EXTRACTION OF TRAPPED GASES IN ICE CORES FOR ISOTOPE ANALYSIS

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Abstract. The use of ice cores for paleoclimatic investigations is discussed in terms of their application for dating, temperature indication, spatial time marker synchronization, trace gas fluxes, solar variability indication and changes in the Dole effect. The different existing techniques for the extraction of gases from ice cores are discussed. These techniques, all to be carried out under vacuum, are melt-extraction, dry-extraction methods and the sublimation technique. Advantages and disadvantages of the individual methods are listed. An extensive list of references is provided for further detailed information.

1. INTRODUCTION

A number of paleoclimatic archives are available for reconstruction purposes, including ocean sediments, peat bogs and lake sediments, tree ring records, historical documents and ice cores. The advantage of ice cores lies in the well ordered and complete collection of climate (H_2O isotopes), climate forcing (greenhouse gases) and solar variability (^{10}Be and ^{36}Cl) information partly with a sub-annual resolution covering the last 500 000 years.

Ice core records with the full width of information can be obtained from sites where melting and sublimation is minimised. Therefore, the central parts of Antarctica and Greenland, as well as some smaller ice caps in the Arctic, are suitable. Ice domes or ridges, where horizontal ice movement can mainly be ignored in interpreting records, are often preferred drilling sites. In contrast most of alpine glaciers are not cold enough and can be used only for certain investigations with parameters which are hardly influenced by melting and associated processes. The feasibility of ice to act as an archive is based on the sequential accumulation of snow, containing a snapshot of the atmosphere's condition. During the transformation — 'snow–firn–ice' — information can be stored in three reservoirs: (1) the water itself — more precisely its isotopic composition — contains a record of climate variability in particular the local temperature; (2) particles and soluble gases are trapped in snow flakes or at the snow surface and record the chemistry of the lower atmosphere; (3) the gases, which are closed off from the free atmosphere when a certain firn density is reached, hence the gas age is different from the age of the surrounding ice.

1.1 Dating

Dating of the ice cores is essential in order to reconstruct the temporal development of any parameter. There are different dating methods: (1) annual layer counting — parameter like the isotopic composition of water ($\delta^{18}O_{ice}$, δD_{ice}), electrical conductivity measurement (ECM), dust or most chemical components (H_2O_2, NH_4 etc.) show seasonal variations; (2) time markers, such as known volcanic eruptions or nuclear weapon tests; (3) ice flow modelling. Annual layer counting is preferred when the accumulation rate is sufficiently high. In deeper

ice, and for low accumulation sites, ice flow modelling combined with time markers from different archives is generally used. A brief description will be given about the accuracy of ice core dating.

1.2 H$_2$O isotopes as temperature indicator

The „key" parameter in any ice core record are the H$_2$O isotope records. Both the oxygen and hydrogen isotope ratios can be measured and yield information about temperature and water vapour history (sources). The principles of using H$_2$O isotopes as a paleothermometer was already discussed by several authors starting with simple Rayleigh distillation [1, 2, 3, 4, 5, 6, 7]. The relationship between H$_2$O isotopes and temperature was derived spatially for Greenland for example by [8]. Despite critical discussion of using such a spatial relation it was actually used by many scientists for temporal variations. Borehole temperature logging in combination with heat diffusion backcalculations has provided a better insight of past temperature changes and hence the long-term temporal relationship between temperature and H$_2$O isotopes. This new calibrations for long-term changes was recently supplemented for short-term events by another calibration technique using nitrogen isotopes (δ^{15}N) of N$_2$ which are partly influenced by thermal diffusion [9, 10, 11].

