

## <sup>14</sup>C STUDIES OF NATURAL ICE

A. T. WILSON

Department of Geosciences, Gould-Simpson 208, The University of Arizona, Tucson, Arizona  
85721 USA

**ABSTRACT.** There are many kinds of natural ice found on our planet. These include glacier ice, ice sheets, cave ice, massive ground ice, ice-wedge ice and permafrost ice. The problems associated with the recovery and dating of the CO<sub>2</sub> and other gases contained in these kinds of ice is reviewed. New data are presented on various kinds of natural ice. How this kind of data can be used to help determine the origin and history of natural ice samples is discussed, along with the kind of paleoclimatic information that might be obtained from natural ice samples.

### INTRODUCTION

In recent years, the ice in polar ice sheets has become an increasingly important source of paleoenvironmental information. Polar ice cores provide perhaps the best way of obtaining samples for study of the Earth's atmosphere at times in the past. Carbon dioxide concentrations are particularly important because as a "greenhouse" gas, CO<sub>2</sub> may have played a major role in controlling the Earth's temperature in the past, and could do the same in the future.

This paper describes a new technique for recovering CO<sub>2</sub> and other gases from natural ice samples. The initial work was aimed at obtaining the air trapped in the ice from high-altitude ice sheets (100 cc kg<sup>-1</sup> ice) and the recovery from this air of the very small quantities of CO<sub>2</sub> (of the order of 40 µg carbon from a 3-kg sample of ice core). The goal of this project was to measure the quantity of CO<sub>2</sub>, its <sup>14</sup>C content and its carbon isotope ratios. This work has now been extended to other forms of natural ice. Because of the quantities needed even for accelerator mass spectrometric (AMS) natural <sup>14</sup>C measurements, previous measurements of <sup>14</sup>C in CO<sub>2</sub> from ice samples were quite limited. The most successful measurements were made by the Swiss group (Andree *et al.* 1986) who measured the <sup>14</sup>C in ice samples with ice masses of *ca.* 20 kg.

Two difficult problems must be overcome to recover the total CO<sub>2</sub> trapped in polar ice and to measure its quantity and <sup>14</sup>C content and stable isotope ratios:

1. Samples of ice core from high-altitude, high-latitude ice sheets contain extremely small amounts of carbon. A kilogram of ice from a polar ice sheet contains *ca.* 12 µg of carbon as CO<sub>2</sub>, depending on the altitude of the ice sheet. Most ice cores have a diameter of only about 10 cm. This makes it difficult to obtain sufficiently large samples of ice for <sup>14</sup>C dating. Conventional AMS <sup>14</sup>C dating requires samples of *ca.* 1000 µg of carbon. Consequently, it was necessary to develop a practical and quantitative procedure for extracting CO<sub>2</sub> from polar ice samples (Wilson and Donahue 1990, 1992), and a precise and sufficiently accurate technique for measuring <sup>14</sup>C in samples containing as few as 35 µg of carbon (Wilson 1992).
2. Polar ice cores may contain a considerable amount of carbon as solid carbonate particles such as wind-blown loess. It is essential to prevent the CO<sub>2</sub> sample from exchanging carbon with, or receiving CO<sub>2</sub> from, carbonate loess.

In this paper a sublimation technique is described which enables one to carbon date the atmospheric gases trapped in ice weighing as little as 0.5–3 kg, the mass depending on its CO<sub>2</sub> content. The sublimation technique also provides insight into the processes by which atmospheric gases become trapped in polar ice sheets. This, in turn, has enabled us to make high-precision measurement of the CO<sub>2</sub> concentrations of the Earth's atmosphere in Glacial times. The results of these studies should

lead to a better understanding of what controlled the pre-anthropogenic CO<sub>2</sub> concentration of the atmosphere.

