

THE FORMATION AND COMPOSITION OF THE GAS CONTENT OF SEA ICE

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ABSTRACT. The different factors contributing to the formation of the gas porosity of sea ice are: (1a) gases captured during the formation of the initial ice cover, (1b) gases released from solution during the initial freezing of sea-water, (1c) the inclusion of gases rising from the sea bottom, (2a) the substitution of gas for brine drained from the ice during times of melting, (2b) the release of gas from the brine within the ice during the course of partial freezing, and (2c) the formation of voids filled with water vapour during the course of internal melting. An analysis is made of each of these processes and it is concluded that processes 1b, 2a, and 2c are important. Process 1c may also be a major effect but it is difficult to evaluate until the rate of gas release from the sea floor is better known. The migration of air pockets into the ice from the overlying snow is shown to be a possible but not a significant effect. Available data on the composition of gas in sea ice are reviewed and it is shown to be significantly different from air. Possible causes for these differences are discussed.

The porosity of sea ice, i.e. the total relative volume of its gas plus its brine inclusions, is one of the factors strongly affecting its strength, as has been shown by Tsurikov (1947) and by Weeks and Assur (1968). In seas with high salinities the effect of the presence of brine within the ice will usually be the dominant factor. However on water bodies with low salinities the effect of the gas included within the ice may be greater than the effect of the brine. Despite its significance there have not been any attempts at a quantitative analysis of the entrapment of gas in sea ice. This paper is an attempt at such a study.

RÉSUMÉ. *La formation et la composition de la teneur en gaz de la glace de mer.* Les différents facteurs contribuant à la formation de la porosité aux gaz de la glace de mer sont: (1a) Les gaz emprisonnés au moment de la formation de la couverture de glace initiale. (1b) Les gaz rejetés à partir de solutions au cours du gel initial de l'eau de mer. (1c) La capture de gaz montant du fond de la mer. (2a) La substitution de gaz à la saumure qui s'écoule de la glace pendant les périodes de fusion. (2b) Le dégagement de gaz depuis la saumure contenue dans la glace pendant la période de regel partiel. (2c) La formation de vides remplis de vapeur d'eau au cours de la fusion interne. On analyse chacun de ces processus et on conclue que les facteurs 1b, 2a et 2c sont importants. Le processus 1c peut également avoir un effet prédominant, mais il est difficile de l'estimer tant que le taux de dégagement de gaz depuis le fond de la mer n'est pas mieux connu. La migration de poches d'air dans la glace à partir de la neige sus-jacente est, montre-t-on, un effet possible mais non significatif. On passe en revue les résultats connus sur la composition des gaz dans la glace de mer et on montre qu'elle est significativement différente de celle de l'air. On discute les causes possibles de ces différences.

La porosité de la glace de mer c'est à dire le volume total relatif de ces inclusions en saumure et en gaz est l'un des facteurs qui affecte le plus sa résistance mécanique comme l'ont montré Tsurikov (1947) et Weeks et Assur (1968). Dans les mers à haute salinité, l'effet de la présence de saumure dans la glace sera d'ordinaire le facteur dominant. Cependant dans les eaux de faible salinité, les effets de la teneur en inclusions gazeuses peuvent l'emporter sur ceux de la saumure. En dépit de son importance, il n'a pas été possible de donner une idée d'une analyse quantitative de la capture des gaz par la glace de mer. Cet article est une tentative vers une telle étude.

ZUSAMMENFASSUNG. *Die Bildung und Zusammensetzung des Gasgehaltes von Meereis.* Die verschiedenen Prozesse, die zur Bildung der Gasporosität von Meereis führen, sind: (1a) Gaseinschluss bei der Bildung der ursprünglichen Eisdecke; (1b) Gasfreigabe aus der Lösung während des Gefrierprozesses; (1c) Einschluss von Gasen, die vom Meeresgrund aufsteigen; (2a) Ersatz der ausfliessenden Sole durch Gas in Schmelzperioden; (2b) Gasfreigabe aus der Sole im Eis während ihres teilweisen Gefrierens; (2c) Bildung von Hohlräumen, die sich im Verlauf des inneren Schmelzens mit Wasserdampf füllen. Die Analyse jedes dieser Prozesse zeigt, dass die Vorgänge 1b, 2a und 2c bedeutungsvoll sind. Prozess 1c kann ebenfalls grössere Wirkung haben, doch lässt sich dies schwer feststellen, solange das Ausmass der Gasfreigabe vom Meeresgrund nicht besser bekannt ist. Die Wanderung von Gaseinschlüssen aus der Schneedecke in das Eis erweist sich als möglicher, jedoch nicht signifikanter Effekt. Vorhandene Daten über die Gaszusammensetzung werden überprüft und zeigen deren beträchtliche Verschiedenheit gegenüber der Luft. Mögliche Ursachen für diese Unterschiede werden diskutiert.