1.3 Isotopes as synchronisation tool

A fact which is obvious from the deep ice cores recovered so far are the fast variations during glacial times. These variations are more pronounced in Greenland ice compared to Antarctica. Based on these changes, which are common for a lot of parameters such as the H$_2$O isotopes, methane and many chemical species etc., one can in principal synchronise ice core records from different sites. However, for a synchronisation one has to differentiate between ice (H$_2$O isotopes), impurities of the ice (chemical species, dust etc.), which underlie both strong local influences and trapped air properties, which are more of global character (short mixing time of the atmosphere of 1–2 years). Two recently established tools are using the global parameters of the isotopic composition of atmospheric oxygen (δ^{18}O$_{atm}$) by [12] and of methane by [13, 14, 15]. Due to the much shorter atmospheric lifetime for methane than for oxygen, methane is a better recorder of short-term variations and hence better suited for exact synchronisation of different records. But even using so called global parameters as synchronisation tool have their difficulties, which are namely coupled with gas-ice age differences as well as the spread of air ages. Both are among others dependent on the local accumulation rate and temperature. When considering only record comparisons within a single ice core, for example δ^{18}O$_{ice}$ with a gas record (CO$_2$, CH$_4$, N$_2$O), then δ^{15}N is very useful since it can be used to derive exact estimates of gas-ice age differences. Similarly, noble gas ratios or noble gas isotope ratios can also be used to estimate this difference [16].

1.4 Isotopes of trace gases as flux markers

Carbon, oxygen, hydrogen and nitrogen isotopes of the most important greenhouse gases CO$_2$, CH$_4$ and N$_2$O — **except** water vapour — are very useful tools for tracing the partitioning of fluxes into the different reservoirs (ocean, atmosphere, biosphere) as shown by several publications as shown below. For detailed information about the importance of biological CO$_2$ pump, CO$_2$ isotope disequilibrium, carbonate dissolution and other part of the global carbon cycle please consult the following selected papers [17, 18, 19, 20, 21, 22, 23, 24]. This list is by far incomplete but it allows you a first approach to this topic.

1.5 Isotopes as indicators of gravitational and thermal diffusion corrections

In the diffusive zone of the ice sheet overlaying firn zone two alteration of the air composition occurs due to external forcing of air movement. First of all the earth's gravitation field leads to an enrichment of the heavy isotopes and elements at close-off depths compared to the free atmosphere. Secondly similarly acts a temperature gradient between surface and close-off depth in that the heavier molecule migrates towards the colder end. Both influences can be studied by looking at the isotopic composition of nitrogen ($\delta^{15}N$) since this parameter is believed to be constant in the atmosphere over time periods of 10^5 years, as generally accepted. Information about this topic can be found in the following publications [25, 26, 27, 28].

1.6 Oxygen Isotope as an indicator of a changing Dole effect

The past atmospheric oxygen isotopic composition of ice cores is a global parameter. Together with the corresponding oceanic $\delta^{18}O$ as measured on sea-sediments, mainly derived from benthic foraminifera, one get an idea of the variation of the so-called Dole effect (i.e. the differences of $\delta^{18}O_{atm}$-$\delta^{18}O_{sea}$) [29] and [30].

1.7 ^{10}Be and ^{36}Cl as solar variability indicators

These two isotope are cosmogenically produced. The production rates of these species are modulated by both the magnetic fields carried by solar wind as well as those associated with the geomagnetic dipole moment. Therefore, a large potential for retrieving information about changes of solar variability as well as changes in the magnetic fields in the past is given for those species.[31, 32, 33, 34, 35].

In the following section we will briefly summarise the principal methods which are used to analyse the above mentioned parameters. We will focus mainly on the gas species and their isotopes rather than on direct measurements of ice matrix components and or chemical inclusions.

2. METHODS

First of all one has to distinguish between techniques used for gas extraction or for chemical and matrix component. For the latter two purposes mainly a melting of ice is adequate. For H_2O isotopes only a simple melting is necessary. For Be and Cl isotopes a chemical absorbent is mounted into the melt water line. However, there are different ice melting devices (melt heads) available, some of them were specifically developed for certain tasks such as CFA (continuous flow technique) which is used to determine parameters such as Ca^{++}, Na^+, Cl^-, NH_4^+, H_2O_2 and many more. But most of engineering time was spent on extraction systems for gases.

There are three main techniques used for extracting gases from ice cores, which will be discussed below. Historically the melt-extraction (1) is the oldest method used, followed by the various dry extraction techniques (2) after having problems with CO_2 contamination (in particular from carbonate dissolution in acidic ice or oxidation of organic acids) with the melt-extraction. The third technique is based on the sublimation of the ice (3) to circumvent the potential contamination problems associated with water chemistry. All three methods have in common that the procedure has to be undertaken under vacuum. For extraction types (1) and (3), the extraction efficiency is close to 100% whereas for extraction (2) it is variable

depending on time, crushed ice particle size and air inclusion state (bubbles, clathrates, mixture of both). The air in the ice is first enclosed in air bubbles which with increasing pressure lower their volume according to rules of a Van der Waal gas. At a certain depth depending on hydrostatic pressure and site temperature the bubbles are transformed into air-hydrates (clathrates), which are somewhat like a football-like cage made-up of water molecules which themselves host gas molecules. Description of the main extraction devices, their advantages and disadvantages as well as their main applications are listed below.