#### PREVIOUS METHODS FOR THE RECOVERY OF CARBON DIOXIDE FROM ICE

Two methods have been used previously to extract CO<sub>2</sub> from polar ice. Fireman and Norris (1982) melted the ice and removed the CO<sub>2</sub> with a stream of helium, then cryogenically isolated the CO<sub>2</sub>. In the melting process, the pH of the solution was maintained at a value chosen to minimize the release of carbonate carbon. The other method (Coachman, Hemmingsen and Scholander 1956; Delmas, Ascencio and Legrand 1980; Barnola *et al.* 1983; Andree *et al.* 1986) involves crushing the ice without melting, so that air is released. The crushing process releases atmospheric gases trapped in voids, but is probably less effective in releasing gases that have penetrated the ice matrix. The recovery of CO<sub>2</sub> by crushing is *ca.* 75%, which is probably not a serious problem for <sup>14</sup>C dating. However, because of possible chemical species and isotope partitioning between the gas and solid phases in the ice, incomplete recovery might be a problem for accurate determinations of CO<sub>2</sub>/air ratios, and of isotope ratios of the CO<sub>2</sub> in the past atmosphere.

#### GAS EXTRACTION BY ICE SUBLIMATION

The evaporation and recondensation of ice in a closed system releases all gaseous and solid components originally trapped in a polar ice sample and allows precision manometric measurement of the gases.

The all-glass system used in this research (Fig. 1) isolates CO<sub>2</sub> and N<sub>2</sub> + O<sub>2</sub> from water vapor. In addition to allowing visual monitoring of the progress of the sublimation, glass has less of a tendency to adsorb gases than stainless steel. The temperature and rate of sublimation can be controlled by irradiating the ice sample with infrared radiation. During sublimation, the water vapor, CO<sub>2</sub>, and other gases released are collected in appropriate cold traps. As long as the water vapor pressure in equilibrium with the ice is below 4.58 torr, the triple point for ice-water-vapor, no liquid water can exist. We usually operate at 2 torr, which corresponds to -10°C. Under these conditions infrared energy can be applied to the ice without danger of the formation of liquid water. With the current apparatus, sublimation of a 3-kg ice core requires 18 hr. Diameter, not length, is evidently the primary factor in determining sublimation time. Thus, with a longer sublimation housing, a 10-kg ice-core sample would require not much longer to sublime. This might be useful for studies of other constituents of the atmosphere.

The gases released from the ice are passed through a series of traps. This is shown in Figure 1, which is a simplified schematic of our apparatus. The procedure is as follows:

1. The sample of ice, with mass ranging from 0.5 to 3 kg, is loaded into the apparatus and the system is evacuated.
2. The core surface is "cleaned" overnight by subliming to waste without the infrared lights off; this discards the outer 10% of the core. This cleaning process removes contaminating gases and any drilling fluid (in our case butyl acetate) from any cracks that may be open to the outside of the core. For accurate AMS measurements of the very small amounts of CO<sub>2</sub> recovered from the ice cores, it is important that the samples be absolutely free of any organic matter. This is because the fragmentation pattern of most organic compounds can contribute ions of mass 45, which has the same mass as <sup>13</sup>CO<sub>2</sub>.
3. The sublimed gases are then diverted through traps A through F, and the infrared lamps are turned on to speed up the rate of sublimation.

4. Traps A and B collect 99.9+% of the water vapor; trap C collects the remainder. All are cooled to -80°C.
5. Atmospheric gases (except water) that were trapped in the core pass through cold traps B and C. The CO<sub>2</sub> (and N<sub>2</sub>O) are collected in traps D or E, which are multipass high-efficiency traps held at liquid nitrogen temperature. The remaining atmospheric gases, with a few exceptions (e.g., H<sub>2</sub> and He), are collected on trap F, which contains molecular sieve held at liquid nitrogen temperature. Trap F has the advantage of allowing the apparatus to operate without the need of an external vacuum system, thus reducing the chance of the loss of a valuable ice core sample in the event of a power failure. Having traps D and E in parallel enables successive samples to be taken for mass spectrometric measurements. At the end of the run the CO<sub>2</sub> is transferred into a constant volume capacitance manometer and its mass is measured. It is then transferred to an attached graphitization line, where the CO<sub>2</sub> is converted to graphite, from which an AMS target is made.

