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AMS RADIOCARBON DATING OF ICE: VALIDITY OF THE TECHNIQUE AND THE PROBLEM OF COSMOGENIC *IN-SITU* PRODUCTION IN POLAR ICE CORES

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ABSTRACT. In the "sublimation technique," carbon dioxide entrapped in ice is recovered by sublimation, converted to graphite and ratio of $^{14}C/^{13}C$ in the CO_2 determined by AMS measurements. We describe here several experiments performed to check the validity of such measurements and to study the effect of cosmogenically produced *in-situ* ^{14}C on the measurements.

INTRODUCTION

Polar ice sheets have become an important source of paleoenvironmental information. Ice cores taken from polar ice sheets provide an excellent opportunity for studying the Earth's atmosphere at times in the past. The most reliable dating of ice cores older than the limit of annual isotopic stratigraphy (9–12 ka BP) may be through ^{14}C measurements on the CO_2 contained in the ice. We have developed a "sublimation" technique for recovering small amounts of CO_2 in atmospheric air entrapped in polar ice cores. The basic technique was reported at the 13th International Radiocarbon Conference (Wilson & Donahue 1989). We discuss here two important questions concerning the ^{14}C dating of the CO_2 entrapped in ice. We study the reliability of the method by determining the ^{14}C ages of known-age samples dated by other methods, and we investigate the effect of *in-situ*, cosmogenically produced ^{14}C that may be present in ice cores.

THE SUBLIMATION TECHNIQUE FOR THE ^{14}C DATING OF ICE CORES

Two serious problems must be overcome to measure successfully the ^{14}C content of CO_2 trapped in polar ice:

1. The core contains extremely small amounts of carbon. A kilogram of ice from a polar ice sheet contains, depending on the surface altitude of the ice sheet, about 15 to 20 μg of carbon as CO_2. Most ice cores are only about 10 cm in diameter, which makes it difficult to obtain very large samples of ice for dating. In addition to making detection of ^{14}C difficult, the small quantities of carbon exacerbate the problem of correcting for background (chemical blank) carbon accumulated during sample processing and target preparation.
2. The polar ice cores may contain a considerable amount of carbon as solid carbonate particles – wind blown loess. It is important to prevent the exchange of CO_2 carbon with carbonate carbon.

Our technique, described in detail in Wilson and Donahue (1989, 1990) enables us to carbon date the atmospheric gases trapped in as little as 0.5–3 kg of ice, depending on its CO_2 content. The technique involves placing the ice sample in a carefully degassed glass vacuum system, "cleaning" the ice by removing the outer few millimeters by sublimation, then subliming the ice completely,

using infrared lamps as an energy source. The water vapor pressure is monitored to ensure that the surface of the ice is always below −10°C. It is important to keep the temperature of the ice well below 0°C to prevent any exchange of sample CO_2 with carbonate loess that might be present in the ice sample. The gases evolved from the subliming ice first pass through a trap at −80°C to remove water. The remaining gases pass through a trap immersed in liquid nitrogen where the CO_2 is recovered. The gases that pass the liquid nitrogen trap are trapped on a molecular sieve held at liquid nitrogen temperatures.

In our apparatus, we can sublime a 3-kg sample of ice core in 18 h. We measure the quantity of water sublimed, the amount of air and CO_2 recovered and the ^{14}C content of the CO_2. From these data, we can calculate the CO_2 concentration of the atmosphere at the time given by our ^{14}C date. So far, we have processed various kinds of natural ice ranging in difficulty from ice from ice caves to ice cores from polar ice sheets.

Ice-cave ice is essentially frozen groundwater that had been in contact with the soil atmosphere and contains >1000 μg of CO_2 carbon kg^{-1} ice. We need only 100-g samples to date this type of ice. At the other end of the scale of difficulty is ice from high-altitude, high-latitude ice sheets. This ice has never been liquid water, and we recover the CO_2 from air trapped in bubbles when the snow was compressed into ice at the firn/ice transition. Since these samples usually come from high altitudes, the air pressure can be significantly lower than that at sea level. These samples contain about 15 μg of CO_2 carbon kg^{-1} ice. Besides the problem of recovery, they present a problem of measuring ^{14}C in samples of very small size.

