APPLICATION OF AMS ^{14}C DATING TO ICE CORE RESEARCH

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ABSTRACT. I describe here the use of the accelerator mass spectrometer (AMS) sublimation technique to ^{14}C-date polar ice cores. An unexpected result of this work has been to extend the understanding of how polar ice sheets entrap and record the past composition of the Earth's atmosphere. This work has led to the discovery of a new phenomenon in which CO_2 and other greenhouse gases can be entrapped in cold (never melted) polar ice sheets.

INTRODUCTION

In recent years, ice has become an increasingly important source of paleoenvironmental information. As part of the second Greenland Ice-Sheet Program (GISP-2), researchers developed a novel experimental technique for use in ice-core research. This technique involves placing the sample of ice in a glass vacuum system, where it is allowed to sublime at low temperature (−10°C) while being irradiated with infrared radiation (Fig. 1). The rate of sublimation can be controlled by adjusting the intensity of the infrared radiation; with the current apparatus, sublimation of a 3-kg ice core requires *ca.* 18 h. During sublimation, the water vapor, CO_2 and other gases released are collected in appropriate cold traps.[1] The amounts and isotope ratios of all the products can be measured. The dust particles are recovered from the ice-core compartment at the end of each run, weighed and stored for future studies.

The technique was initially developed to recover the very small amounts of atmospheric CO_2 ($1\ \mu M$ of $CO_2\ kg^{-1}$ ice or $12\ \mu g$ of C as $CO_2\ kg^{-1}$ ice) uncontaminated by carbonate dust (loess) present in ice cores. This CO_2 is converted to graphite, a target prepared for accelerator mass spectrometry (AMS) and its $^{14}C/^{13}C$ ratio determined. Wilson and Donahue (1990) described the technique, which is useful for ^{14}C dating of ice and has been used on polar ice cores, glacial ice, buried ice and ice-cave ice. The sublimation technique enables one to determine accurately the actual amounts of the various atmospheric gases trapped in an ice core and their isotopic composition. This information can be useful in determining the origin of the ice (*e.g.*, glacial *vs.* frozen groundwater). The results derived using the sublimation technique reveal that current views on the entrapment of atmospheric gases in polar ice cores may be seriously in error. I show here how those views should be modified.

The sublimation technique for the ^{14}C dating of ice cores not only yields a sample of CO_2 for conversion into graphite, but also allows measurement of its quantity and the values of $\delta^{13}C$ and $\delta^{18}O$. The air entrapped in the ice-core sample is also measured and recovered, allowing the determination of its ppmv CO_2 value and composition.

CAN THE SUBLIMATION TECHNIQUE BE USED FOR CHEMICAL ANALYSES?

One of the surprising results of my research on the late Holocene part of the GISP core was that significantly more (*ca.* 25% more) CO_2 was recovered than could be accounted for by the air that was recovered. Where did this "extra" CO_2 come from? Acceptable ^{14}C dates were obtained (Table 1), so it could not have come from the contemporary atmosphere. Mass spectrometric analysis showed

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[1] The presence of liquid-phase water during the gas-extraction process could promote release of CO_2 from any carbonate present in the ice. As long as the water vapor pressure in equilibrium with the ice is below 4.58 mbar, the triple point for ice-water-vapor, no liquid water can exist. The equipment is usually operated at a pressure of 2 mbar, which corresponds to −10°C. Under these conditions, infrared energy can be applied to the ice without danger of the formation of liquid water.

