Analysis and interpretation of gas content and composition in natural ice

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Abstract. The influence of ice formation and transformation on gas content and composition in temperate ice is studied. The concentration and composition of gas in newly formed temperate ice provides information on the gas trapping mechanisms. During ablation the gas content is highly influenced by water in the intergranular vein system. Based on gas analysis results the amount of water with which the trapped gases have been in contact is estimated. Experiments were mainly done on core samples from Griesgletscher (Swiss Alps). For the analysis of N\textsubscript{2}, O\textsubscript{2}, and Ar sufficient gas is contained in samples of 3-8 g of ice, but also samples of 300-1000 g were analysed.

1. INTRODUCTION

Gas content and composition analysis provides information on the environmental conditions at the time of formation of glacier ice and on the history of a given piece of ice. The interpretation of the analytical data, however, has to be based on the knowledge of gas occlusion mechanisms and possible transformation effects afterwards.

For cold ice it is assumed that the gas composition in air bubbles is close to atmospheric, at least as regards the main components. There is essentially no migration of the gases in the ice, if not too small a piece is considered.

Temperate glacier ice is completely different. Already after occlusion the gas composition differs significantly from the composition of the atmosphere, and considerable variations in gas content and composition have been observed. From the occlusion to the ablation tongue these variations are amplified by the water in the intergranular vein system.

The significance of gas analysis work on natural ice has been emphasized already by Coachman et al. (1958a, b). Our attention was drawn to the problem of gases in temperate glaciers, when we tried to collect Ar and CO\textsubscript{2} for dating alpine glaciers by \textsuperscript{14}C and \textsuperscript{39}Ar measurements. In a first attempt, based on measurements of a few sparse samples, gas behaviour models have been discussed (Alder et al., 1969; Bucher et al., 1971; Weiss et al., 1972). For the present work we have analysed 160 samples from one particular alpine glacier and 30 samples from other alpine glaciers. We have measured the total gas content and the fraction of the three dominant components N\textsubscript{2}, O\textsubscript{2} and Ar. The models can now be developed on a much broader base, though still more information has to be obtained. In a next step we will have to study how far the results obtained on the one glacier are representative for other glaciers.
2. THE PRINCIPAL MECHANISMS AND A GAS REMOVAL MODEL

2.1. The occlusion of air in glacier ice
Practically all gas in natural ice is concentrated in air bubbles, as long as the hydrostatic pressure does not exceed 60–80 b. Scholander et al. (1953) have quoted that bubble free ice contains less than 0.03 cm$^3$ gas at STP per kg ice, i.e. $10^{-3}$ times the concentration usually found in natural ice. We shall first discuss two simple extreme cases of gas occlusion:

1. A cylinder of water freezes from one end; the other end is open to the atmosphere (bulk process). In equilibrium with the atmosphere water dissolves 29.0 cm$^3$ of air per kg of ice at STP. When freezing starts, the water close to the ice-water boundary becomes supersaturated. If supersaturation becomes about 30 fold, bubbles are formed, grow and get trapped by the growing ice (Carte, 1961; Bari and Hallett, 1974). The number and size of trapped bubbles depends mainly on the freezing rate. A high rate favours the formation and occlusion of bubbles. The gas composition is close to the composition of air dissolved in water. But in addition the gas composition in the bubbles depends on the diffusion constant of the different gas components in water. Compared with Ar, the diffusion of O$_2$ is faster and the diffusion of N$_2$ is slower (Houghton et al., 1962).

2. Cold dry snow is overburdened by fresh snow, sintered and transformed into ice. The transformation of cold ice grains into a solid mass of ice is effectuated by elimination of pore space and reduction of surface area, as Anderson and Benson (1963) have described. Since this transition is a geometrical process, the composition of the trapped gas is close to air composition (Raynaud and Lorius, 1973). Any initial gas content of the ice grains is small compared to the value of about 100 cm$^3$ gas per kg of ice generally resulting in this compaction process.

In a temperate glacier both processes take place. Meltwater penetration from the surface and refreezing in cold winter snow resembles the bulk process, as well as the freezing of water in crevasses. The densification of firn and its transformation into ice in temperate glaciers resembles sintering of cold firn, though in temperate firn the grains are 'lubricated' by water and sintering is faster. The pore space between the ice grains is filled with air and water. The water originates partly from the surface, partly from internal melting due to frictional heat. Surface water is saturated with air and has little effect on the gases in the pore space. Internal melting mostly takes place in the active layer just above the transition zone of firn into ice (Lliboutry, 1971). If the internal meltwater gets into contact with the air in the pore space, it dissolves a part of the air. Then it is pressed out due to the difference of hydrostatic pressure between the firn and the water. The more soluble gases are therefore depleted in the remaining gas.

