CORRECTION OF AIR-CONTENT MEASUREMENTS IN POLAR ICE FOR THE EFFECT OF CUT BUBBLES AT THE SURFACE OF THE SAMPLE

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ABSTRACT. Air content (V) of polar ice has been used as an indicator of the past elevation of the ice sheets. A calculation is presented to correct V measurements performed on ice samples for the effect of cut bubbles at their surface. The results indicate a correction ranging from 1 to 10% for cubic ice samples with about 3 cm length. The correction depends mainly on the size of the bubbles. The theoretical calculation is experimentally verified. The statistical noise linked with the presence of a finite number of bubbles in the ice samples is evaluated. The influence of such a correction on the V profiles measured on polar ice cores is discussed. The method in this paper can also be used for correction of ice-density data obtained by the hydrostatic method.

INTRODUCTION

The air content (V), also called total gas content, of polar ice is a sensitive indicator of the elevation at which the ice was formed and hence provides a sort of "palaeoaltimeter" (Raynaud, 1982). This air is trapped as bubbles when the snow transforms into ice. Deeper in the ice sheet, several hundred meters below the surface, the gas molecules become entrapped as gas-hydrates (clathrates) and the bubbles progressively disappear. Nevertheless, after a deep ice core is drilled, the hydrostatic pressure surrounding the core decreases to 1 atmosphere. The ice relaxes and cavities containing air re-appear. Thus, when an ice sample is cut (generally in a cubic form) for V measurement, some bubbles (and/or cavities) are open at its surface and the corresponding air is lost. As stressed in previous works (Raynaud, 1982; Higashi and others, 1983), this loss may be a possible source of error when measuring V profiles. It is possible to correct the V measurements for this gas lost by a calculation involving the measured V value, the size of the sample, and the size and shape of the bubbles. Bubble size, and hence gas lost, generally decreases with depth at a given site. Bubble size also depends on the origin site of the ice (generally, colder sites have a larger number of smaller bubbles). This means that the gas-loss correction could be important when comparing V measurements at different depths along the same core or from different sites.

Two very similar approaches for estimating this correction have been developed simultaneously and

independently at the Arctic and Antarctic Research Institute (AARI) in Leningrad and at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) in Grenoble. The first approach, more simple to use, gives a mean statistical result. The second approach also indicates how sensitive the result is to the random distribution of a finite number of bubbles in the cube, and could be easier to extend to bubble shapes which are not taken into account in this paper. The calculation is also applied to some V results, and is finally compared to the approach by Higashi and others (1983). The discussion will be mainly restricted to bubbly ice; the case of deep ice with cavities resulting from clathrate relaxation will be mentioned in the section dealing with the experimental test of the calculation.

DESCRIPTION OF THE TWO CUT BUBBLES CORRECTION METHODS

Principles

The calculation is based on a statistical relation (Saltikov, 1976) which links the ratio n_c/n_t to $\langle H \rangle$, where n_c is the number of cut bubbles that appear on a unit surface area, n_t the number of bubbles per volume unit, and $\langle H \rangle$ the mean size of a convex bubble (that is to say, the mean distance between two parallel planes oriented at random, and tangential to the bubble). Saltikov demonstrated that for convex bubbles placed and oriented randomly in space, with the same shape but any size spectrum:

$$n_c/n_t = \langle H \rangle. \tag{1}$$

In the case of a cubic sample with length A (surface area = $6A^2$ and volume = A^3), Equation (1) leads to:

$$N_c/N_t = 6\langle H \rangle / A \tag{2}$$

where N_t is total number of bubbles in the cube (including cut bubbles) and N_c is number of cut bubbles. N_c/N_t can therefore be calculated knowing $\langle H \rangle$ and A.

Another approach to estimating N_c/N_t is to place at random in a cube the centres of N_t bubbles having all the same size and shape. A criterion for finding the cut bubbles is defined as a function of the distance between the centre of a bubble and each surface of the cube. This criterion is dependent on the size, the shape, and the spatial orientation of the bubbles. Using it, a computer program tests each bubble and then counts the bubbles which are cut (N_c) . The effect of the random distribution of a finite number of bubbles in the ice cube will be evaluated by comparing the results of different runs with the same parameters. Only bubbles with the same size will be considered here, but a bubble-size spectrum has also been taken into account by making some small modifications to the computer program. No difference has been observed by introducing a mean bubble size or when using a full bubble-size spectrum.