(1) Melt extraction

The ice is melted by heating the ice under vacuum, therefore releasing the occluded gases from the bubbles. Slow refreezing of the water forces the gases to leave to the headspace of the extraction chamber (usually glass containers made up from two parts sealed with either a synthetic product or soft metal), which are then either cryogenically condensed (by a closed-cycled helium cooler or a liquid helium) or compressed. To optimize the gas extraction efficiency the heating/refrezeeing cycle is repeated up to three times. References describing this technique are [36, 37, 38, 39]. In recent times this technique was modified to process rather small samples (10–20 g of ice) for methane concentration analysis and isotope and elemental measurements of the main air components [40, 41, 14] and [10, 42].

Advantages:
- close to 100% extraction efficiency
- simple and fast extraction
- no or hardly detectable fractionation for close to 100% extraction efficiency

Disadvantages:
- cannot be used for highly water soluble gas species (e.g. CO_2)
- contamination potential via water chemistry
- contamination by ad/disorption processes
- water vapor transport effects
- extraction efficiency has to be checked to prevent fractionations due to different solubilities

Applied to the following species:
- CH_4 and N_2O concentration (latter is rather surprising)   [14], [43], [44]
- $\delta^{18}O_{atm}$, $\delta^{15}N$ [42], [10]
- elemental ratios of main air components (O_2/N_2, AR/N_2)   [10]
- noble gas ratios (Kr/Ar, Xe/Kr)   [16]
- $\delta^{18}O_{ice}$ (ice melting only)   [45], [46]

(2) Dry extraction

Several techniques for dry extraction have been suggested and are actually in use. In the following these different types of dry extraction systems are briefly described and noted for which purpose they are used. General advantages/disadvantages compared to the melt-extraction can be given as:

Advantages:
- no interaction with wet chemistry (when working at low temperatures, <-15°C, lower temperatures usually result in lower contaminations)
- combinations of trace gas analyses including CO_2 on the same sample are possible
- close to 100% extraction of opened air bubbles

Disadvantages:

- incomplete gas extraction (depending on the size ratio of remaining ice particles and the mean bubble or clathrate distance; especially important for clathrate ice)
- contamination problems associated with moving parts (for example: metal-metal friction produces methane)
- contamination problems associated with desorption processes, especially from metal surfaces (therefore good preconditioning is necessary) or the whole extraction system has to be heated to minimize adsorption/desorption processes, especially for CO2.

Needle-crusher

Another technique developed at Bern by [47] is the needle-crusher for small ice samples of less than 20g. Under vacuum an array of needles is repeatedly pneumatically driven into the ice sample splitting it into small pieces, releasing thereby the enclosed air. This air is then expanded into an infra-red laser absorption spectrometer cell, where the CO_2 concentration is determined. The extraction efficiency is of the order of 80% for bubble ice and around 45–70% for clathrate ice [*48*].

A similar technique is in use at Scripps [49]. We evacuate the crusher and crush the ice (4–6 cm^3) at –70°C, and condense the whole liberated air sample at about 20 K into mini-cold traps cooled by a closed cycle He refrigerator. We admit three standard air gases (165–328 ppm CO_2)over the crushed ice for every three samples to closely simulate the standardization procedure to the ice air extractions. These standard gases are then treated identical to the samples. The traps containing samples and standards are subsequently warmed to –70°C, the gas is mixed with a bellow assembly (to overcome stratification due to different condensation temperatures) and dispensed into the IR cell by the bellow assembly. Measurements are made by tunable diode laser spectroscopy on a single vibrational-rotational line. Each sample is measured at exactly the same pressure and temperature. Our depth resolution is about 1 cm.

Advantages:

- fast crushing technique for small samples (<20g)
- good extraction efficiency for bubble ice
- very well reproducible

Disadvantages:

- not well suitable for clathrate ice (increasing CO_2 concentration with time)

Applications:

- for CO_2 concentration its isotopic composition

Ball-mill

The ball-mill was developed by [50] to test whether another extraction technique than the previously described needle-crusher would lead to similar results. The ice is powdered by balls within a stainless steel container thus pulverizing the ice and releasing the air. The depth resolution due to the larger sample size is somewhat less.

