GAS EXTRACTION FROM POLAR ICE CORES: A CRITICAL ISSUE FOR STUDYING THE EVOLUTION OF ATMOSPHERIC CO₂ AND ICE-SHEET SURFACE ELEVATION

by

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ABSTRACT

The measurement of gases enclosed in polar ice cores provides valuable information concerning the history of the ice sheets and their environment. The extraction of gases from ice is a critical step in the experimental procedure. We found that the most efficient methods of gas extraction for 20 to 50 g samples were ice melting and controlled refreezing of the melt water for the total gas content and ice crushing for the CO_2 content. These two experimental methods are described in detail.

It is shown, in particular, that ice is easily contaminated by carbonate dust during sample preparation. This contamination introduces an excess of CO_2 when gases are extracted using a procedure involving ice melting.

1. INTRODUCTION

When firn is transformed into air-tight ice by natural sintering of firn grains near the ice surface, a portion of the surrounding atmosphere becomes trapped in the pores between the grains. The barometric conditions and the gaseous composition of the atmosphere prevailing when the firn pores close off are thus reflected in the volume and composition of the air enclosed in the ice. Consequently, measurements of gases enclosed in polar ice cores provide valuable information about the past history and environment of the ice sheets, including past surface elevations of the ice sheets from the total gas content (Raynaud and Lebel 1979, Raynaud and others 1979, Raynaud and Whillans 1982), and the evolution of the atmospheric CO_2 over the last tens of thousands of years from the CO_2 content (Berner and others 1980, Delmas and others 1980).

Nevertheless, a portion of the gases extracted from ice may have an origin different from the gaseous atmosphere trapped during ice formation. Solid trace constituents may be decomposed and generate gases during gas extraction. Actually, extraction of gases from ice is the most critical step in the experimental procedure. The aim of this paper is to review the different methods tested in our laboratory and to describe and discuss in detail those which appear to be the most efficient.

2. GAS EXTRACTION FOR THE VOLUMETRIC DETERMINATION OF THE AIR TRAPPED IN ICE

The first requirement for measuring accurately the volume of atmospheric air enclosed in ice is to achieve a complete extraction. The total gas content V measured in cold polar ice is of the order of $0.1~cm^3 = 100~mm^3$ STP g^{-1} of ice. The natural variations observed are generally a few per cent of V. The composition of the total gas is very close to the atmospheric composition, except for CO_2. This CO_2 deviation, due to the decomposition of contaminating carbonate dust (section 3), is too small (about 0.1% of the total volume) to affect air volume measurements.

For total gas content determinations, we used two extraction methods: melting of ice in kerosene, and extraction of gases in a vacuum. The first method is described in detail by Langway (1958). The experimental uncertainty is about ±7%. The study of V variations in ice generally requires more accurate measurements, which are obtained by extracting the gases in a vacuum.

We have tested and used the latter method in our laboratory, following several different procedures (Raynaud 1977, Raynaud and Delmas 1977, Lebel 1979): (i) sublimating ice, (ii) melting ice, and (iii) melting ice and refreezing the melt water. All these procedures generally lead to accurate (± about 1%) relative measurements, but there are systematic differences between results obtained with different procedures (Raynaud and Lebel 1979). Because of the systematic nature of these differences, the total gas content variations in ice deduced from the results of a single procedure are not affected and V changes obtained by different procedures may be compared. A major difference between the procedures tested is the amount of water vapour in contact with the drying agent (P_2O_5 or $Mg(ClO_4)_2$) or trapped by condensation (in a cold trap) during gas extraction. Gas-solid interactions occurring during trapping of water vapour are probably the main cause of the systematic differences observed between the different procedures.

Currently we use the procedure involving ice melting and refreezing. This procedure reduces considerably the amount of water vapour in contact with the drying agent and is the most efficient (best

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relative precision and least time-consuming). The analytical method has already been described in Lebel (1979) and was used, in particular, for measurements reported by Raynaud and Lebel (1979) and Raynaud and Whillans (1982).

The main steps in the procedure are as follows. (i) At about -15°C, the ice sample is prepared, weighed accurately (20 to 25 ± 0.01 g) and placed in a glass vessel ((1) in Fig.1). (ii) With the extraction line (Fig.1) pre-evacuated, the glass vessel is connected to the line and evacuated for 20 min through the liquid N_2-trap (9). Then the stopcock of (1) is closed and the ice melts. (iii) During melting, most of the gases escape above the melt water and a certain gas fraction remains dissolved. The water is then slowly refrozen (refreezing time is 30 to 40 mins). Cooling is obtained by the Peltier effect with thermoelectric modules. The bottom of the vessel is especially designed in order to provide a perfect contact with the top of the modules. In this way, dissolved gases migrate towards the ice-water interface as the ice grows and at the end of the refreezing process the vessel contains gas-free ice with the extracted gases above. (iv) The stopcock of (1) is opened again, the extracted air dried through the P_2O_5 traps (4) and collected in a volumetric gas burette (6) using an automatic Toepler pump (5). During this last step, only a small amount of water vapor is transferred to the P_2O_5 traps because water in the glass vessel is in the form of ice maintained at low temperature. The traps (4) are filled with granular P_2O_5. To obtain reproducible results, the P_2O_5 has to be changed after about 20 extractions.