Summarizing we can say:

1. In ice formed by sintering of cold, dry firn we expect about 100 cm$^3$ of gas per kg of ice with a main composition very close to atmospheric.

2. In ice formed by freezing a bulk of water saturated with air we expect less than 30 cm$^3$/kg with a composition similar to that of air dissolved in water. The more soluble gases are enriched.

3. In ice formed by sintering in a temperate firn zone we expect ice with a gas content lower than 100 cm$^3$/kg and a composition close to atmospheric, but reflecting depletion of the more soluble gases.
2.2. The removal of gas from temperate glacier ice

Temperate glaciers have an intergranular drainage system (Nye and Frank, 1973). It is difficult to estimate the efficiency of this system, since in a flowing glacier the channels are blocked and re-opened continuously (Lliboutry, 1971; Nye and Mae, 1972). The water filling the channels is either penetrating from the surface or produced by internal melting due to heat of friction.

If one of the channels touches an air bubble, part of the gas will get dissolved in the water, the fraction depending on the saturation degree of the water, on the bubble pressure, and on the duration of contact. Water flowing downwards may be saturated at a certain depth. Nevertheless, reaching a deeper layer, it can dissolve more gas, because there the gas pressure in the bubbles is higher. The pressure increases by about 0.09 b per m depth increase. According to Henry's law and taking into account the different solubilities of the components, 1 kg of water can dissolve 2.7 cm³ STP additional gas of atmospheric composition per each m depth increase.

The dissolution effect of water flowing through a temperate glacier and that of internal meltwater can be compared roughly as follows:

Water flowing through a glacier at a rate of $10^{-4}$ m per year (Lliboutry, 1971) can dissolve as much gas as $10^{-3}$ kg of gas free meltwater in contact with air bubbles at a pressure of 1 b in 1 kg of ice.

Heat of internal friction produces practically gas free meltwater, which in deep strata is particularly efficient regarding dissolution of gases in the immediate neighbourhood. Our opinion is that removal by locally formed meltwater is the dominant mechanism which leads to the observed gas contents and gas compositions.

2.3. A gas removal model

The model describes the development of gas content and gas composition in a mass element of a temperate glacier. Initial gas contents and compositions are taken from analysis of ice samples of the accumulation area.

The model is based on the following assumptions:

1. Any loss of gravitational energy is continuously used for meltwater production.
2. This meltwater is gas free and dissolves a part of the gases in the mass element according to Henry's law. The actual bubble pressure is approximated by the ice pressure.
3. Further interaction of the meltwater with gases in the glacier is neglected. Interaction of surface water flowing through the glacier is also neglected.

In a future version of this model we will consider a more realistic distribution of meltwater production. In addition we plan to include the influence of the water in the drainage system on gas content and composition.

In our calculations we use the following symbols:

- $m_0$: mass of a given piece of ice at the starting point [kg],
- $m(h)$: mass of this piece of ice at a depth of $h$ metres [kg],
- $g$: gravitational constant, 9.810 m/s²,
- $C$: heat of fusion of ice, $3.338 \times 10^5$ J/kg at STP,
- $L_i$: Bunsen's absorption coefficient of the gas $i$ in water [cm³ m²/kg N],
- $p_i$: partial pressure of the gas $i$ [N/m²],
- $V_i(h)$: volume of the gas $i$ in the mass element $m(h)$, reduced to STP [cm³].
\( \rho \) density of bubble free ice, 0.9168 kg/cm\(^3\) at STP,
\( p_0 \) atmospheric pressure [N/m\(^2\)],
\( h(x), x, \delta(x), b, h_0, x_1 \): cf. Fig. 1.

The loss of mass by melting due to gravitational energy is

\[
\frac{dm}{dh} = -\frac{m(h)g}{C} \quad (1)
\]

or as a function of \( m_0 \)

\[
\frac{dm}{dh} = -\frac{m_0 g}{C} \exp\left(-gh/C\right) \quad (2)
\]

The infinitesimal amount \( dm \) of gas-free meltwater will dissolve the volume \( dV \) from gas \( i \) and remove it from the ice:

\[
dV_i = -L_i \frac{V_i}{\sum_j V_j} \left( \rho g \delta(x) + p_0 \right) dm \quad (3)
\]

Thus we get the following system of differential equations:

\[
dV_i = -L_i \frac{V_i}{\sum_j V_j} \left( \rho g \delta(x) + p_0 \right) \frac{m_0 g}{C} \exp\left(-gh(x)/C\right) dh \quad (4)
\]

This differential equation system can be solved analytically and leads to transcendent functions. Our solutions were obtained by stepwise, numerical integration.