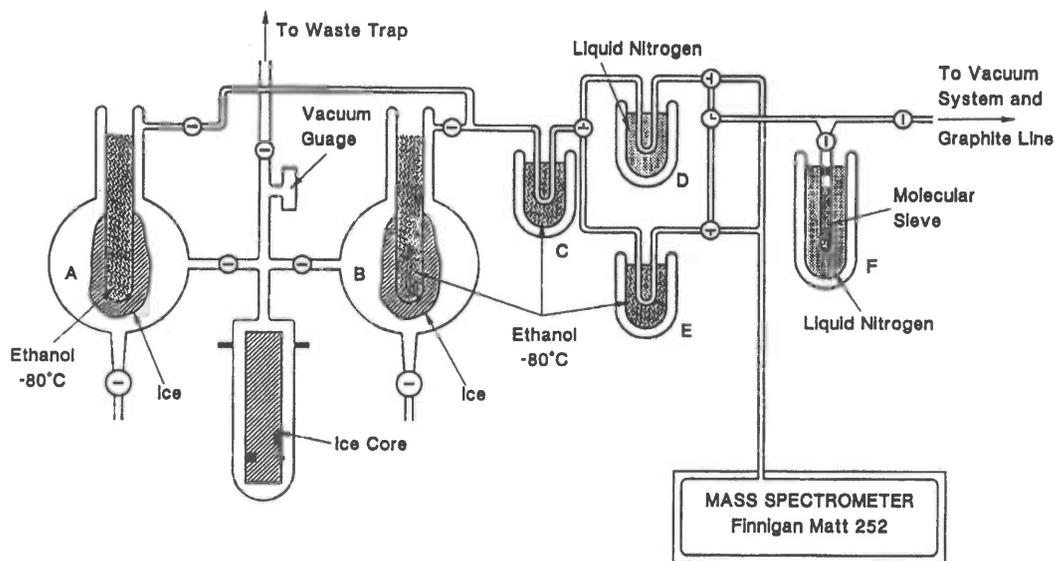


Fig. 1. Apparatus for the sublimation of ice cores to measure <sup>14</sup>C/<sup>13</sup>C, δ<sup>13</sup>C and δ<sup>18</sup>O of entrapped CO<sub>2</sub>

### Determination of Apparatus Blanks

The sublimation apparatus was specially designed to enable measurement of blanks, *i.e.*, the amount of CO<sub>2</sub> and the level of <sup>14</sup>C that derive from any source other than the ice sample itself. For example, the air and CO<sub>2</sub> blank can be determined by subliming ice on to condenser (or trap) A and then conducting a blank run where this ice is re-sublimed through the ice-core-containing vessel to condenser B. The amount of CO<sub>2</sub> (and air) obtained on such runs is called the "apparatus blank", and was <0.02 μmol of CO<sub>2</sub> per day. The reason this blank is so low is because we do the "cleaning" and the actual run at a relatively high partial water vapor pressure (1 torr). In a glass vacuum line, water tends to displace any CO<sub>2</sub> adsorbed on the walls of the apparatus.

If this re-sublimation is performed after a run on a core containing a large quantity of carbonate loess while the solid remains in the bottom of the sublimation chamber, one can estimate an upper level for the contribution of CO<sub>2</sub> this loess could add to the sample, or the sample blank, discussed in more detail below.

In ice-core work, contamination of the outer layers of the core is a concern. This can be studied by "peeling" layers off the ice core and measuring their released gases separately. As stated above, the core is cleaned by allowing it to sublime overnight without the infrared lights. This procedure discards *ca.* 10% of the outer part of the ice core. The sample gases are then collected in at least two cuts representing outer and inner portions of the ice core. The fact that all cuts yield the same CO<sub>2</sub>/air ratio is convincing evidence that the technique is robust and the core samples are not contaminated. If the carbonate loess had contributed significant CO<sub>2</sub> to the sample, one would expect the inner sample to give a higher apparent CO<sub>2</sub>/air ratio than the outer sample, as more carbonate would be available for interaction.

### Carbonate Loess Contribution

The incorporation of CO<sub>2</sub> from the carbonate loess in the core is a special type of blank problem that could arise from sublimation of Greenland ice cores. For example, at the end of the sublimation run on glacial ice from Greenland, 5 mg of calcium carbonate dust might remain at the bottom of the "ice-core compartment" of the apparatus. During re-sublimation of pure gas-free ice from one condenser to the other at a constant vapor pressure of 1 torr, up to 0.02 μmol of CO<sub>2</sub> can volatilize from the carbonate loess in the bottom of the ice chamber. This would add <1 ppmv to the CO<sub>2</sub> measurement and have virtually no effect on the δ<sup>13</sup>C.

