vostok, ice containing fossil air from between 18 and 26 ka is found between 400 and 600 m, which is well above the depth at which the bubbles begin to form clathrates.

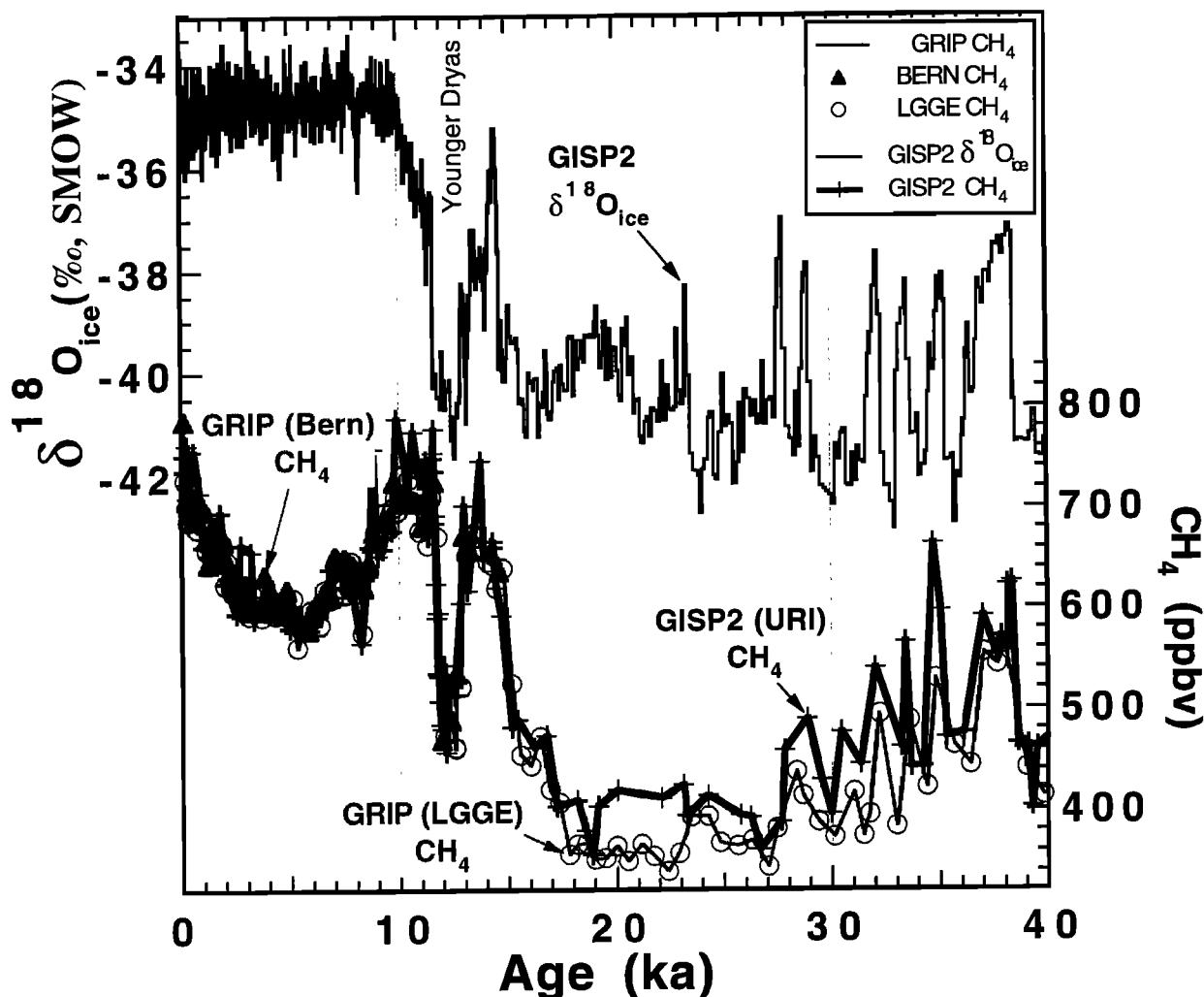


Figure 3. Isotopic temperature ( $\delta^{18}\text{O}_{\text{ice}}$ ) [Grootes *et al.*, 1993; Stuiver *et al.*, 1995] and  $\text{CH}_4$  records from the GRIP [Blunier *et al.*, 1993; Chappellaz *et al.*, 1993; Blunier *et al.*, 1995] and GISP2 [Brook *et al.*, 1996] ice cores covering the last 40ka. The timescale for all records is that of the GISP2 core. All  $\text{CH}_4$  data have been corrected for blanks and normalized to the NOAA scale using normalization factors in Table 4. None of the  $\text{CH}_4$  data have been corrected for gravitational fractionation. This correction is less than 3 ppbv and will not affect the difference between the two records as the correction is nearly the same for both cores. Note the excellent agreement between the records between 0 and 9ka. Prior to 9ka, URI  $\text{CH}_4$  data appear to be ~50 ppbv higher than the corresponding GRIP data during cold periods.

## Conclusions

The ice-core air extraction techniques have been shown to produce similar results for the ice tested (relatively shallow ice from a cold, moderate accumulation rate site in central Greenland). The  $\text{CO}_2$  standard scales at the various laboratories agreed with the NOAA scale within  $\pm 0.38\%$ . For  $\text{CH}_4$  analyses, all laboratory standards agreed within  $\pm 2\%$ . The average  $\text{CO}_2$  and  $\text{CH}_4$  values measured on the intercalibration ice (corrected for the slight differences in working standards) were  $283 \pm 13$  ppmv and  $748 \pm 10$  ppbv, respectively. The  $\text{CO}_2$  data show excessive scatter which we believe is related to  $\text{CO}_2$ -producing impurities in Greenland ice.

The  $\text{CH}_4$  results from the intercalibration ice showed subtle differences between the five laboratories which measured  $\text{CH}_4$ . The standard deviation of all measurements

about the mean  $\text{CH}_4$  value ( $\pm 10$  ppbv) is comparable to the overall analytical uncertainty for the  $\text{CH}_4$  measurements, suggesting that much of the observed scatter is the result of analytical uncertainties as opposed to artifacts associated with the extraction procedures. However, results from the dry extraction techniques (CSIRO and Bern) are, on average, 20 ppbv higher than the average results of the melt extraction techniques and are 26 ppbv higher than the mean LGGE results. These differences are slightly more than can be explained by the known measurement errors. While we have not been able to identify the cause of this discrepancy, we believe that the blanks we determined for some of the extraction procedures may be slightly underestimated for actual ice core samples. Therefore, when comparing  $\text{CH}_4$  records from different laboratories at high precision levels (i.e.,  $< 20$  ppbv), the interlaboratory differences in calibration scales and extraction procedures need to be taken into account.

The elemental and isotopic compositions of O<sub>2</sub>, N<sub>2</sub>, and Ar trapped in the intercalibration ice were measured by two laboratories. The  $\delta^{15}\text{N}$  of N<sub>2</sub>, the  $\delta^{18}\text{O}/\text{N}_2$ , and the  $\delta^{\text{Ar}}/\text{N}_2$  data from the two laboratories were consistent with one another within analytical uncertainties. The average  $\delta^{18}\text{O}$  of O<sub>2</sub> data from URI were 0.12‰ lower than the Bern values. Estimates of the  $\delta^{18}\text{O}$  of the atmospheric O<sub>2</sub> between 1817 and 1832 A.D. were in complete agreement ( $\delta^{18}\text{O}_{\text{atm}} = 0.03 \pm 0.01\text{‰}$ ) with previous measurements.

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