Either by counting the cut bubbles or by using Equation (2), a value of the ratio N_C/N_t is obtained. Let V_{meas} be the measured value of air content and V the air content corrected for the cut bubbles at the surface of the sample. On average, the bubbles are cut in their middle, and the gas lost corresponds to the gas volume included in $N_C/2$ bubbles. The percentage of gas lost is then obtained from:

$$(V - V_{\text{meas}})/V = N_{\text{c}}/(2N_{\text{t}})$$
 (3)

and V is given by:

$$V = V_{\text{meas}} / (1 - N_{\text{c}} / (2N_{\text{t}})).$$
 (4)

The effects of edges and corners of the cube are neglected as the bubble size is much smaller than A. To determine the ratio N_c/N_t , the bubble shape has to be known.

Equation (3) can easily be extended to samples of any arbitrary form:

$$(V - V_{\text{mass}})/V = (1/2)(n_c/n_t)(s/v)$$
(5)

where s is the surface of the sample and ν is its volume. Nevertheless, for the sake of simplicity, we will only consider here, for the calculation, cubic samples.

Choice of simple bubble shapes

From ice-core observations in the depth range extending from a few tens of meters to a few hundreds of meters below the close-off level, the most simple suitable bubble geometries appear to be spheres and cylinders. The cylindrical type bubbles (generally found together with almost spherical bubbles) can be found oriented in the same direction (this is the case when the ice motion is important). They are also found in the case of newly formed ice without any preferred orientation. Deeper, but above the clathrate-formation zone, the bubbles are generally spherical. We have therefore considered three kinds of bubbles: spherical bubbles, cylindrical bubbles all oriented in the same direction (taken parallel to a side of the cubic sample, which leads to a minimum evaluation of the gas loss), and cylindrical bubbles oriented at random.

Calculations for spherical bubbles

For spherical occlusions of any size spectrum, $\langle H \rangle$ is equal to the mean diameter of the bubbles $\langle D \rangle$. According to Equations (2) and (3), the percentage of gas lost can then be obtained as a function of measurable quantities from:

$$(V - V_{\text{meas}})/V = 3\langle D \rangle / A, \tag{6}$$

In order to write the computer program, one needs to define a criterion for finding the cut bubbles. We consider spherical bubbles with the same diameter (D). The bubbles located partly (i.e. cut at the surface) or completely in the cube have their centres located in a volume $(A + D)^3$ (see Fig. 1). N'_t centres of bubbles are introduced in that volume $(N'_t = N_t + N_c/2)$. A bubble is cut if, and only if, the distance between its centre and one surface of the cube is smaller than D/2. This criterion allows one to determine N_c . In practice, a Cartesian marker is used, with its origin located at the centre of the cube and whose axes are the three normals to the sides of the cube. The three coordinates X_i (i = 1,2,3) of each bubble centre are chosen at random at the interval [-(A + D)/2, +(A + D)/2]. The criterion for finding the cut bubbles is:

for at least one of the
$$X_i$$
, $|A/2 - X_i| \le D/2$ or



Fig. 1. Position of the cut spherical bubbles and of their centres in the cube.

 $|X_i + A/2| \le D/2$. The value of N_c/N_t can be obtained by counting N_c . Equation (3) becomes:

$$(V - V_{\text{meas}})/V = (N_c/2)/(N_t' - (N_c/2)).$$
 (7)

Calculations for cylindrical bubbles all oriented in the same direction

The orientation of cylindrical bubbles with respect to the faces of the cube is shown in Figure 2. The bubbles are considered as cylinders all having the same base diameter D and the same length L, their axes being parallel to a side of the cube.



Fig. 2. Position of the oriented cylindrical bubbles in the cube.

Equation (1) cannot be applied directly, but similar equations are easily obtained:

 $n_c/n_t = D$ for the four lateral sides of the cube,

and $n_c/n_t = L$ for the top and bottom sides of the cube.

The following relations are then obtained for the whole cube:

$$N_{\rm C}/N_{\rm t} = (4A^2D + 2A^2L)/A^3$$
, which leads to:
 $(V - V_{\rm meas})/V = (2D + L)/A.$ (8)

To write the computer program, the case of oriented

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cylinders is very similar to the case of spheres. The $N'_{\rm t}$ bubbles are placed in the volume $(A + D)^2(A + L)$, and a bubble is cut if its centre is located at a distance which is less than D/2 from a lateral side of the cube or at a distance less than L/2 from the top or the bottom sides of the cube. With this criterion, $N_{\rm c}$ can be found and $(V - V_{\rm meas})/V$ is determined using Equation (7).