Intermediate between these two extremes is temperate alpine glacier ice. The surface snow that ultimately forms these glaciers has usually undergone some melting and refreezing, which leads to the incorporation of atmospheric CO_2 into the ice crystals. With polar ice-core samples, we normally use 2–3 kg samples, and we can now routinely run 60-μg graphite samples in our AMS facility. Smaller samples are precisely diluted with ^{14}C-free CO_2, to bring the AMS target size to about 60–100 μg. We have run polar ice samples as small as 1 kg in the "bomb pulse" zone where the activity is high and the spatial resolution in the ice core is of concern. This work was undertaken to determine the "offset" between the age of the air and the age of the ice that entraps it. In polar-ice cores, the age of the ice that is entrapping the air may have fallen as snow hundreds (in the case of Greenland ice cores) to many thousands of years ago (in the case of ice cores from the central part of the Antarctic Ice sheet).

VALIDITY OF THE ^{14}C DATING OF ICE

Ice-Cave Ice

Caves containing bodies of ice occur in many parts of the world. Little is known about the mechanics of the ice bodies in these caves, and many questions remain unanswered. How long has ice been in these caves? Did the ice survive the Medieval Warm period? What is the distribution of the age within the ice body? Does the ice contain any paleoclimatic information? ^{14}C dating of the ice may provide a way of obtaining the answers to some of these questions. The ice is very easy to date, as it contains, by polar ice core standards, very large quantities of CO_2. Thus, samples of only 100 g are required. Presumably, the ice is frozen groundwater that has been in contact with the soil atmosphere, which is high in CO_2 due to the respiration of plant roots. The question is, if we recover CO_2 from this "cave ice" and determine its $^{14}C/^{13}C$ ratio, do we calculate a valid date for the ice? We have dated many samples from the ice caves in New Mexico, and, in the course of this work, were able to obtain dates for both a normal sample (bird feather, twig) and the ice that entrapped it. The data are given in Table 1. One can see that the ^{14}C dates of the conventional

materials are the same as the CO_2 entrapped in the ice that encloses them. This gives us confidence that the dates we are obtaining from the ice samples not associated with organic remains are also valid.

TABLE 1. Radiocarbon Dating Carbon Dioxide of Ice from the Candelaria Ice Cave, New Mexico

Sample no.	Source of CO_2	^{14}C date (yr BP)
AA-6022	Ice	55 ± 60
AA-6023D2	Bird feather in ice sample AA-6022	25 ± 70
AA-4915	Ice from base of deposit	1780 ± 60
AA-6021	Ice from base of deposit	1860 ± 60
GX-15919	Twig embedded in ice sample AA-6021	1810 ± 100

RADIOCARBON DATING OF POLAR ICE CORES

An excellent source of known-age air entrapped in polar ice is air that is just older than atmospheric weapons tests. Wilson and Donahue (1990) determined the depth in the GISP-2 core at which bomb-produced ^{14}C is present. By choosing samples from depths just below this level, we are assured that they contain air that was in the atmosphere between AD 1900 and 1940. The ^{14}C content of this air is precisely known from tree-ring studies. One would expect that measurements on samples from this depth would provide a sensitive check of the validity of our technique.

However, the fact that polar ice can contain some cosmic-ray-produced, *in-situ* ^{14}C complicates these considerations. Lal *et al.* (1990) reported the observation of cosmogenic *in-situ* ^{14}C in ablating ice from the Allen Hills area of Antarctica. In addition, Lal and Jull (1990) calculated that a considerable amount of *in-situ* ^{14}C could be formed on the surface of an accumulating ice sheet. Their calculations show, for example, that if all *in-situ* ^{14}C produced in the surface snow at the GISP-2 site were retained during the firnification process to be entrapped in the ice below the firn/ice transition, a correction of 1.6 ka would have to be made to our results. If even a small fraction of *in-situ* ^{14}C were to be retained through the firnification process, important corrections would have to be made to determine ice-core ages from measurements on sublimed CO_2. To study the effects of this *in-situ* ^{14}C, we used samples of the GISP-2 ice core from depths just below the region containing the nuclear weapons pulse, the region just below 90 m (Wilson & Donahue 1990). Results of measurements on CO_2 extracted from two samples at this depth are shown in Table 2.