Die Porosität des Meereises, d.h. das totale relative Volumen seines Gas- und Solegehaltes, ist einer der Faktoren, von dem vor allem seine Festigkeit abhängt, wie Tsurikov (1947) und Weeks und Assur (1968) gezeigt haben. In Meeren mit hohem Salzgehalt dominiert gewöhnlich der Einfluss des Vorhandenseins von Sole im Eis. Hingegen dürfte in Wasserkörpern mit geringem Salzgehalt der Einfluss des im Eis eingeschlossenen Gases höher sein als der der Sole. Trotz seiner Bedeutsamkeit wurden keine Versuche zur Quantitativen Analyse des Gaseinschlusses im Meereis unternommen. Die vorliegende Arbeit möchte diese Lücke schliessen.

PROCESSES RESULTING IN GAS ENTRAPMENT IN SEA ICE

Savel'yev (1963) has proposed dividing the processes involved in the formation of the gas content of sea ice into syngenetic (connected with phenomena occurring under the ice at the time of its formation and growth), and epigenetic (occurring within the ice cover itself). To these should also be added a third group of phenomena which occur at the upper boundary of the ice cover and lead to the entrapment of gas. These latter processes will be called exogenetic.

Savel'yev (1963) has referred to the following three processes as syngenetic:

- 1a. The entrapment of gas within the primary ice layer at a time when it consists of separate crystals that have not, as yet, frozen together. This gas is presumed to be captured partly from the atmosphere and partly from the water.
- 1b. The release of gas from solution during the further freezing of sea-water. This process occurs continuously during ice growth in all the freezing areas of the oceans.
- 1c. The inclusion in the ice of gas bubbles which rise from the sea bottom, primarily as the result of the decomposition of organic matter. Such inclusions are distinguished by their lenticular form, whereas other inclusions are commonly cylindrical or pear-shaped (Kheysin and Cherepanov, 1968; Bari and Hallett, 1974).

It is also possible to imagine four epigenetic processes which result in the formation of gas inclusions:

- 2a. The substitution of air for a part of the brine which, during the course of ice melting, drained downward out of the ice when the initially closed brine pockets change into interconnected vertical brine channels. Zubov (1945) and Savel'yev (1963) consider this to be a cardinal process in the development of the gas porosity of sea ice. Zubov (1945, 1957) even developed a table that allowed the computation of the changes in the bulk density of the ice that result from such substitution. However this process can only occur in the uppermost layers of the ice cover, those above sea-level, because at locations below sea-level sea-water will substitute for the brine.
- 2b. The release of gas from entrapped brine as the result of its further freezing.
- 2c. The formation of water-vapour-filled pores during internal ice melting. When melting occurs on the walls of brine pockets, the volume of melt water that is produced is less than the volume of ice that melts. As a result voids can be formed on the upper ends of the brine pockets. These voids are then quickly filled with vapour as the result of the partial evaporation of ice and brine.
- 2d. The formation of gaseous inclusions from oxygen produced through photosynthesis by algae living in the ice. The possibility of this phenomenon was first noted by Zubov (1945); the latest studies by Buynitskiy (1973) have confirmed this possibility.

There are also two exogenic processes that would result in the formation of gaseous inclusions:

- 3a. The capture of air during the formation of "infiltration" ice, i.e. the ice produced if the snow cover on top of the ice sheet becomes saturated with either sea-water or melt water and then refreezes.
- 3b. The possible migration of air inclusions from the snow cover into the underlying ice cover. Zubov (1945), Savel'yev (1963), and Kheysin and Cherepanov (1969) have noted that when a vertical temperature gradient is present in the ice sheet, sublimation will occur at the warm ends of the air inclusions with the deposition of water vapour occurring at the cold ends. This causes the air bubbles to migrate in a direction opposite to the direction of heat flow. It is only natural to suggest that this phenomenon should result in the migration of air bubbles that originally formed in the snow into the ice.