Our calculations are based on a model glacier which is shown in Fig. 1. The mass elements flow along parabolas. The maximum vertical thickness of the glacier is 250 m. Then

\[
\delta(x) = 0.1667x - 2.778 \cdot 10^{-5} \cdot x^3 - b
\]

\[
h(x) = h_0 - 2.778 \cdot 10^{-5} \cdot x^3 - b
\]
In Table 1 we give model calculated gas contents and compositions for various distances $x_1$ from the terminus for two typical initial gas contents. The initial composition is equal to the composition of the atmosphere.

<table>
<thead>
<tr>
<th>$b$ [m]</th>
<th>$x_1$ [m]</th>
<th>Relative mass loss by internal melting [%]</th>
<th>Initial gas content Ar/N$_2$ [cm$^3$/kg]</th>
<th>Final gas content Ar/N$_2$ [cm$^3$/kg]</th>
<th>Initial gas content O$_2$/N$_2$ [%]</th>
<th>Final gas content O$_2$/N$_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>3000</td>
<td>0.0</td>
<td>10.00</td>
<td>1.19*</td>
<td>26.8*</td>
<td>1.19*</td>
</tr>
<tr>
<td>200</td>
<td>1658</td>
<td>1.3</td>
<td>8.76</td>
<td>1.01</td>
<td>23.6</td>
<td>1.17</td>
</tr>
<tr>
<td>150</td>
<td>1102</td>
<td>1.8</td>
<td>6.70</td>
<td>0.73</td>
<td>18.4</td>
<td>1.12</td>
</tr>
<tr>
<td>100</td>
<td>675</td>
<td>2.3</td>
<td>4.18</td>
<td>0.41</td>
<td>11.6</td>
<td>1.07</td>
</tr>
<tr>
<td>50</td>
<td>316</td>
<td>2.6</td>
<td>1.37</td>
<td>0.10</td>
<td>3.7</td>
<td>1.01</td>
</tr>
<tr>
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<td>0</td>
<td>2.9</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
<td>0.95</td>
</tr>
</tbody>
</table>

* Ratios of initial gas composition, equal to atmospheric.

It is of special interest to note that for low initial gas contents the variations of both gas content and composition are much stronger than for high initial concentrations. As expected the ratios Ar/N$_2$ and O$_2$/N$_2$ decrease with increasing maximum depth of the flow line. Ar and O$_2$ are more soluble in water than N$_2$.

3. SAMPLE COLLECTION AND ANALYTICAL METHODS

3.1. Description of the sampling sites, sample collection, transport and storage
For our investigations we selected the Griesgletscher (Fig. 2) which is situated near Nufenenpass (Canton Wallis, Switzerland). This glacier has a simple, regular shape, a single firn zone and an ablation zone without larger Gletscherschrunds. The total length is 5.4 km. The highest part of the accumulation area lies at an altitude of 3300 m a.s.l., the firn line between 2850 and 2700 m. The ablation tongue ends in an artificial lake at 2356 m. Samples were taken from nine sites in the ablation area.

Further samples were taken close to the terminus (about 2000 m a.s.l) of the Unteraargletscher (Bernese Oberland). They represent much older ice than could be collected on the Griesgletscher.

Samples from the transition zone of firn to ice had to be collected in the Kesselwandferner (Oetztaler Alps, Austria), where we were allowed to sample at the bottom of a firn pit at 3280 m. The pit was described by Ambach and Eisner (1966), the actual depth is about 30 m. On top of the newly formed ice a 2-m deep water layer had to be pumped off before the samples could be collected.

All samples were taken with a SIPRE core auger. Immediately after augering, the cores were sealed in plastic hoses and placed in a freezer at $-25^\circ$C. After freezer transport to Bern, the samples were stored at $-25^\circ$C before further treatment.

3.2. Gas extraction and analysis
Immediately before analysis, in a freezer room ($-22^\circ$C $\pm$ 5°C), the core samples were cut with a band saw to the appropriate size. Very occasionally during
preparation the formation of cracks was observed; cracked samples were rejected.