The amount of gas that can be extracted by a second ice melting-controlled refreezing cycle is negligible (0.1 to 0.3% of the total amount of gas) and we can assume that gas extraction is complete after only one cycle.

Sources of experimental error in the relative measurements of total gas content in ice are mainly the amount of ice sublimated when the glass vessel (1) is first evacuated and the accuracy of the volumetric burette. The influence of these sources of error was evaluated experimentally and the corresponding experimental error on the V results is <±1%.

To check the relative precision of our measurements, we performed comparative determinations of V on natural samples which are assumed to enclose very similar amounts of air (Raynaud and Lebel 1979). The
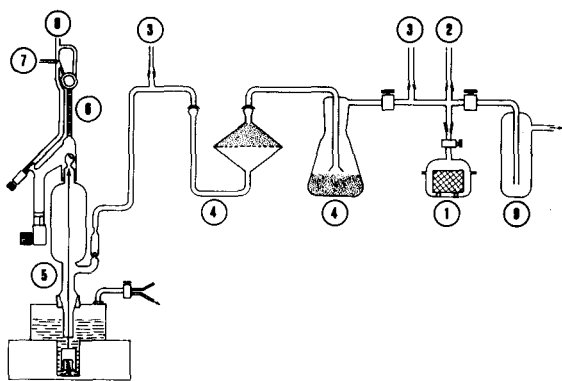

Fig.1. Standard gas extraction line used for total gas content and CO_2 measurements.
(1) sample vessel,
(2) inlet for gas calibration,
(3) Pirani gauge,
(4) P_2O_5-trap,
(5) Toepler pump,
(6) gas burette with divisions of 0.02 cm³ STP,
(7) outlet towards the gas chromatograph,
(8) outlet towards the atmosphere,
(9) liquid N_2-trap.

difference between comparable measurements never exceeds 2% and is on the average 0.7%.

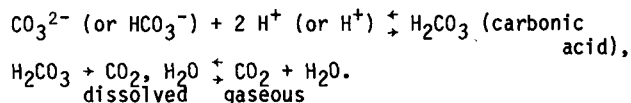## 3. GAS EXTRACTION AND CO_2 CONTENT IN POLAR ICE
3.1 Carbonates and the contamination problem

Based on a present-day atmospheric CO_2 concentration of 340 parts per million by volume (vpm) and a total gas content in ice of 0.1 cm³ STP g⁻¹, the calculated volume of CO_2 in 1 kg of ice would be 34 μℓ of CO_2, i.e. 1.5 μmol. This value is comparable with the concentrations (range 0.5 to 4 μmol kg⁻¹) of the other major trace constituents or ions (H^+, SO_4^{2-}, NO_3^-, Cl^-, Na^+) generally found in Antarctic ice (Delmas and others in press). The determination of chemical concentrations at such low levels is very difficult, mainly because of contamination problems during sampling, sample handling, and laboratory work.

In the case of major atmospheric gases (N_2, O_2, Ar, and CO_2), such problems have been disregarded until now. However, the case of CO_2 is special as it can be generated from carbonates. Carbonate is a common constituent of continental dust, particularly in sedimentary areas where it is a significant neutralizing agent of natural atmospheric acids. If care is not taken in sample preparation, carbonate dust may be inadvertently incorporated in the ice, most likely in the form of solid particles deposited on the surface.

If the gases are extracted by ice melting, carbonated particles remain in the melt water in a soluble or insoluble form. These particles may then slowly react with the natural acidity of the sample or be rapidly destroyed by sulphuric acid which may be added to the melt water in order to improve extraction of CO_2 (Raynaud and Delmas 1977).

When a carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) dissolves in acidic water, the following equilibria occur:

$$CO_3^{2-} \text{ (or } HCO_3^-) + 2 H^+ \text{ (or } H^+) \leftrightarrows H_2CO_3 \text{ (carbonic acid)},$$

$$\underset{\text{dissolved}}{H_2CO_3} + CO_2, H_2O \leftrightarrows \underset{\text{gaseous}}{CO_2} + H_2O.$$

The more acid the solution, the more easily these equilibria are displaced to the right and CO_2 is freed. It can be calculated that 106 μg (1 μmol) of sodium carbonate decomposes giving 22 μℓ (STP) of CO_2. This value must be compared to a "normal" CO_2 content of ice (~34 μℓ of CO_2, 1.5 μmol). If special care is not taken in handling the ice sample, a contamination of 1 μmol is very feasible. In this case, the measured CO_2 content is increased by 66%.