In considering the different mechanisms that can possibly contribute to the formation of the gas porosity of sea ice, one should remember that it is currently impossible adequately to estimate the quantity of oxygen liberated by algae. It is also difficult to estimate the volume of air that will be included in infiltrated ice in as much as it is unknown what part of the air will be displaced by water.

Syngenetic processes

Process 1a has been investigated by Matsuo and Miyake (1966) who considered the gas content of a primary ice cover composed of horizontally elongated crystals with a random c -axis orientation. We will refer to this layer as the transition layer. It is reasonable to assume that the water trapped between these initial crystals will contain a large amount of dissolved air. There are also probably a number of air bubbles that are initially trapped as well. Matsuo and Miyake also suppose that atmospheric gas diffuses into this layer and obtain, from the diffusion equation, the following expression for the concentration of gas in the ice:

$$C - C_w = (C_\infty - C_w)[1 - \exp(-\beta st/V_t)], \quad (1)$$

where C is the content of a given gas in the ice at time t with time $t = 0$ taken at the beginning of freezing and C_∞ is the content at $t = \infty$, C_w is the concentration of the same gas in the water, V_t is the volume of the transition layer within the limits of area s , and β is the absorption coefficient which is equal to 0.340, 0.346, and 0.76 cm min^{-1} for nitrogen, oxygen, and CO_2 respectively (at a temperature of 0°C). Assuming that the two principal components of the gas entrapped in the ice are nitrogen and oxygen, we can write the following equation for the gas porosity of the ice v_i

$$v_i = C_N + C_O = C_\Sigma, \quad (2)$$

where i is the number of the process.

It is obvious that $s/V_t = h_t$ where h_t is the thickness of the transition layer. In this case, on the basis of Equation (1) we have

$$v_{1a} = C_{\Sigma w} \exp(-\beta t/h_t) + v_\infty [1 - \exp(-\beta t/h_t)]. \quad (3)$$

Here $C_{\Sigma w} = C_{Nw} + C_{Ow}$ and the coefficient β can be taken as approximately 0.342 cm min^{-1} or $2.34 \times 10^{-4} \text{ cm d}^{-1}$.

In Equations (1) and (3), C_∞ and v_∞ are unknown. Matsuo and Miyake did not determine them and their determination would require quite long experiments. Judging from the observations made by Savel'yev (1963) during three months in the Arctic, v_∞ can be more than 0.050. Our own observations made during a 101 d period on the White Sea gives v_∞ greater than 0.112.

Process 1b is caused by the release during freezing of a part of the gases that were initially dissolved in the sea-water. During freezing the salinity and density of the upper layer of the sea of thickness z are raised because of the rejection of salt by the growing ice sheet. This causes what Zubov (1945) has termed the vertical winter circulation. Assuming that this process is basically one-dimensional, if as a result the salinity of the portion of the water column involved in the vertical circulation s_z can be raised by dS_w over the area s during the time dt , then as a consequence the solubility of some gas can be lowered by dL . In this case a gas with a volume $s dL$ can be released from the water column s_z , and the gas concentration in the ice layer that has formed dh will be

$$C = \frac{s_z dL}{s dh} = z \frac{dL}{dh}. \quad (4)$$

If the increase in the depth of the winter circulation layer is neglected in comparison with the value of z , we can determine z from

$$\text{or, } \left. \begin{aligned} dm &= -dm_w, \\ S dM &= -S_w dM_w, \end{aligned} \right\} \quad (5)$$

where dM is the mass of ice in layer dh , dm is the mass of salts included in it, S is its salinity, $-dm_w$ and $-dM_w$ are the decreases in the masses of salt and of water within the limits of the layer z , and S_w is the salinity of the water. The mass changes dM and $-dM_w$ can be expressed in terms of dh , z , s , the ice density δ , and the increase in the water density $d\rho$:

$$dM = \delta s dh,$$

and

$$-dM_w = sz d\rho.$$

Substituting these values in Equation (5), we obtain

$$z = \frac{\delta S dh}{S_w d\rho}, \quad (6)$$

and from Equations (4) and (6)

$$C = \frac{\delta S dL}{S_w d\rho}. \quad (7)$$

Let us now consider the concentration within the ice of the two main gases that are dissolved in the sea-water by writing Equation (7) as