TABLE 2. Samples from the GISP-2 Ice Core

Sample No.	Depth (m)	$F^*_{measured}$	$F_{tree\text{-}ring}$	Ratio ice/tree
AA-5293D4	90.6	0.98 ± 0.03	0.978 ± 0.005	1.002 ± 0.03
AA-6323	91.4	0.992 ± 0.008	0.978 ± 0.005	1.014 ± 0.009
			Weighted average	1.013 ± 0.009

$$^*F = \frac{(^{14}C/^{13}C)_{sample};\ \delta = -25‰}{(^{14}C/^{13}C)_{1950};\ \delta = -25‰}$$

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From the results presented in this table, two observations can be made. By the time the snow at the surface of Summit (GISP-2 ice core) has moved down to the firn/ice boundary, essentially all of the cosmic-ray-produced *in-situ* ^{14}C in CO_2 has escaped to the atmosphere. Our results indicate that less than 3% of the ^{14}C in the CO_2 recovered with our system could be from cosmogenic *in-situ* ^{14}C. Presumably, the *in-situ* ^{14}C escapes to the atmosphere during the recrystallization involved in the firnification process.

Perhaps the most important result of this work was that it provided an important check on our technique for the ^{14}C dating of polar ice cores. For an ice sample with a precisely known date, our results agree within our experimental errors, which in the best case, are less than 1%, with results obtained from tree-ring measurements. This provides evidence that, at least in the Holocene portion of the GISP-2 core, we have not overlooked some important phenomenon. This also gives us some confidence that our procedure for ^{14}C dating the air trapped in polar ice cores does enable us to produce correct dates for the Holocene portion of the GISP-2 core. It is interesting to note that our dating of the undiluted CO_2 from the 5-kg ice sample used in this work provided results of comparable accuracy to routine AMS ^{14}C dating of more conventional materials.

The production and retention of cosmogenic *in-situ* ^{14}C in ice cores can depend sensitively on the geographical location at which those cores were drilled. For example, Lal and Jull (1990) calculate that, because of the low accumulation rate in the Antarctic, cosmogenic *in-situ* ^{14}C at the site of the Vostok core should be approximately ten times that at Summit in Greenland (GISP-2). We have recently performed an experiment similar to the one described above for a sample from a depth of 112 m at Vostok. This depth should correspond to an air age of about 600 yr. One would expect the specific activity of the carbon in the CO_2 in the air extracted from this ice core sample to be about 93% of "modern" (1950). We found it to be 2.344 ± 0.013 times "modern." Our measured result is

$$F_{\text{measured}} = 2.344 \pm 0.013 ,$$

so that the ratio

$$\frac{F_{\text{ice-measured}}}{F_{\text{air-expected}}} = 2.344/0.93 = 2.52 .$$

It is clear that a great deal of cosmic-ray-produced *in-situ* ^{14}C is retained in the Vostok core, and any ^{14}C dating of this core will have to correct for this phenomenon. However, a correction can be made, so that accurate dates can be obtained, at least for the Holocene. Our Vostok sample was stored in a trench at Vostok for about one year. Depending on the degree of shielding it experienced, a fraction between 0 and 1/3 of the cosmogenic ^{14}C that we observed could be from "post-coring" cosmic-ray-induced reactions.

A comparison of experimental and calculated results (Lal & Jull 1990) for the Vostok core indicates that as much as 25% of the *in-situ* ^{14}C cosmogenically produced in the surface snow at Vostok is retained through the firnification process, and is present in ice below the firn/ice transition. This result was obtained using the fact that ice contains about 15 μg of carbon trapped as CO_2 kg^{-1} of ice, and assuming that *in-situ*-produced ^{14}C is 50% in CO and 50% in CO_2 (Lal *et al.* 1990). Whereas almost none of the original ice matrix at Summit is retained, the situation is very different at Vostok, possibly due to the fact that the firn at Vostok is 25°C colder than at Summit (GISP-2).

The above measurements at 112 m in the Vostok core provide *in-situ* ^{14}C corrections, which must be applied to any ^{14}C dating of the Vostok core in Holocene times. It is likely that the correction will be different during glacial times, when conditions were colder and accumulation rate was less. It is also possible that some cosmogenic *in-situ* ^{14}C was retained in GISP-2 ice during glacial times, when the temperature and accumulation rate were lower than they are now. The possible presence of cosmogenically produced *in-situ* ^{14}C must be carefully considered when interpreting ^{14}C age measurements of polar ice.

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