Our present knowledge of the chemical composition (Delmas and others in press) of Antarctic snow clearly demonstrates that natural carbonates are highly improbable in snow, particularly at central Antarctic locations, and have never been detected in clean samples (Legrand 1980). Only contaminated samples have been found to be carbonated. This contamination was assessed by titrating in detail the carbonate or acid content of an ice core (Dome C, 111 m depth). It was shown that it is a typical surface contamination, probably caused by handling the sample in the cold room during band-saw trimming. The sample (a cube of ice) was placed in a clean glass funnel and allowed to melt slowly. Several successive melt-water fractions were recovered and titrated separately. The titration method used, which was developed in our laboratory (Legrand and others to be published*), measures the concentrations (±0.2 μEquiv. ℓ⁻¹) of strong acids (pH<7) or of (bi)carbonates (pH>7) in natural precipitations. In this titration method, the influence of atmospheric CO_2 is eliminated.

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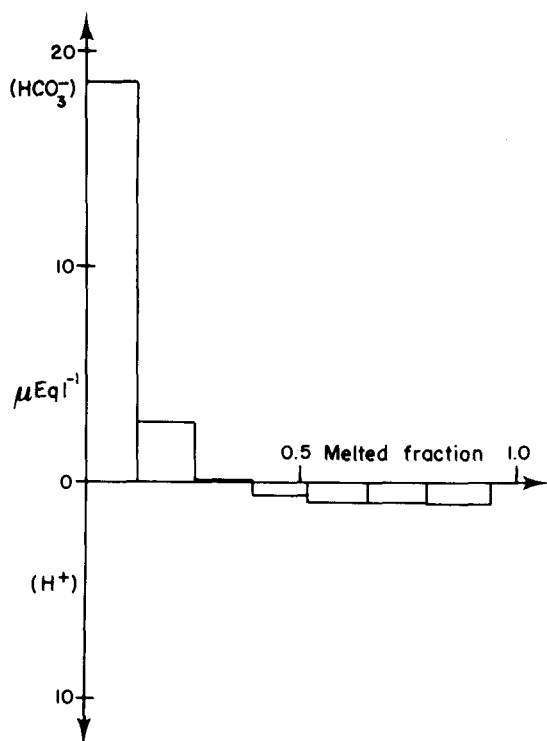
Fig.2. Study of the superficial carbonate contam-
ination of an ice-core sample. The first fract-
ions of melt water recovered contain (bi)carbon-
ates. The inner part of the core is slightly
acid and is most probably free of contamination.

The diagram in Figure 2 clearly demonstrates that
the external part of the ice sample is heavily con-
taminated and that the "normal" acidity of the ice
can be obtained only by analysing the inner core of
the sample cube. By adding the (bi)carbonate found
for each fraction, we calculate a corresponding total
amount of CO_2 of nearly 2.2 µmol, an amount which
can be compared to that which is assumed to be in the
air bubbles (1.5 µmol). This comparison clearly
shows that the measured carbonate contamination may
easily double the natural CO_2 content of the ice.
In this particular case, the CO_2 content determined
after melting the sample and extracting the gases
would probably be higher than 800 vpm.

When the sample is not prepared just before gas
extraction, contamination may be even more important
and explain the very high CO_2 values found by Raynaud
and Delmas (1977) for certain levels in the Camp
Century core. On the other hand, if the volume of the
sample is bigger (300 g, for example (Berner and
others 1980)), surface contamination may be reduced
and corresponding excess CO_2 lowered. It must be
noted that the long complete extraction times (>1 h)
reported by these authors is most probably explained
by slow destruction of the carbonated particles and
displacement of the above chemical equilibria (Stumm
and Morgan 1970) by the natural acidity of the melt
water. The composition of the "first fraction" (as
defined by Berner and others (1980)) can be assumed
to approximately reflect that of the bubbles.

We therefore conclude that excess CO_2 generally
measured when gases are extracted by melting ice is
satisfactorily explained by inadvertent contamination
of ice samples during preparation. Furthermore, dis-
persion of the CO_2 values thus obtained could be
also linked to this artifact.

Preparation of samples in ultraclean conditions
at -15°C being difficult, we tried to wash thoroughly
the solid sample with a pure liquid (alcohol, de-

ionized water, and acidified deionized water were
used) in order to remove superficial contaminated ice
layers. The CO_2 content of the extracted gases was
considerably lowered. It seemed, however, that a res-
idual contamination still remained (Delmas and others
1980).