Advantages:

- fast and easy for middle sized samples (50g>sample <100g)
- good crushing efficiency for both bubble and clathrate ice

Disadvantages:
- not suitable for methane measurements (methane production by metal-metal friction)
- potential of sealing the gas outlet by ice powder

Applications:
- mainly for CO_2, also used for nitrous oxide (N_2O)

Ice mill
The ice mill was especially developed for carbon isotope measurements on CO_2. It was design by [51] for ice samples between 100 to 1000g, making it ideally for extraction of a few microliters of carbon dioxide for mass-spectrometric measurements using a dual inlet system. It furthermore was used for a few radiocarbon measurements. The ice is crushed in a evacuated stainless steel container by a milling cutter. The escaping air from the opened bubbles is collected by condensation at 15K with a closed-cycled helium cooler (Leybold-Heraeus or CTI Cyrogenics).

Advantages:
- large size sample possible
- controllable particle size by additional weights
- fast extraction time and condensation time (<12min)
- tested and suitable for isotope measurements

Disadvantages:
- potential of strong contaminations for CH_4, CO_2, N_2O after removing of ball-bearing silver coating within the ice mill
- rather long time for pre-conditioning

Applications:
- mainly for carbon isotopes ($\delta^{13}C$, $\delta^{18}O$)   [60], [20]
- $\delta^{15}N$, $\delta^{18}O_{atm}$ [52]
- elemental ratios such as $\delta O_2/N_2$, dAr/N_2 etc.

Cheese Grater (taken from CO_2 -Paper by [53])
The technique quickly extracts air from the bubbles without melting the ice or exposing the released air to moving metal components, both of which could influence the trace gas composition [54, 55]. Briefly, samples weighing 500–1500 gram are prepared by selecting crack-free ice and trimming away the outer 5–20 mm. Each sample is sealed in a polyethylene bag flushed with high purity nitrogen and cooled to $-80^{\circ}C$. It is then placed in the extraction flask where it is evacuated and then grinded to fine chips. The released air is dried cryogenically at $-100^{\circ}C$ and collected cryogenically in electropolished stainless steel "traps", cooled to about $-255^{\circ}C$ by a closed-cycle helium cooler. The precision is extremely good due to the large sample size which is applicable for high accumulation rate sites.
The measuring procedure at Scripps for $\delta^{13}CO_2$ uses a somewhat similar techniques for liberating the air. About 200 g of carefully trimmed ice is crushed under vacuum in a rotary, inwardly spiked stainless steel cylinder (about 5 L volume) in a $-27^{\circ}C$ freezer for 30 minutes.

Advantages:

- fast extraction and condensation method (<10min)
- large sample processing is possible (up 1400g)
- tested for several trace gas concentrations and isotope species
- low contamination (at least true for the system at DAR, Aspendale)

Disadvantages:

- lower sample limit is around 200g at least for the Australian Cheese Grater Technique (since a remaining ellipsoidal ball of around 70g is present after crushing)

Applications:

- CO_2 , CH_4, N_2O, CO, H_2
- $\delta^{13}C$, $\delta^{18}O$ on CO_2, C-14, $\delta^{13}CH_4$

New ice mill

A sample of up to 20g is crushed in a sealed container by a milling cutter and the gas escaping from the opened bubbles is flushed with helium to a Porapak column where it is stored until its injection into the gas chromatograph. To avoid any contamination with CH4 produced by friction in the gear section, a helium-flushed rotary feed-through is used. CH4 analyses on ice samples of about 10g from the last 1000 years give precise and reproducible results [56].

Advantages:

- very small sample can be processed (5g<sample<20g)
- hardly no contamination
- direct gas trapping and injection to the chromatograph

Disadvantages:

- rather difficult in maintenance

Applications:

- so far for methane
- potential for CO_2 and N_2O

(3) Sublimation technique

[57] and [58] recently reported the use of sublimation of the ice as a technique for extraction of air samples from ice cores. They applied this technique to extract air samples for the determination of the isotopic composition of CO_2. More recently, [59] used a similar gas extraction approach combined with a frequency-modulated high-resolution infrared absorption spectrometer with tuneable diode lasers (FM-TDLAS) for analysing trace gas concentrations of CO_2, CH_4 and N_2O.