$$C_N = \frac{\delta S dL_N}{S_w d\rho},$$

and

$$C_O = \frac{\delta S dL_O}{S_w d\rho}.$$

Because of Equation (2) we have

$$v_{1b} = \frac{\delta S dL_\Sigma}{S_w d\rho}. \quad (8)$$

Here v_{1b} is the ice porosity which is formed as the result of process 1b and

$$L_\Sigma = L_N + L_O. \quad (9)$$

Note that Equation (8) includes the ice density which is itself connected to the porosity by means of the relation

$$\delta = \delta_p(1 - v_i), \quad (10)$$

where δ_p is the density of pure ice. Therefore instead of Equation (8) we have

$$v_{1b} = \left[\frac{\delta_p S dL_\Sigma}{S_w d\rho} \right] / \left[1 + \frac{\delta_p S dL_\Sigma}{S_w d\rho} \right]. \quad (11)$$

As has been pointed out by Tsurikov (1976), the ratio of the salinities of ice and of water (S/S_w) is related to the rate of growth of the ice cover ($w = dh/dt$) in the following manner

$$S/S_w = [Cl]/[Cl]_w = 7w^3/(7w^3 + 10.30) = f(w). \quad (12)$$

Therefore

$$v_{1b} = \delta_p \frac{dL_\Sigma}{d\rho} f(w) / \left[1 + \delta_p \frac{dL_\Sigma}{d\rho} f(w) \right]. \quad (13)$$

We will use the empirical formulae for the nitrogen and oxygen saturation of sea-water developed by Fox (see Zubov, 1957) in which the results are expressed in dimensionless units. These are

$$L_N = \{18.56 - 0.428 \theta + 0.007452 \theta^2 - 0.00005494 \theta^3 - (0.2149 - 0.00711 \theta + 0.000095 \theta^2)[Cl]_w\} \times 10^{-3}, \quad (14)$$

and

$$L_O = \{10.291 - 0.2809 \theta + 0.006009 \theta^2 - 0.0000632 \theta^3 - (0.1161 - 0.003922 \theta + 0.000063 \theta^2)[Cl]_w\} \times 10^{-3}, \quad (15)$$

where θ is the temperature of the water and $[Cl]_w$ its chlorinity. Newer equations are available for the dependence of the oxygen solubility on temperature and chlorinity; for instance those of Green and Carrit (UNESCO, 1973). However they are complicated and inconvenient to use. Also for the present purposes the differences between the values of L_O calculated by the formulae of Fox and of Green and Carrit are negligible (for $\theta = 0^\circ C$, they do not exceed 0.8% of the quantities themselves, which does not have a great effect on our approximate calculations).

The water temperature at the lower surface of the ice is at the freezing point τ , the exact value of which is dependent on the water composition. The dependence between these two quantities can be simply expressed by using a formula of Miyake (1939)

$$\tau = -0.10271 [Cl]_w. \quad (16)$$

Taking this into account, we can rewrite Equations (14) and (15) as

$$\left. \begin{aligned} L_N &= 18.63 \times 10^{-3} - 171.0 \times 10^{-6} [Cl]_w - \\ &\quad - 0.651 \times 10^{-6} [Cl]_w^2 - 100.1 \times 10^{-9} [Cl]_w^3, \\ \text{and} \\ L_O &= 10.291 \times 10^{-3} - 87.3 \times 10^{-6} [Cl]_w - \\ &\quad - 0.402 \times 10^{-6} [Cl]_w^2 - 66.4 \times 10^{-9} [Cl]_w^3, \end{aligned} \right\} \quad (17)$$

from which we obtain

$$\left. \begin{aligned} dL_N &= -171 \times 10^{-6} d[Cl]_w - 1.302 \times 10^{-6} [Cl]_w d[Cl]_w - \\ &\quad - 300.3 \times 10^{-9} [Cl]_w^2 d[Cl]_w, \\ \text{and} \\ dL_O &= -87.3 \times 10^{-6} d[Cl]_w - 0.804 \times 10^{-6} [Cl]_w d[Cl]_w - \\ &\quad - 199.2 \times 10^{-9} [Cl]_w^2 d[Cl]_w. \end{aligned} \right\} \quad (18)$$