Our sublimation procedure is presently designed to analyze relatively large samples of ice. This requirement is dictated by the demands imposed by <sup>14</sup>C analysis. If only CO<sub>2</sub>/air ratios were required, our system could be modified to use much smaller quantities of ice. The present apparatus recovers the water, the CO<sub>2</sub> (plus N<sub>2</sub>O), and the atmospheric gases that can be trapped on a molecular sieve at liquid nitrogen temperatures. It would be a relatively simple matter to modify the system to recover for study other compounds of interest, *e.g.*, CH<sub>4</sub> and CO.

### Discussion of Possible Errors in the Determination of Past Atmospheric Composition

The errors involved in determining the CO<sub>2</sub>/air ratio of the atmosphere at some time in the past from an ice core sample are of two kinds:

1. Errors associated with the analytical procedure itself. These kinds of errors are the easiest to deal with. They were determined by measuring and combining the errors in each step of the analytical procedure and were found to be ± 3 ppmv, or *ca.* 1.5%. This value was confirmed by running multiple cuts on ice core samples. It was found that the individual results agreed within this error. The calibration of the measuring transducers on the apparatus was confirmed by running a standard air sample kindly supplied by Pieter Tans of NOAA.
2. Problems associated with the CO<sub>2</sub>/air ratio of the recovered gases not being representative of the past atmosphere. For example, this could occur if CO<sub>2</sub> were added to, or removed from, the ice core sample during its passage from the zone of closing to the point of recovery. Delmas (1993) suggested that some of the anomalously high values of CO<sub>2</sub> found in some Greenland cores might be the result of the reaction of slightly acidic ice with the carbonate loess contained in the ice. This would be an example of this type of problem. Loss of accuracy of this second kind may derive from the use of invalid assumptions about the system.

One can use indirect evidence that one's data are probably valid. For example, in the sublimation of the Greenland glacial cores:

- a) The amount of carbonate varies from sample to sample as one goes down the ice core, yet the CO<sub>2</sub>/air ratio falls on a smooth curve.

- b) The scatter of the data from the curve through the points is close to what is calculated for the precision of the actual lab analysis itself (see 1 above), which suggests that other errors are either small or constant.

The present apparatus recovers the water, the CO<sub>2</sub> (plus N<sub>2</sub>O) and the atmospheric gases that can be trapped on a molecular sieve at liquid nitrogen temperatures. It would be a relatively simple matter to modify the system to recover for study other compounds of interest, e.g., CH<sub>4</sub> and CO. The ratio of air to CO<sub>2</sub> yields an accurate ±3 ppmv measure of the CO<sub>2</sub> concentration of the Earth's atmosphere during Glacial times. The ratio of air to the amount of ice sublimed gives information on the altitude of the ice sheet at times in the past.

**APPLICATIONS OF THE SUBLIMATION TECHNIQUE TO OTHER TYPES OF NATURAL ICE**

So far we have processed many types of natural ice; a partial list is given in Table 1. One can see that the amount of CO<sub>2</sub> and air per kilogram of ice varies greatly among the different types of natural ice. On the one hand, we have ice from the very cold polar ice sheets, where the only CO<sub>2</sub> comes from bubbles of mechanically entrapped samples of the past atmosphere. At the other extreme is ice from ice caves with 70 times more CO<sub>2</sub> per kilogram of ice (cave ice is discussed in detail below). These latter samples are presumably frozen groundwater that has been in equilibrium with CO<sub>2</sub>-rich soil gases. Intermediate between these two extremes is ice from temperate glaciers, where summer melt has incorporated dissolved atmospheric CO<sub>2</sub> into ice crystals on refreezing. An interesting question we hope to investigate is: Can the CO<sub>2</sub> and air content (and air composition) of low-altitude polar glaciers yield paleoclimatic information on past summer temperatures? For example, did the Medieval Warm Period produce warmer summer days in the Antarctic Dry Valley areas?