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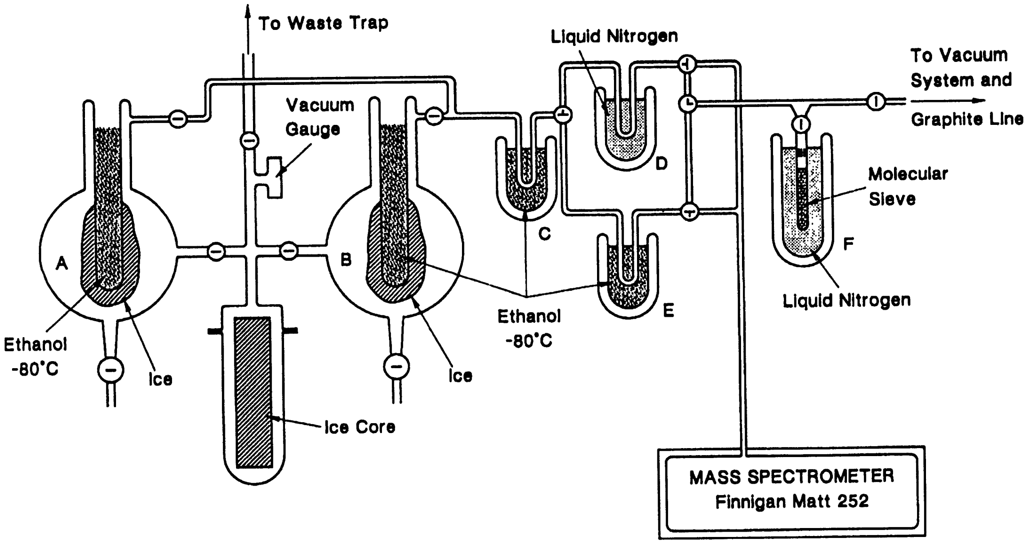

Fig. 1. Apparatus for the sublimation of ice cores to measure $^{14}C/^{13}C$, $\delta^{13}C$ and $\delta^{18}C$ of entrapped CO_2

TABLE 1. Dates on Some Samples of Polar Ice Cores

Core	Depth (m)	CO_2 C in Ice (μg kg^{-1})	^{14}C date of CO_2 (yr BP)	Calendar date (BC)	Layer date* (BC)
Newall	60	28	1730 ± 85		
Newall	80	30	2400 ± 160		
Newall	127	26	2730 ± 120		
Newall	165	20	3300 ± 125		
GISP-2	727	17†	3262 ± 79	1904–1563	1350
GISP-2	894	19†	3589 ± 105	2370–1846	2380
GISP-2	1108	18†	4782 ± 78	3945–3540	3868

*From the data of Meese *et al.* (1994)

†From the air content of these ice core samples, one would have expected *ca.* 13.5 μg kg^{-1} of CO_2 carbon.

that the CO_2 was as pure as the very pure CO_2 used for the mass spectrometer reference gas, except for small quantities of nitrous oxide. It definitely was not contaminated to 25%. The calibration of the measuring gauges was checked by running a 349 ppmv air standard supplied by the National Oceanic and Atmospheric Administration (NOAA). This value was in the range of the CO_2/air ratios recovered from the Holocene section of the GISP-2 ice core. The accuracy of a measurement of the CO_2/air ratio on the sublimation apparatus was ± 3 ppmv.

Measurement of Quantities of Air and CO_2 and CO_2/Air Ratios

At the end of the run, the CO_2 was cryogenically purified and transferred to a part of the vacuum system that had small volume and that included a capacitance pressure gauge. The amount of CO_2 was computed from the known volume, pressure and temperature. The quantity of air was determined by removing the liquid nitrogen from the small tube (*ca.* 3-ml volume) containing the molecular sieve and allowing it to expand into a relatively large, precisely known volume (1–3 liters). Complete desorption was ensured by heating the small tube that contained the molecular sieve to 320°C. This relatively large volume included the same capacitance pressure gauge that was used to measure the CO_2. Measurement of pressure and temperature give the quantity of air recovered. This arrangement allows CO_2/air ratios to be determined very precisely, especially if the volumes are chosen so that the same part of the measuring range of the capacitance gauge is used for both the air and the CO_2.

Determination of Apparatus Blank

The sublimation apparatus (Fig. 1) was specially designed to enable measurement of blanks, *i.e.*, the amount of CO_2 and the level of ^{14}C that derive from any source other than the ice sample itself. For example, the air and CO_2 blank can be determined by subliming ice onto condenser (or trap) A and then re-subliming this ice through the vessel containing the ice core to condenser B. In a glass vacuum line, water tends to displace CO_2 adsorbed on the walls of the apparatus (Zumbrunn, Neftel and Oeschger 1982). The amount of CO_2 obtained is the apparatus blank, which is < 0.02 µmol of CO_2 per day. If this re-sublimation is performed after a run on an ice-core sample 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_2 this loess could make to the sample during the run, *i.e.*, the sample blank, discussed in more detail below.