To obtain the density of sea-water we will use the empirical equation of Knudsen (Forch and others, 1902)

$$\rho = 1 + \sigma_d \times 10^{-3} + (\sigma_0 + 0.1324)[1 - A(\theta) + B(\theta)(\sigma_0 - 0.1324)] \times 10^{-3}, \quad (19)$$

where σ_0 is the relative density for $0^\circ C$, σ_d is the relative density of distilled water, and $A(\theta)$ and $B(\theta)$ are functions of temperature. σ_0 can be expressed as a function of the chlorinity of the sea-water by

$$\sigma_0 = -0.069 + 1.4708 [Cl]_w - 0.001570 [Cl]_w^2 + 0.0000398 [Cl]_w^3, \quad (20)$$

and σ_d , $A(\theta)$, and $B(\theta)$ vary with temperature as

$$\sigma_d = \frac{(\theta - 3.98 \text{ deg})^2}{603.570} \frac{\theta + 283 \text{ deg}}{\theta + 67.26 \text{ deg}}, \quad (21)$$

and

$$\left. \begin{aligned} A(\theta) &= (4.7867 - 0.098185 \theta + 0.0010843 \theta^2) \times 10^{-3}, \\ B(\theta) &= (18.30 - 0.1864 \theta + 0.01667 \theta^2) \times 10^{-6}. \end{aligned} \right\} \quad (22)$$

Because in the case we are considering $\theta = \tau$ and τ is associated with the chlorinity of the water via Equation (16), we can solve Equations (19) to (22) neglecting the terms in $[\text{Cl}]_w$ with powers higher than the third. Differentiating the resulting equation we obtain

$$d\rho = \frac{-4.50[\text{Cl}]_w^2 d[\text{Cl}]_w - 0.025[\text{Cl}]_w d[\text{Cl}]_w - 2.42 d[\text{Cl}]_w}{2.670[\text{Cl}]_w^2 - 3.500[\text{Cl}]_w + 1.140} + \frac{+1.4709 \times 10^{-3} d[\text{Cl}]_w - 4.95 \times 10^{-6} [\text{Cl}]_w d[\text{Cl}]_w - 2.24 \times 10^{-6} d[\text{Cl}]_w}{(23)}$$

By means of Equations (18) and (23), the values of $dL_N/d\rho$, $dL_O/d\rho$, and $dL_\Sigma/d\rho$ given in Table I can be calculated. The results obtained by graphically interpolating the derivatives (Fig. 1) can then be substituted in either Equation (11) or Equation (13) to determine the ice porosity v_{1b} .

TABLE I. THE DERIVATIVES $dL_N/d\rho$, $dL_O/d\rho$, AND $dL_\Sigma/d\rho$

$[\text{Cl}]_w$ ‰	$dL_N/d\rho$ $\times 10^{-3}$	$dL_O/d\rho$ $\times 10^{-3}$	$dL_\Sigma/d\rho$ $\times 10^{-3}$
2	3.3	1.7	4.0
3	10.0	5.1	15.1
5	32.6	17.0	49.6
7	65.2	34.5	99.7
9	95.0	50.2	145.2
10	114.4	61.3	175.7
11	141.1	76.6	217.7
13	177.4	94.8	242.2
15	200.0	112.4	312.4
17	200.0	112.4	312.4
19	200.1	114.8	314.9
20	200.7	115.7	316.4

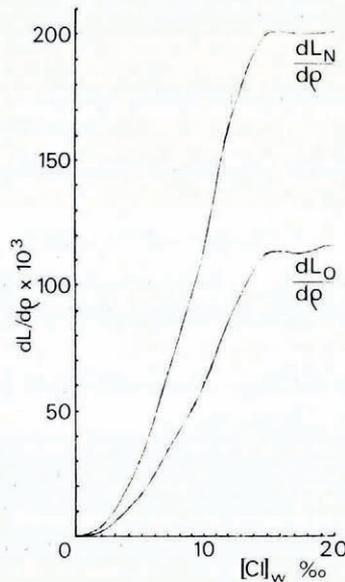


Fig. 1

Process 1c, i.e. the gas release from the sea bottom, can be treated by assuming that the rate of release is constant

$$dv/dt = A = \text{const.}$$

Hence in the time interval dt a gas volume equal to dV is released and will accumulate at the base of the ice sheet. In addition

$$dV = A dt, \tag{24}$$

and from Stefan's (1891) analysis of ice growth

$$dh/dt = k_i(\tau - \theta)/\Lambda h, \tag{25}$$

and

$$dt = \Lambda h dh/k_i(\tau - \theta), \tag{26}$$

where k_i is the thermal conductivity of ice, θ is the temperature of the upper boundary of the ice, and Λ is the quantity of heat necessary for the formation of 1 cm³ of sea ice at a temperature equal to the freezing point of sea-water τ . From Equations (24) and (25) we now have