**TABLE 1. Examples of Various Types of Natural Ice Studied Using the Sublimation Technique**

	μg CO <sub>2</sub> -C kg <sup>-1</sup>	Air kg <sup>-1</sup>	<sup>14</sup> C age (yr BP)	<sup>18</sup> O CO <sub>2</sub> -H <sub>2</sub> O‰	Comments
<i>Ice Sheet Samples</i>					
1) GISP1948	12.7	100.3			1 and 2 true glacial samples only mechanically trapped air. 3 and 4 Holocene samples have additional CO <sub>2</sub> .
2) GISP2289	10.9	99.3			
3) GISP1164	17.8	92.6			
4) GISP1363	17.2	92.5			
<i>Glacier Samples</i>					
5) Fountain Gl	14.7	26.8	10,600	44.8	Regular polar glacier Ice never melted, lost much air
6) Stagnation Gl	20.1	4.1	1700	54.1	
7) Lateral Moraine Stagnation Gl	38.9	5.4	6000	50.7	Ice never melted
<i>Cave Ice</i>					
8) Reno Ice Cave	230	14.8			Little N <sub>2</sub> O Zero N <sub>2</sub> O Zero N <sub>2</sub> O
9) Reno Ice Cave	152	11.1			
10) NM Ice Cave	1920	11.8			
<i>Arctic Massive Ground Ice</i>					
11) Sermilik	2118	87.9	32,000	46.8	Little N <sub>2</sub> O Zero N <sub>2</sub> O Zero N <sub>2</sub> O
12) Pen. Point	494	25.5	20,500	44.3	
13) Pen. Point	549	60.4	20,000	43.7	

In the Arctic, there are large deposits of “ground ice” of controversial origin (see discussion below). With the sublimation technique, we can very easily determine if this ice is of glacial origin (air content *ca.* 100 cc kg<sup>-1</sup> and low CO<sub>2</sub> content) or from frozen groundwater (low air content and very high CO<sub>2</sub> content). We can also measure the <sup>14</sup>C-specific activity of this CO<sub>2</sub> and determine the time of formation. It is also possible that this technique could become a universal method for dating geomorphic features in the Arctic. Many features are ice cored, or are impregnated with ice. If the CO<sub>2</sub> in this ice is <sup>14</sup>C dated, one may gain insight into the time of formation of these features.

### CAVE ICE

In many parts of the world there are massive bodies of ice in natural caves: in Austria, New Mexico, Idaho and Nevada, to mention a few. Little is known as to how this ice was formed, its age, or whether it contains any information on past climate. We have used the sublimation technique to study samples of cave ice from New Mexico and Nevada. These ice samples are much easier to work with than high altitude polar ice cores because they are formed from frozen groundwater, and therefore contain relatively large amounts of CO<sub>2</sub>.

Some of the basic questions about these deposits of ice are:

1. How old is this cave ice?
2. Does it record any paleoclimatic information?

Preliminary work suggests that there may be two types of cave ice deposits:

1. The first type is found in a cave where the mean temperature is below zero, but the summer temperature is slightly above zero. During summer, liquid groundwater flows onto the top of the ice body and forms a shallow layer that freezes during winter. We will call this the “frozen-lake” type deposit. In this type of deposit the bottom of the ice is frozen onto the underlying rock, and the bottom layers of ice could be very old. Such ice bodies are difficult to study without a great deal of effort.
2. The second type of ice body has a flat top on which groundwater flows in summer, to be frozen during winter. The ice body itself is not frozen to its base but “loosely” sits in the bottom of the cave—often a lava tube. The mean temperature of the bottom of the cave is probably slightly warmer than the caves that hold the frozen-lake-type deposits. We will call this type of deposit an “ice block” deposit, in that it is a flat-topped block of ice sitting in the bottom of a cave. An example of such a deposit is the Candelaria Ice Cave in New Mexico. This cave is a lava tube, and the flat-topped ice body rests loosely in the bottom of the cave. There is a large enough space beneath the ice body and the rock for a person to climb under the ice body to sample the base of the ice. The <sup>14</sup>C date of the CO<sub>2</sub> in two samples from the base of this ice body were 1780 ± 60 BP and 1860 ± 60 BP, respectively. The <sup>14</sup>C date of a twig embedded in the latter sample was <sup>14</sup>C dated at 1810 ± 100 BP. Surface ice from the deposit gave a <sup>14</sup>C date of 55 ± 60 BP. A bird feather embedded in this surface ice sample gave a <sup>14</sup>C date of 25 ± 70 BP. These data suggest that the deposit is not a relic from some previous climate but is more or less in steady state. Presumably, the ice freezes onto the surface and slowly moves down through the ice body during many hundreds of years to be lost by ablation from the bottom of the ice body. Clearly, this ice body survived the Medieval Warm Period in this area. It is difficult to understand how such an ice body could have originally formed without postulating that it formed at a colder time as a “frozen lake” type deposit. As the climate warmed, it presumably became isolated from its base except at points where it is supported by the base and the walls of the lava tube.