Contamination of Ice Core

Contamination of the outer layers of the ice core is problematic. This can be studied by "peeling" layers off the ice core and measuring them separately. The core is cleaned by subliming to waste overnight, and the sample is taken as at least two cuts. The fact that both cuts yield the same result indicates that it is valid.

Carbonate Loess

The incorporation of CO_2 from carbonate loess in the core is a special problem that could arise from the sublimation of Greenland ice cores. For example, at the end of a sublimation run on glacial-age ice from Greenland, 5 mg of carbonate-containing dust might remain at the bottom of the "ice-core compartment" of our apparatus. During an 18-hr-long re-sublimation of pure gas-free ice from one condenser to the other at a constant vapor pressure of 1 mbar, up to 0.02 µmol of CO_2 can volatilize from the carbonate loess in the bottom of the ice chamber. This would add <1 ppmv to the CO_2 measurement and have virtually no effect on the $\delta^{13}C$ measurement.

CONSEQUENCES FOR ICE CORE RESEARCH

The above results suggest that the entrapment of CO_2 and other gases in cold (never melted) polar ice is more complex than previously assumed. These results invalidate the assumption that *the ice in the matrix of ice that entraps bubbles of atmospheric air in the "zone of closing" contains no* CO_2 *or other "greenhouse" gases*, particularly for the Holocene section of the GISP core. I have called the CO_2 entrapped in the matrix of ice surrounding the bubbles "matrix CO_2".

To check this conclusion, I ran samples of firn from above the "zone of closing" in the GISP-2 and Vostok ice core in the sublimation apparatus. As the new hypothesis predicted, the samples did contain the expected amount of CO_2, together with nitrous oxide and a small quantity of air. The air was only 1–2% of what would have been expected from a similar weight of normal ice core (*i.e.*, the firn-ice contained only 1–2 cc kg^{-1} instead of the 100 cc kg^{-1} normally found in polar ice from below the firn/ice transition). The air was enriched in oxygen and the CO_2 was depleted in ^{13}C (–13‰ on the PDB scale).

In hindsight, the phenomenon of "matrix" gases in cold (never melted) polar firn is probably not that unexpected. It is well known to most light-isotope geochemists that, if one freezes water in a vacuum system from a non-condensable gas that contains CO_2, some of the CO_2 will be trapped in the resulting ice.

As was pointed out by Fireman and Norris (1982), high-altitude polar ice can contain relatively large amounts of *in-situ* produced ^{14}C. This ^{14}C is produced in the ice crystals by nuclear spallation of oxygen by cosmic rays. Wilson and Donahue (1992) showed that, at least in the Holocene part of the GISP-2 ice core, all the *in-situ* produced $^{14}CO_2$ had been removed. Presumably, resublimation processes associated with firnification under Holocene conditions in the GISP core involve the complete recrystallization of all the ice crystals. During this process, the *in-situ* $^{14}CO_2$ and ^{14}CO enter the firn gas phase, where they are diluted and ultimately escape to the free atmosphere. An interesting point is that this perhaps gives us a technique for studying firnification processes. In some ice cores, *e.g.*, the Holocene section of the Vostok (Antarctica) ice-core, some *in-situ* $^{14}CO_2$ is retained, which means that some of the original ice crystal matrix has survived recrystallization.