$$dv = A\Lambda h dh/k_i(\tau - \theta).$$

Here the value Λ is equal to the density of sea ice δ multiplied by the latent heat of pure ice λ and by a factor which gives the mass of pure ice in 1 g of sea ice. According to Tsurikov (1975), this factor is equal to or larger than 0.1. Hence $\Lambda \geq 0.1\lambda\delta$ and

$$dv \geq \frac{A\lambda\delta}{10k_i(\tau - \theta)} h dh. \tag{27}$$

It should be noted that if in this equation $\tau = \theta$, i.e. if the temperature gradient is equal to zero, ice growth stops.

Now consider the porosity of some layer, say $h_2 - h_1$. In this case we must integrate Equation (27) within the limits of 0 to v_{1c} and h_1 to h_2 . As a result we have

$$v_{1c} \geq \frac{A\lambda\delta}{20k_i(\tau - \theta)} \Delta h^2,$$

where $\Delta h^2 = h_2^2 - h_1^2$. Now taking Equation (10) into account we have

$$v_{1c} \geq \left[\frac{20k_i(\tau - \theta)}{A\lambda\delta\Delta h^2} + 1 \right]^{-1}, \tag{28}$$

and if we wish to consider the porosity of the complete thickness of the ice cover, then $h_1 = 0$ and

$$v_{1c} \geq \left[\frac{20k_i(\tau - \theta)}{A\lambda\delta\Delta h^2} \right]^{-1}. \tag{29}$$

Epigenetic processes

Process 2a (i.e. the substitution of air for a part of the brine) occurs during the course of ice melting, when closed brine pockets change into interconnected channels that extend through the ice sheet. The process should be analysed starting from a knowledge of the volume of substituted brine. The relative volume of brine in the complete thickness of the ice cover is equal to the ratio of the brine volume V_b to the total ice volume considered

$$v_b = V_b/sh.$$

By analogy, the relative volume of brine in the portions of the ice above water-level and below water-level must be

and
$$\left. \begin{aligned} v_{b0} &= V_{b0}/sz_0, \\ v_{bu} &= V_{bu}/sz_u, \end{aligned} \right\} \tag{30}$$

where z_u and z_o are draft and free-board of the ice relative to sea-level. Because $V_{b0} = V_b - V_{bu}$, according to the last three equations we have

$$V_{b0} = shv_b - sz_u v_{bu} = [hv_b - (h - z_o) v_{bu}] s,$$

and from Equation (30) we obtain

$$v_{b0} = \frac{[hv_b - (h - z_o) v_{bu}] s}{sz_o} = \frac{h}{z_o} v_b - \left(\frac{h}{z_o} - 1 \right) v_{bu}. \quad (31)$$

From Archimedes Principle, if the ice is not covered with snow, it follows that

$$Mg = M_w g, \quad (32)$$

where M and M_w are the masses of ice and displaced water respectively and g is the acceleration due to gravity. The assumption about the absence of snow on the ice is reasonable because the snow cover usually melts before significant melting starts within the ice itself. We then rewrite Equation (32) as

$$\delta h = \rho z_u = \rho(h - z_o),$$

where

$$h/z_o = \rho/(\rho - \delta). \quad (33)$$

As the brine in the above-water part of the ice is replaced by air we can rewrite Equation (31) as

$$v_{2a} = \frac{hv_b}{z_o} - \left(\frac{h}{z_o} - 1 \right) v_{bu},$$

and then substituting from Equation (33)

$$v_{2a} = \frac{\rho v_b}{\rho - \delta} - \left(\frac{\rho}{\rho - \delta} - 1 \right) v_{bu}. \quad (34)$$

Next taking Equation (10) into account we obtain

$$\delta_p v_{2a}^2 + (\rho - \delta_p + \delta_p v_{bu}) v_{2a} - \rho v_b + 2\rho v_{bu} + \delta_p h v_{bu} = 0,$$

which, when solved as a quadratic equation, becomes

$$v_{2a} = \frac{1}{2} \frac{\rho}{2\delta_p} \frac{v_{bu}}{2} \pm \left(\frac{\delta_p}{2} \frac{\rho^2}{2\delta_p} + \frac{\delta_p v_{bu}}{2} - \rho - 5\rho v_{bu} + 4\rho v_b - 2\delta_p v_{bu} \right). \quad (35)$$