We have prepared two kinds of samples:

1. **Small samples in the range of 3–10 g.** The samples were weighed, placed in a brass flask with copper sealing and flushed with ultrapure helium. After melting the samples were transferred into a stripping column, where the gases were extracted and analysed with a gas chromatograph in a similar way as described in earlier publications (Bucher et al., 1971; Weiss et al., 1972). The lower useful working limit of this system is about 0.05 cm³ gas STP per kg ice, if 7-g samples are analysed, the precision of the results is ± 5 per cent. Each sample was determined for absolute content of N₂, O₂, Ar and CH₄.

2. **Large samples in the range of 300–1000 g.** We started gas extraction from larger core samples in order to find good average values in samples, where a detailed analysis reveals strong scattering of gas content and gas composition, to control the effects of opening bubbles and channels while cutting core samples, and to overcome difficulties with the analysis of other gases (e.g. CO₂). The large samples were placed in a glass extraction flask, which was evacuated to clean the sample surface from adsorbed gases. During melting and till boiling the released gases were pumped with a Toepppler pump through four stages of cooled
water traps into a small storage cylinder, where the total gas content was measured. From the cylinder we injected the gases into the gas chromatograph for analysis.

### 3.3. Complementary investigations

Before analysis most samples were inspected and classified for the following qualities:

1. bubble number density,
2. bubble distribution (groups, chains, layers),
3. dominant bubble form (oval, cylindric, irregular, dust content),
4. bubble orientation (random, aligned, intracrystalline),
5. smallest and largest bubble diameter,
6. average crystal size.

These qualities together with the results of gas analysis were transferred onto computer punch cards.

### 4. RESULTS

#### 4.1. Results of the total gas determinations

Figure 3 shows all total gas content determinations for the different sampling sites.

#### 4.2. Results of gas composition determinations and model calculations

Figure 4 shows the gas composition determinations of the Griesgletscher sites in comparison with model calculations. On the top right diagram the shape of the three curves is given by the model parameters (cf. Fig. 1) and the different initial gas compositions. The initial total gas content as a further parameter gives the speed with which the composition changes. We point out that a random distribution initially dispersed around a central point is stretched out along a gas removal curve.

The Kesselwandferner data are similar to the data of site 1, also with respect to other observed data (bubble forms and distribution, crystal forms). The composition of the Unteraargletscher samples is similar to site 8, although the total gas content is a quarter of that of site 8.

On site 2 of the Griesgletscher, samples were determined with an anomalously low O$_2$-content. There, the gas contained 0.27–0.89 per cent CH$_4$, which presumably originated from methane producing bacteria. Reactivation of the bacteria, however, failed because the bacteria may not have survived freezer temperatures.* In many other samples traces of CH$_4$ were detected, but not more than about 50 vol.-ppm. Yet, this is $10^2$ times more than Robbins et al. (1973) measured in cold ice.

### 5. DISCUSSION OF THE RESULTS

The samples from the transition zone of firn to ice (Kesselwandferner) and those of relatively young ice (Griesgletscher, site 1) show, that already in newly formed ice the better soluble gases are depleted. In addition, a strong dispersion of gas content and composition is observed. The depletion effect can be explained

* Personal communication by Zehnder (EAWAG Dübendorf, 1975), who did the Hungate tests (cultivation of CH$_4$-bacteria on special culture media under a CO$_2$-H$_2$-atmosphere).
qualitatively by the sintering model of temperate firn (section 2.1). In comparison to Ar, O\textsubscript{2} is more depleted than may be expected from the difference in solubility. This can be explained qualitatively by the higher diffusion velocity of O\textsubscript{2}, allowing O\textsubscript{2} to escape preferentially during the occlusion by sintering. However, we have not yet attempted to describe the occlusion mechanisms in a quantitative model.

From the samples taken in the Kesselwandferner additional information on gas occlusion is obtained. In the 30-m deep firn pit two kinds of samples were collected. The sample from the wall was not soaked with water, since the 2-m deep water well was pumped out before sampling. Yet, the samples from the bottom were taken from water soaked firn. Immediately after collection all samples were chilled with dry ice. Gas analysis of small samples shows no significant differences, whereas the large sample from the wet core has a higher gas content, indicating a contribution by gases which originally were dissolved in intergranular water. Chains of oblong bubbles were observed visually between the grains. Only by extraction of large samples could the gases contained in grain channels be collected for analysis. During preparation of the small samples many of these channels were opened and the gases were lost while flushing.

The changes of gas content and composition during ablation as observed in the ice cores from the different sites on the Griesgletscher are described surprisingly well by our simple gas removal model (cf. Fig. 4, especially bottom diagrams). The good agreement may be partly accidental. In particular for the upper layers the meltwater production is overestimated. In these layers the water flowing through the intergranular vein system may be the dominant effect of gas removal.