3.2 Crushing the ice

We have developed a gas extraction method where
the ice remains in the solid state in order to recover
only the bubbles. By this means, the solid carbonates
and the natural acids of the ice are not allowed to
react and to free excess CO_2.

The ice samples are cut from the centre of the
core with a band-saw. Their weights are in the range
30 to 50 g. All operations are done in a cold room
(cutting at -15°C, crushing at -40°C). The stainless
steel cylindrical container (volume 150 ml), in which
the ice is crushed, has two distinct parts (Fig.3).

Fig.3. Stainless-steel container
used to crush ice samples and
recover air from the bubbles.

A stopcock was fitted at the top of the upper part.
The assembly of the two parts is made airtight using
an indium wire. Stainless-steel balls are added to
the solid sample. The air is rapidly evacuated by
connecting the container, maintained at about -40°C,
to the vacuum line (10^{-2} torr). The evacuated vessel
is then closed, transferred to the cold room and
mounted on the crushing apparatus. This apparatus
acts by imparting an up-and-down motion (several
hundred cycles min^{-1}) to the vessel. The ice is
very finely pulverized by the metal balls. The
optimal crushing time was determined experimentally
(Fig.4). After 30 s the amount extracted is relati-
vely small. Note that the CO_2 content measured
depends neither on extraction rate nor on crushing
time. This shows that a total extraction of the air
bubbles is not necessary to get reproducible CO_2
values. Finally, by adding a small amount of $NaHCO_3$
powder to the ice sample just before crushing, it
was checked that solid contaminants do not alter the
CO_2 measurements.

After crushing, the stainless-steel container
(maintained at about -40°C) is connected to the
extraction line. Extracted gases are dried and colle-
cted in the gas burette as described in section 2.
CO_2 concentrations are measured by gas chromato-
graphy (Silicagel column, thermistor detector). The
method is calibrated by using synthetic air standards
with CO_2 contents in the 150 to 400 vpm range. The
overall error of the method is estimated to be about
10%*.

This procedure was used by Delmas and others
(1980) in order to describe past variations of atmo-
spheric CO_2. CO_2 values thus obtained from ice
(160 to 350 vpm) bracket the present-day CO_2 atmo-
spheric content. Furthermore, very similar profiles
(CO_2 concentrations vs age) were obtained at two
different Antarctic locations. These results are a

* We are currently improving the chromatographic
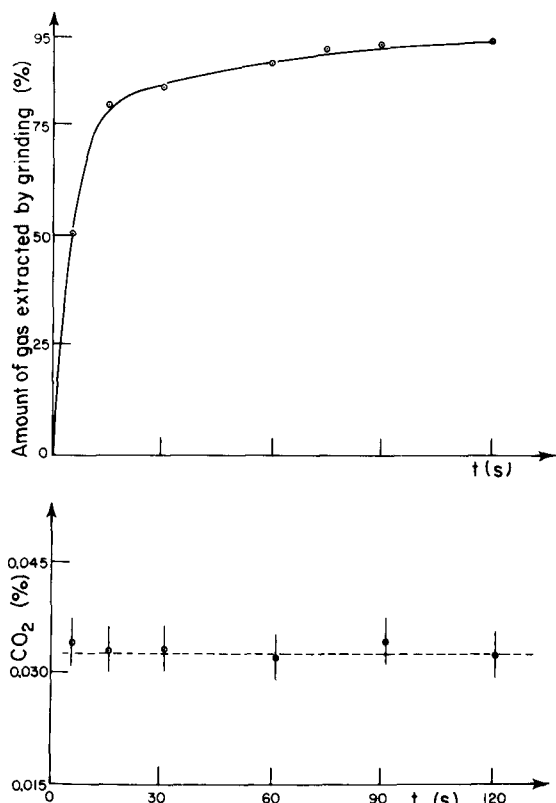determination method in order to reduce the experi-
mental error.

Fig.4. Extraction rates and CO_2 content of gases extracted after increasing crushing times (Dome C ice, 111 m depth).

good indication that the CO_2 variations in the air bubbles of polar ice are related to the composition of the past atmosphere.

4. CONCLUSION

For measuring the volume of atmospheric air trapped in polar ice, the most suitable and reproducible gas extraction method tested in our laboratory consists of melting the ice and controlled refreezing of the melt water in a vacuum.

In the case of CO_2 measurements in ice, carbonate contamination during sample preparation satisfactorily explains the high CO_2 values formerly observed. This contamination precludes the use of gas extraction methods involving ice melting, at least in the case of small samples. Ice crushing in a vacuum appears to be the most suitable means of obtaining consistent past atmospheric CO_2 values from polar ice.

ACKNOWLEDGEMENTS

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