The other cave from which we have dated samples is the Reno Cave, near Reno, Nevada. One sample was contemporary; the other gave a <sup>14</sup>C date of 1700 BP.

To summarize:

1. Cave ice is a little-understood geological phenomenon that can be studied with the use of <sup>14</sup>C dating and other isotopic techniques.
2. At least some of the ice in cave ice deposits is many hundreds of years old, and may contain paleoclimatic information. At least the two cave ice deposits discussed in this paper survived the Medieval Warm Period.
3. Organic material (a twig and a feather) embedded in the ice gave similar <sup>14</sup>C dates to those obtained from the <sup>14</sup>C dating of the CO<sub>2</sub> contained in the ice. This is evidence that the ice dates are reliable.

### **OCCURRENCE OF MASSIVE GROUND ICE**

Massive ground ice is a widespread phenomena that has been identified throughout the Arctic. Deposits occur in many places throughout the continuous permafrost regions. In these regions, the absence of massive ground ice is guaranteed only in areas where the bedrock is at or very near the surface. In Eurasia, massive ground ice is mostly found in many of the river valleys and throughout the northern peninsulas. In North America, massive ground ice has predominantly been found in the Mackenzie Delta and recently glaciated areas in the high Arctic.

The properties of massive ground ice vary depending on the origin and subsequent history (Mackay 1989; Fujino *et al.* 1988). Due to the variety of developmental processes, the stratigraphic relationship with the enclosing sediment often cannot provide definitive answers to its origin. Initial studies characterized these ice bodies as being typically overlain by a thin (2–5 m) layer of fine-grained sediment covered by tundra vegetation, and underlain by more permeable sand saturated with groundwater (Mackay 1973). However, more recent work has shown that the stratigraphic relationships of ice and its enclosing sediments can vary considerably (Dallimore and Wolfe 1988; Mackay 1989).

The physical properties, such as ice crystal size and orientation and internal bedding planes, can provide some genetic evidence. Segregated ice tends to have larger, oriented crystals, but this is a function of the freezing rate, and the rate of water flowing to the freezing front (Gell 1978). Buried glacier ice tends to have higher gas contents; however, if the ice was formed by regelation at the base of a glacier, the ice content and crystallography could vary appreciably.

As the gas content is trapped in the ice body from the time of formation, its chemistry and isotopic signature offer the best chance of determining the origin and absolute age of the ice (see Moorman, Michel and Wilson 1996). In general, the gases in buried glacier ice will have a chemical and isotopic signature similar to that of the atmosphere, and segregated ice will contain gases similar to that of the groundwater associated with local soils.

### **Evidence for Massive Ground Ice as Relics of Continental Glaciation**

Grosswald (1980) describes moraines, striations, erratics, post-glacial tectonic rebound, and extensive “proglacial” lakes as evidence for extensive continental glaciation during the late Wisconsinan in northern Eurasia (see also Hughes, Denton and Grosswald 1977). <sup>14</sup>C dates on shells and organics in or underlying “glacial sediments” indicate that this final glaciation was centered on the continental shelves between 18,000 and 9000 yr ago.

The timing of glacier ice buried in the Canadian Arctic is less certain, and could range from early to late Wisconsinan in age. The Yaya Lake ground ice described by Dallimore and Wolfe (1988) is considered to be beyond the limit of late Wisconsinan glaciation (Rampton 1988b). Therefore, if the glacial limits are correct, this ice must have a pre-late Wisconsinan age if it is of glacial origin.

The current situation is that Canadian researchers contend that many of the large tabular bodies of buried ice in the Arctic, which are often tens of meters thick and several km<sup>2</sup> in area, are “segregated ice” formed by *in-situ* freezing of groundwater (Mackay 1973), although some may be of glacial origin. On the other hand, Russian researchers (Grosswald 1980, 1993; Solomatin and Konjachin 1992) advocate that massive ground ice in northwestern Siberia is buried glacial ice from a major late Wisconsinan ice sheet centered on the Kara Sea continental shelf. This Kara Ice Sheet is proposed to have extended southward onto the delta of the Ob River, thus damming it and the Yenisei River to form very large lakes. The outflow of these proglacial lakes is proposed to have been sequentially through the Aral, Caspian and Black Seas, and ultimately into the Mediterranean.