APPLICATION TO THE ^{14}C DATING OF ICE CORES

For ^{14}C dating of ice samples, the "matrix CO_2" phenomenon must be considered. In the Holocene section of the GISP-2 ice core, 25% of the CO_2 recovered in the sublimation apparatus (the matrix CO_2) is probably almost the same age as the ice with which it is associated. This is based on the assumption that most of the matrix CO_2 was incorporated near the top of the ice sheet, where the temperature gradients are steeper. The remaining 80% of the CO_2 came from the bubbles of air entrapped in a matrix of ice as it passed through the "zone of closing". In the case of the GISP ice core, this ice formed from snow that had fallen 220 yr before. Wilson and Donahue (1990) determined this figure by locating the nuclear weapons testing pulse in the GISP-2 ice-core. In the case of this core, the correction is not large, because of the relatively high accumulation at Summit during Holocene times. Ice cores from warmer regions, such as the Newall ice core, which comes from an elevation of 1500 m in the McMurdo Dry Valley region of Antarctica, have even more CO_2 (Table 1). In addition to matrix CO_2, ice cores may also contain ice lens material. During the warmest/sunniest days of some summers, melting may occur on the *névé* of the Newall Glacier. The meltwater would flow down into the colder underlying snow to refreeze. During the brief period when the water is not frozen, it can take up atmospheric CO_2, the amounts of which can be quite large by ice-core standards. To avoid this problem, scientific ice cores (*e.g.*, GISP-2) are drilled in the coldest locations available. Melt layers represent a good source of CO_2 for ^{14}C dating, provided the atmospheric CO_2 does not have an opportunity to exchange with carbonate loess that may be present. Since most mineral carbonate has a $\delta^{13}C$ very different from that of atmospheric CO_2, $\delta^{13}C$ measurements on the CO_2 can help determine if there is a problem. The Newall ice core has an air/ice offset of *ca.* 900 yr, which would be the age of the CO_2 associated with the entrapped air. The remaining (and larger) part of the CO_2, which would be matrix CO_2 and any ice lens CO_2, would have the same age as the ice with which it is associated.

IN-SITU ^{14}C PRODUCTION IN HIGH-ALTITUDE ICE SHEETS

As has been pointed out by Fireman and Norris (1982), there must be significant quantities of $^{14}CO_2$ and ^{14}CO produced at the surface of high-altitude ice sheets. (See also Lal and Jull 1990; Lal *et al.* 1990). This was dramatically demonstrated when I attempted to determine "blank" runs on the sublimation apparatus using old (^{14}C- free) ice core samples from Vostok Station, with rather mixed results. I discovered that ice-core samples stored on the surface acquired $^{14}CO_2$ as a result of cosmicray bombardment. Vostok is situated right on the south magnetic pole at an elevation of 4000 m. I obtained a sample of the 3G Vostok ice-core from a depth of 1479 m (expected age: 100 ka yr; Barnola *et al.* 1987). This core was stored at the surface in a plywood shed from January 1985 to January 1992. The CO_2 recovered from this core should not have contained any ^{14}C because of its age. In fact, the CO_2 obtained by sublimation had a ^{14}C-specific activity greater than Modern and was very close to the HOxII, NIST Standard Reference Material 4990C for ^{14}C dating. Obtaining reasonable ^{14}C dates from the Holocene part of the GISP ice core implies that little *in-situ* ^{14}C is retained. To check this important conclusion, Wilson and Donahue (1992) determined the depth in the GISP-2 ice core at which bomb-produced ^{14}C is present. By choosing samples from depths just below this level, they were assured that they contained air that was in the atmosphere between AD 1900 and 1940. The ^{14}C-specific activity of the CO_2 in this air is precisely known from tree-ring studies. These results agree within experimental uncertainties, which, at best, are $<1\%$, with results obtained from tree-ring measurements (Stuiver and Reimer 1993). This provides valuable glaciological information about the firnification process—for example, that no original ice crystals remain. How much of the original *in-situ* ^{14}C survives provides information about the firnification process.

CONCLUSION

The use of AMS to determine the ^{14}C-specific activity of the very small amounts of CO_2 that can be recovered by subliming polar ice cores, together with $\delta^{13}C$, have shown that the entrapment of CO_2 and other gases in polar ice cores is more complex than has been assumed. In particular, the ice matrix that entraps the bubbles of atmospheric air can contain important quantities of CO_2 and other "greenhouse gases". This is an important phenomenon, and must be taken into consideration when using polar ice cores to ascertain the concentration of past atmospheric "greenhouse" gases.

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