Calculations for cylindrical bubbles oriented at random The geometry is illustrated in Figure 3. In this case, Equation (1) can be used by taking:

$$\langle H \rangle = (2L + \pi D)/4$$
 (Saltikov, 1976)

where L and D are the mean length and base diameter of the cylindrical bubbles. Equations (2) and (3) then yield the following relationship:

$$(V - V_{\text{meas}})/V = 3(2L + \pi D)/(4A).$$
 (9)



Fig. 3. Cylindrical bubbles oriented at random. $(L^2 + D^2)^{0.5}$ is the diagonal of the bubble.

With the computer program, we consider only cylindrical bubbles with uniform length and diameter. The three coordinates of each bubble centre are taken at random. The three Cartesian coordinates of the vector corresponding to the bubble axis are chosen at random between -1 and 1, and then normalized. As shown in Figure 3, the centres of the N'_t bubbles have to be placed in a volume $(A + (L^2 + D^2)^{0.5})^3$, but all the bubbles located at a distance smaller than $(L^2 + D^2)^{0.5}$ from a side of the cube (let N_d be their number) are not cut (see bubble 1 in Figure 3). We have the following relation between N_t and N_t : $N_t' = N_t + N_d/2$. The criteria for finding cut bubbles and N_c still have to be determined. As shown in Figure 4, a bubble is cut if the distance between its centre and a side of the cube is less than d (see Fig. 4). d can be calculated as a function of L, D, and the considered side of the cube:

$$d = (L/2) |K_i| + (D/2)(1 - K_i^2)^{0.5}.$$

The criterion according to which N_c can be counted is then:

for at least one of the X_i ,

$$|A/2 - X_i| \le d \text{ or } |X_i + A/2| \le d.$$

Thus, the ratio N_c/N_t is obtained by counting the N_c and N_d bubbles and, according to Equation (3),

$$(V - V_{\text{meas}})/V = (N_{\text{C}}/2)/(N_{\text{t}}' - (N_{\text{d}}/2)).$$
 (10)



Fig. 4. Criterion for finding the cut bubbles. The figure plane is defined by the centre of the bubble, the bubble axis, and the normal direction to the considered side of the cube, D, L, and \vec{K} are defined in the text.

Several other bubble shapes could be taken into account. A criterion for selecting the cut bubbles or a value of $\langle H \rangle$ would have to be determined in each specific case.

Case of two types of bubble shapes in an ice sample

The two shapes can be, for instance, spheres and cylinders oriented at random. This case is often observed in newly formed ice. In Table I, the necessary parameters are defined, and expressed for spheres and cylinders oriented at random.

By assuming that air pressure is identical both in spherical and cylindrical bubbles, the percentage of gas lost is obtained from:

$$(V - V_{\text{meas}})/V = [pR_1v_1 + (1 - p)R_2v_2]/[pv_1 + (1 - p)v_2].$$
(11)

Then, the detailed formulae are obtained by replacing R_1 , v_1 , R_2 , and v_2 by their expressions given in Table I.

SENSITIVITY OF THE CALCULATION RESULTS TO THE DATA

The percentage of gas lost: $100(V - V_{meas})/V$ depends on the length A of the ice cube, and on the size and shape of the bubbles. The key parameters for the correction are the size and shape of the bubbles as well as the percentage of spherical and cylindrical bubbles which are measured on thin sections. For ice samples considered in this study, the percentage of spherical bubbles is generally between 40 and 100%, the mean diameter of both spherical and cylindrical bubbles is between 0.1 and 0.6 mm, and the mean length of cylindrical bubbles is between 0.5 and 2 mm. These ranges all lead to gas losses varying between 1 and 10% of the air content. Because the correction is less than 10% of the V value, a 10% error resulting from bubble measurements will lead to an error less than 1% in the corrected air-content value.

Because the mass M of the sample is measured during air-content experiments, and the ice-core density profiles are generally known, the length A of the cube can be obtained from M and the density (ρ), and A can also be measured directly. The uncertainty in the determination of A results in a negligible error on the calculated gas lost.