Tsurikov (1976) concluded that the formation of through channels occurs only after the relative brine volume on every horizon of the submerged portion of the ice reaches a value of at least 0.044. Then assuming that v_{bu} is equal or greater than its minimum, we can obtain an estimate of the maximal value for v_{2a} from Equation (34). First we note that the density of pure ice δ_p only changes from 0.917 (at 0°C) to 0.922 (at -23°C) and if we take an average value of $\delta_p = 0.92$ the possible error from this source will not be more than 0.3%. Also, although the density of sea-water varies with temperature and composition, if we consider its value to be $\rho = 1.00$ the possible error due to this is less than 3%. Taking these approximate values into account, Equation (35) can be written as

$$v_{2a} = -0.063 \pm (-1.362 + 4v_b). \quad (36)$$

If from the two roots of Equation (36) we select the one which gives the increase of v_{2a} that depends on the increase in v_b as in Equation (34), we obtain

$$v_{2a} = 4v_b - 1.425. \quad (37)$$

Process 2b considers the release upon further freezing of gas that is dissolved in brine trapped within sea ice. During the course of freezing, sea-water with a mass of ρV_w turns into pure ice with mass $\delta_p V_p$ and brine with mass $\rho_b V_b$. From this we can write

$$\rho V_w = \delta V = \delta_p V_p + \rho_b V_b, \quad (38)$$

where V_w is the volume of the frozen water, and V , V_p , and V_b are the volumes of the sea ice, pure ice, and brine respectively. During this process some of the gas that was initially dissolved in the unfrozen sea-water having a concentration of C_w will still remain in the brine where the gas concentration has now reached saturation concentration L and some will come out of solution resulting in gas-filled pores within the ice. Therefore

$$C_w V_w = L V_b + C V, \tag{39}$$

where C is the relative gas content of the ice.

From Equation (38) we have

$$V_w = \delta V / \rho,$$

and, as has been demonstrated by Tsurikov and Tsurikova (1972), the relative mass of brine in the ice $\rho_b V_b / \delta V$ is equal to the ratio of the chlorinity of sea ice to that of the brine

$$\rho_b V_b / \delta V = [Cl] / [Cl]_b. \tag{40}$$

Now, substituting the last two equations in Equation (39), we have

$$C = \frac{\delta C_w}{\rho} - \frac{\delta L [Cl]}{\rho_b [Cl]_b}, \tag{41}$$

and, taking Equation (2) into account

$$v_{2b} = \frac{\delta}{\rho} (C_{Nw} + C_{Ow}) - \frac{\delta}{\rho_b} (L_N + L_O) \frac{[Cl]}{[Cl]_b}, \tag{42}$$

where C_{Nw} and C_{Ow} are the concentrations of nitrogen and oxygen in the sea-water before it freezes. Now denoting $C_{Nw} + C_{Ow} = C_{\Sigma w}$ and substituting the value of δ as obtained from Equation (10) into Equation (41) we obtain

$$v_{2b} = \left[\frac{\delta_p}{\rho} C_{\Sigma w} - \frac{\delta_p L_{\Sigma} [Cl]}{\rho_b [Cl]_b} \right] / \left[1 + \frac{\delta_p}{\rho} C_{\Sigma w} - \frac{\delta_p L_{\Sigma} [Cl]}{\rho_b [Cl]_b} \right]. \tag{43}$$

This equation includes the densities of brine ρ_b , sea-water ρ , and pure ice δ_p all of which are variables. However the possible error resulting from taking $\rho_b = 1.10$ cannot be more than 7% ($\rho_b = 1.00$ at $-0.2^\circ C$ and 1.19 at $-23^\circ C$). The errors resulting from assuming $\rho = 1.00$ and $\delta_p = 0.92$ are even less, as stated earlier 0.3 and 3.0% respectively. Hence as an approximation we can obtain from Equation (43)

$$v_{2b} = \left[0.92 C_{\Sigma w} - 0.84 L_{\Sigma} \frac{[Cl]}{[Cl]_b} \right] / \left[1 + 0.92 C_{\Sigma w} - 0.84 L_{\Sigma} \frac{[Cl]}{[Cl]_b} \right]. \tag{44}$$