With increasing distance from the firn line the individual data are dispersed increasingly in gas composition. Mass elements with smaller initial gas content are more affected by gas removal during flow in the glacier than mass elements with high initial content.

Future work on temperate ice should follow the following lines:

1. **Modelling:** consideration of location of meltwater production—inclusion of the effect by water flowing through the vein system—application of the model on removal of chemical impurities—calculation of gas content and composition and of chemical impurities in the intergranular water.

2. **Experimental work:** extension of the studies to glaciers with different characteristics (different in altitude, slope, length)—analysis of gas content and chemical impurities in water and in cores from deeper boreholes, possibly down to the bedrock.

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REFERENCES


DISCUSSION

Lambert:
Did you measure CO₂ in the bubbles?

Bucher:
We made preliminary analyses of CO₂ on samples from large extractions, and it is planned to go on and improve the technique. However, we point out that CO₂-analysis in ice, especially in temperate ice is a crucial point. In temperate ice CO₂ might strongly be affected by organic activity. The presence of organic activity is demonstrated by the samples which showed very low O₂-contents and considerable amounts of CH₄.

Glen:
I can see that your model is reasonable for a simple glacier such as Griesgletscher. In a large glacier, particularly one with one or more ice falls, the ice at the lower end has a banded structure which appears to be formed at depth by islands of bubbles in layers that are probably due to air trapped when crevasses closed. Such bubbles would be a complication. Do you agree? Were any of the glaciers you studied ones where this applied?
Buchner:
We are aware of the complication crevasse trapped bubbles bring. Another complication would be bubbles forming by percolation in cold firm. Just to overcome this we choose the Griesgletscher, where sintering is the main trapping mechanism. For a more complicated glacier we would either have to show that sintering is still dominant or have to adjust the initial values of our calculations.

Raynaud:
You have already measured higher Ar concentrations in temperate glacier ice than in the atmosphere (Jungfraujoch). Do you have any new results confirming this effect?

Buchner:
We suspect that the samples from Jungfraujoch which have a higher than atmospheric Ar concentration were formed by freezing saturated percolation water in the cold ice cap of Jungfraujoch, as published earlier. In samples from site 1, Griesgletscher, and from the firn pit on the Kesselwandferner the mean Ar concentration was dispersed around atmospheric Ar concentration, i.e. we found samples enriched in Ar by as much as a factor 1.2.

Oeschger:
The physical processes which may be responsible for removal of chemical traces were treated in the paper by Glen and Homer and the following discussion. The gas removal model shown in our paper could be applied in a similar way to the removal of chemical traces. I would like to ask Glen, if he sees the possibility of parameterizing the physical processes which are responsible for removal of chemical traces in such a way that they can be used for a semi-empirical removal model.

Glen:
I agree, it would be valuable to cooperate, but I do not think we are in a position to parameterize our model—we would need to know much more than we do about the recrystallization process, and in particular how frequently recrystallization occurs. This is not very susceptible to theoretical or even laboratory studies and might well be best investigated in the field.

Weiss:
Does your model imply that all meltwater is equilibriated with all gas bubbles? Your calculation of the amount of meltwater as a function of the release of potential energy by change in elevation seems to give the right amount of $O_3/N_2$ and $Ar/N_2$ ratio deduction. This result would be altered, either if some of the bubbles did no equilibrate with this meltwater, or if there were additional melting from other heat sources.

Buchner:
We understand the interaction of the meltwater with the bubbles in the glacier as a stochastic process, i.e. on its way through the glacier a certain bubble may equilibriate with meltwater for several times or not at all. Our analytical results are in each case the mean of dozens or hundreds of bubbles and the model calculations start from these mean values. Moreover the amount of meltwater assumed in our model is a very rough estimate. Therefore, it is not worthwhile to take smaller effects into consideration.
Delmas:
You made the assumption that the different speeds of diffusion of gases in ice could explain the effects observed during trapping. But the phenomena in snow are very slow. Do you not think that, for this reason, the effects due to diffusion are unimportant?

Bucher:
Our model concerns only gas removal after trapping. The various gas contents and compositions in ice just after bubble formation are taken as given initial values. However, we tried to explain quantitatively their dispersion, the depletion of $O_2$, and the depletion of more soluble gases in newly formed temperate ice. There we have to consider the diffusion of gases in meltwater, which is one possible process, which, as we think, is more important than adsorption. But explaining the details of the micro-processes involved and quantitative calculations would need considerable additional efforts.