	TABLE I	
Parameter	Spherical bubbles	Cylindrical bubbles oriented at random
Per cent in number	100 <i>p</i>	100(1 - p)
Bubble volume	$v_1 = \pi D_{\rm S}^3/6$	$v_2 = \pi D_c^2 L_c / 4$
$N_{\rm c}/(2N_{\rm t})$ statistical approach	$R_1 = 3D_{\rm S}/A$	$R_2 = 3(2L_{\rm c} + \pi D_{\rm c})/(4A)$
$N_{\rm c}/(2N_{\rm t})$ computer-program approach	$R_1 = N_{\rm c} / (2N_{\rm t}' - N_{\rm c})$	$R_2 = N_{\rm c}/(2N_{\rm t}' - N_{\rm d})$

Notations: subscript s refers to spherical bubbles (D_s) , and subscript c refers to cylindrical bubbles (D_c, L_c) .

INFLUENCE OF THE RANDOM DISTRIBUTION OF BUBBLES

Comparison of the results obtained with the statistical/ computer-program approaches

This comparison (see Table II) is a simple test of coherence. The result of the statistical approach is compared to the mean result of ten computer runs performed with each set of parameters. It is performed on fictious cases, with a fixed value for A (A = 2.7 cm). The percentages of gas lost have been calculated for several bubble sizes and shapes. The results illustrate the range of gas loss which can be involved. The difference between the results of the two approaches shown in Table II is smaller than the experimental uncertainties linked with the V measurements, and are thus negligible.

TABLE II

Bubble size	Computer-program approact mean gas lost	Statistical approach gas lost	
mm	%	%	
Spherical bubble	es alone		
$D_{\rm s} = 0.1$ $D_{\rm s} = 0.6$	1.2 6.6	1.1 6.7	
- Oriented cylindi	rical bubbles alone		
$D_{c} = 0.1 L_{c} =$	= 0.5 2.5	2.6	

10.0

 $D_{\rm c} = 0.6$ $L_{\rm c} = 1.5$ 10.0

Cylindrical bubbles oriented at random alone

$D_{c} = 0.1$	$L_{\rm c} = 0.5$	3.7	3.7
$D_{\rm c}^{\rm c} = 0.6$	$L_{c}^{o} = 1.5$	14.2	13.6

Notations: D, diameter; L, length; s, sphere; c, cylinder.

Scattering of the computer-approach results

Because of the random distribution of the bubbles in the cube, two different runs with the same parameters will not give exactly the same result. A sensitivity study has been performed in the case of one depth level of the Byrd Station ice core and of another level of the Vostok ice core.

In the case of the Byrd Station core, we made the study for the 116 m depth level. According to Gow (1968), the characteristics of this level are: $\rho = 0.907 \,\mathrm{g\,cm^{-3}}$, spherical bubbles with $D_{\mathrm{S}} = 0.49 \,\mathrm{mm}$, and about 230 bubbles cm⁻³ of ice. Measured V is 0.108 cm³ g⁻¹ (Raynaud and Whillans, 1982). Taking into account these numerical values and assuming $M = 20 \,\mathrm{g}$, the results of ten runs performed indicate V values ranging between 0.1132 and 0.1144 cm³ g⁻¹. For the Vostok core at 169 m depth: $\rho = 0.9065 \,\mathrm{g\,cm^{-3}}$ (Salamatin and others, 1985), spherical bubbles with $D_{\mathrm{S}} = 0.35 \,\mathrm{mm}$ and about 430 bubbles cm⁻³ of ice (Barkov and Lipenkov, 1984; Lipenkov, 1989), measured

random distribution of the bubbles in the sample is large of enough to explain a significant part of the scattering (about 1%) observed when measuring V at LGGE on ice samples ith taken in the same horizontal layer of a core.

V is 0.081 cm³ g⁻¹ (unpublished data obtained at LGGE). With M equal to 20 g the results of ten runs lead to V values in the range 0.0836–0.0841 cm³ g⁻¹.

In the two cases, the scatter of the results due to the

EXPERIMENTAL TEST OF THE CALCULATION

One way to check the validity of the calculation is to measure V on several samples with similar weights but different shapes and taken from the same ice (supposedly homogeneous in air content). We selected an ice core known to have reproducible V measurements. Four samples were prepared from the same horizontal slice of ice, two were cubic (about 3 cm by 3 cm by 3 cm) and two were made each of six parallelepipeds (about 1 cm by 1 cm by 3 cm). The bubbles were spherical with a mean diameter of 0.36 mm. The corresponding V measurement results are given in Table III. Since V_{meas} , s (surface), and v (volume of the sample) are known, we can calculate from Equations (1) and (5) the V values.