The sublimation extraction technique utilises sublimation of the ice sample in a high-vacuum apparatus at temperatures well below the triple point of ice-water-vapour (0°C). The energy needed for the sublimation is transferred to the ice sample by near infrared irradiation. The released water vapour and the air from the bubbles are refrozen in consecutive cold traps at temperatures appropriate to separate both components. The air is cryogenically trapped at 14K with a closed-cycled helium cooler. The temperature of the ice during sublimation is

monitored via the water vapour pressure above the ice and kept below $-20°C$ (equivalent to 1hPa vapour pressure) to prevent melting and the formation of the quasi-liquid layer on the ice surface at temperatures between $-4°C$ and $-2°C$ and at the interface between the ice and glass. This prevents chemical reactions in the liquid phase from producing excess CO_2 from carbonate dust.

Advantages:
- No contamination from liquid phase chemical reactions under careful maintained conditions
- 100% extraction efficiency

Disadvantages:
- Rather long sublimation times (30–45min for 50g ice)
- Additionally long pre-conditioning time required
- contamination problems due to wall desorption processes
- contamination potential by accumulation of chemicals and particulates

Applications:
- applied for radiocarbon analyses on CO_2
- CO_2, CH_4, N_2O

(4) Steps following the gas extraction (example $\delta^{13}C$ on CO_2)

Detailed information for $\delta^{13}C$ on CO_2 measuring procedure at SIO

The measuring procedure at Scripps for $\delta^{13}CO_2$ uses a somewhat similar techniques for liberating the air. About 200 g of carefully trimmed ice is crushed under vacuum in a rotary, inwardly spiked stainless steel cylinder (about 5 L volume) in a $-27°C$ freezer for 30 minutes. The CO_2 thus liberated from the ice is extracted in a glass vacuum line by passing it through a $-90°C$ acetone/liquid nitrogen (LN) cooled trap to remove water and two $-196°C$ traps to retain CO_2. The CO_2 is transferred from the first LN trap to the second by warming the first to $-90°C$ (and similarly to the third) and ultimately trapped into a Pyrex tube at $-196°C$ which is flame sealed. We introduce multiple times standard air of precisely known isotopic $^{13}CO_2$ over the uncrushed ice before and later over the crushed ice and retrieve and treat it identically to the ice air samples. We observe a small reproducible negative fractionation which we correct for. The samples (standards and ice air) are analyzed on a VG Prism II IRMS for the isotopic composition of C and O. The performance of the mass spectrometer is frequently calibrated against NIST standards (NBS 19, 16, and 17) and the Netherlands standards GS 19 and 20, and we have a numerous set of equally calibrated secondary standards (both air and carbonate standards, for atmospheric and marine work). Typically we run 3 to 4 standards for 15samples to monitor and correct minor short term variations of machine performance over a day. Other corrections made to the raw isotopic data include a correction for the ^{17}O isotope (Craig correction), gravitational correction (using $\delta^{15}N$ data when available). An additional N_2O correction is based on measurements of mixtures of CO_2 and N_2O to arrive at the specific correction for our machine. We use the published values of N_2O concentration in ice air as the raw data from which we calculate the corrections for N_2O.

Our precision on a single sample is about 0.075 per mil for $^{13}CO_2$. Including the errors for the gravitational correction by ^{15}N, it becomes 0.085 per mil. However duplicate and triplicate analyses indicate errors of 0.060 and 0.049 per mil, respectively.

(5) Additional remarks:

Problems of sample handling, transfer, and storing

It is a general experience that the more manipulations and handling steps a sample has to go through the larger will be the potential to get contaminated. Therefore, a condensed and slim but still sufficient sampling procedure is a first step to expect reproducible results. Secondly, it is important to follow a very strict protocol when processing a sample since many handling steps have often time- or pressure-dependent characteristics (such as adsorption/desorption or extraction efficiencies etc.). Thirdly, fractionation inherently belong to sample gas expansion manipulations, therefore great attention has to be paid to this steps. In particular by introducing samples into a analyzer systems (gaschromatographs or mass spectrometers) this has to be in mind. Fourthly, there are a lot of effects associated with measuring procedures as well, which is thoroughly discussed at least for mass spectrometer analysis in [17].

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