Field investigations have not resolved the disparate interpretations for the origin of these massive ice bodies. It is possible that different occurrences of massive ground ice have different origins. The new sublimation technique can provide data and <sup>14</sup>C dates that can help resolve this problem. Some typical data are shown in Table 1.

#### CRITERIA FOR IDENTIFYING THE ORIGIN AND HISTORY OF AN ICE SAMPLE

Using the sublimation technique, one processes a sample of ice and obtains the following:

1. The amount of air per kilogram of ice.

Glacier/ice sheet ice contain relatively large quantities of air, of the order of 100 cc kg<sup>-1</sup>. This can be lowered somewhat if the ice sample has undergone regelation at the base of the glacier or ice sheet. Groundwater or surface water contains only a fraction of this air content.

- 2a. The amount of CO<sub>2</sub> kg<sup>-1</sup> ice.

The amount of CO<sub>2</sub> associated with high-altitude polar ice, where no melting or recrystallization has taken place, is about one μmol kg<sup>-1</sup>—for example, central Greenland during the full glacial. During the Holocene in central Greenland, where the firn samples are completely re-crystallized, this value rises to 1.5 μmol kg<sup>-1</sup>. Groundwater contains a hundred times these levels.

- 2b. Measurements on the sample of CO<sub>2</sub>.

The isotope ratios can be determined. If there is N<sub>2</sub>O in the ice, this is collected with the CO<sub>2</sub>, and its amount can be determined (at mass 30 on the mass spectrometer) when the carbon isotope ratios are measured. Soil gas is high in N<sub>2</sub>O and significant quantities indicate water that has been associated with a biologically active soil. Interestingly enough, if the oxygen of the CO<sub>2</sub> has not come into isotope equilibrium with the water, it indicates that the sample has never melted.

Using these criteria, one can look at the data shown in Table 1 and determine the source of some typical ice samples:

- a. Samples 1 and 2 are given as typical samples of ice from a very cold ice sheet. They represent ice formed during the last glacial on the surface of the Greenland ice sheet. The only air and CO<sub>2</sub> comes from the mechanical entrapment of atmosphere at the firn/ice transition.

- b. Samples 3 and 4 are given as typical samples from the Greenland Ice Sheet during Holocene times. There is less air because the temperature is warmer and the altitude is higher. There is more CO<sub>2</sub> because the firnification processes lead to the recrystallization of the snow, which leads to the trapping of atmospheric CO<sub>2</sub> (see Wilson 1995).
- c. Arctic glacier samples. Sample 5 is a typical glacier. The <sup>18</sup>O results tell us that most of the ice has been melted at some point. Air has been lost as a result. Samples 6 and 7 have never been subjected to melting but have lost most of their air due to cracking.
- d. Cave ice. Samples 8, 9 and 10 are presented as typical examples of ice formed from frozen groundwater. These samples show high CO<sub>2</sub>, low air and high nitrous oxide.
- e. Arctic Massive Ground Ice. As discussed in the text, the big question is whether these large ice deposits are the remnants of past ice sheets or the products of the freezing of groundwater. As can be seen from Table 1, this massive ground ice appears to have too much air to be frozen groundwater. However, there also appears to be much too much CO<sub>2</sub> for it to be unmodified glacial or ice sheet ice.

It is clear that we should measure the composition of this “air” to see if it is the same as the atmosphere. Oxygen, nitrogen and the noble gases have very different solubilities in water, so that the “air” in groundwater has a composition easily distinguishable from the atmosphere. It would be possible to introduce CO<sub>2</sub> into the ice by a mechanism observed by the author while camped below the snow line on glaciers in both Greenland and Antarctica. Basically, the mechanism is as follows: the ice shrinks in the winter and forms cracks. In the spring a thin layer of meltwater forms on the surface of the ice and flows into the cracks and freezes. This meltwater would absorb CO<sub>2</sub> from the atmosphere and carry it into the ice, leading to glacier ice with higher air/ice ratios and higher CO<sub>2</sub>/ice ratios than would be found in true glacier ice.

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