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Sample shape	$V_{\rm meas}$	\$	v	V
	cm ³ g ⁻¹	cm ²	cm ⁸	cm ³ g ⁻¹
Cube	0.114	50.9	24.7	0.118
Cube	0.114	52.0	25.9	0.118
Six parallelepipeds	0.107	83.7	18.1	0.117
Six parallelepipeds	0.105	90.7	20.4	0.114

The 2% difference in V between cubic and other samples is much smaller than the difference observed between the uncorrected V values, and is small enough to be explained by the experimental errors on V_{meas} , s, v, and D_{s} .

A similar approach can be used for gas-loss corrections in the case of ice with relaxation cavities. For geometrical reasons and because in relaxed ice all the gas is not necessarily included in the cavities, our calculation based on bubble size and shape measurements cannot be applied. For samples with such cavities, we suggest V measurements are performed with different sample shapes. The gas loss, which is proportional to the surface area of the sample, can be evaluated from these measurements by using Equation (5).

APPLICATION IN THE CASE OF YOUNG ICE

Bubbles are generally larger in newly formed ice. With depth, the bubbles tend to become progressively smaller because of enhanced load and ice compaction. This makes the correction for cut bubbles most important for V

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measurements performed on shallow newly formed ice. A good illustration of that is provided by the V measurements (unpublished data from the LGGE) performed on the 204 m long core taken at D-57 in East Antarctica. At this site, the air is completely trapped in the ice below 75 m depth. Table IV shows the results of the mean V measurements as well as the bubble characteristics for the 100 and 200 m depth levels. Note the important difference (11%) between the V measured at 100 and 200 m. After correcting for cut bubbles (Table IV), the difference in V is reduced to 1%, which is comparable to the experimental precision.

TABLE IV

Depth	Per cent spherical bubbles	D _s	D _c	L _c	$V_{ m meas}$	V
m		mm	mm	mm	cm ³ g ⁻¹	cm ³ g ⁻¹
100	51	0.31	0.28	1.9	0.096	0.108
200	100	0.14			0.107	0.109

COMPARISON WITH OTHER CALCULATIONS

Higashi and others (1983) corrected their total gas-content measurements for bubble cutting using a calculation based on volume (ν), surface (s), and density (ρ) measurements on about 25 samples from the same ice-core section. They calculated a surface-correction factor $\alpha = \pi/s$, where π is the volume of the open pores. Because $(V - V_{\text{meas}})/V$ is the ratio between the volume of the open pores and the total volume of the pores, and knowing α and ρ , the percentage of gas lost can be obtained from:

$$(V - V_{\text{meas}})/V = \alpha s/[M(1/\rho - 1/\rho_i)]$$
 (12)

where M is the sample mass, and ρ_i is the density of bubble-free ice.

No assumption is made on the bubble shape and the precision of the correction does not depend on the size or shape of the bubbles. However, this method requires long and precise measurements of sample surfaces, volumes, and densities in order to get a sufficiently precise value for α .

We measured V at LGGE on pieces of the Mizuho ice core (kindly provided by Dr Nishio), one of the cores studied by Higashi and others, and we calculated both the Higashi and others and the LGGE corrections for cut bubbles on these measurements. The results are given in Table V.

The decrease in $(V - V_{meas})/V$ with depth is primarily due to decreasing bubble size with depth. The results presented in Table V indicate that the two correction methods are in agreement.

The same kind of correction can be applied to ice-density measurements (Higashi and others, 1983; Nakawo and Narita, 1985).

CONCLUSION

The different correction methods for cut bubbles discussed here are in good agreement. As illustrated by the D-57 results, the magnitude of the correction, which ranges from 1 to 10%, decreases rapidly with depth. We demonstrate that this correction is important for samples taken above 200 m depth, but can be neglected between about 300 m and the depth where clathrates appear.

TABLE V

Depth	Calculation method ($V = V_{\rm meas})/V$
m		%
60	Japanese method; Equation (12)	11
75	LGGE calculation; Equation (11) an Table I	d 9
85	LGGE calculation; Equation (11) an Table I	d 6
93	Japanese method; Equation (12)	5

Data used: at 60 and 93 m depth, ρ and α are tabulated in Higashi and others (1983), ρ_i at -15.4°C is 0.91869 (Bader, 1964). At 75 m depth we found 64% spherical bubbles, $D_s = 0.39$ mm, $D_c = 0.32$ mm, $L_c = 1.5$ mm, A = 2.85 cm; at 85 m depth there are 84% spherical bubbles, $D_s =$ 0.33 mm, $D_c = 0.29$ mm, $L_c = 1.1$ mm, A = 2.85 cm.

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