I know of no determinations of the solubility of gases in the brine formed from freezing sea-water. Therefore to obtain values of L_N and L_O we have used Equation (17) even though this equation can only be used with confidence to chlorinity values corresponding to sea-water ($[Cl]_b < 20\%$) and to temperatures above $-2.0^\circ C$. Values of L_N and L_O so calculated are presented in Table II and are positive only to some limiting $[Cl]_b$ value which appears to lie in a range between 83 and 86%. This corresponds to a freezing temperature of between

TABLE II. LIMITS OF BRINE SATURATION BY NITROGEN AND OXYGEN

$[Cl]_b$ %	τ °C	L_N $\times 10^{-3}$	L_O $\times 10^{-3}$	L_{Σ} / L_N
1	-0.1	18.4	10.3	1.56
10	-1.0	16.8	9.1	1.60
20	-2.0	14.8	8.5	1.64
50	-5.3	8.5	4.6	1.54
100	-13.2	-9.1	-4.8	1.54
				Weighted mean: 1.56

−8.4 and −8.8°C. Furthermore, from Table II we can see that the value of L_{Σ}/L_N changes only slightly. Therefore taking its value as 1.56 we can simplify Equation (44) to

$$v_{2b} = \{0.92C_{\Sigma W} - 1.32L_N[\text{Cl}]/[\text{Cl}]_b\} / \{1 + 0.92C_{\Sigma W} - 1.32L_N[\text{Cl}]/[\text{Cl}]_b\}. \quad (45)$$

Values of L_N and L_O for different values of the chlorinity of the brine are given in Figure 2.

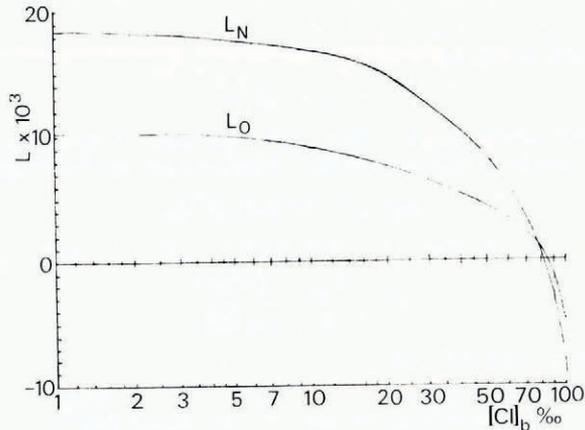


Fig. 2

Process 2c is concerned with the formation of pores that are filled with water vapour. As ice temperatures decrease during a period of ice growth, ice gradually freezes out of the brine so that the brine composition will change to the specific composition that is in equilibrium with ice at the new temperature. The volume of ice that is formed will be more than the volume of brine that it has replaced. As a result strains will occur in the ice causing stresses which can exceed the strength of the ice and result in the formation of cracks. In the opinion of Savel'yev (1963) these cracks quickly refreeze.

In the course of the following rise of temperature $d\theta$, a part of the ice that forms the walls of the brine pockets will be dissolved and the volume of brine will increase by dV_b , a volume which is less than the volume of melted ice dV_p . If cracking of the ice took place on the previous cooling cycle and the cracks refroze, a void with the volume

$$dv = dV_p - dV_b \quad (46)$$

can appear on the upper ends of the brine pockets. These voids are quickly filled with water vapour as a result of the partial evaporation of ice and brine.

It is obvious that $V_p = M_p/\delta_p$. Also if we neglect the relatively small mass of crystallized salts and assume that $M = 1$, we have $M_p + M_b = 1$ and hence $V_p = (1 - M_b)/\delta_p$, so

$$V_p = \frac{1}{\delta_p} - \frac{\rho_b}{\delta_p} V_b,$$

and

$$dV_p = -\frac{\rho_b}{\delta_p} dV_b.$$

Then instead of Equation (46) we can write

$$-dv = \left(\frac{\rho_b}{\delta_p} + 1 \right) dV_b,$$

or, taking Equation (40) into account,

$$-dv = \left(\frac{1}{\delta_p} + \frac{1}{\rho_b} \right) d([Cl]/[Cl]_b).$$

This equation can be integrated between the limits 0 and V_{2c} or $([Cl]_b)_0$ and $([Cl]_b)_2$, taking into account that $d[Cl] = 0$ in as much as the chlorinity of the ice is not dependent on temperature. As a result we have

$$v_{2c} = \left(\frac{1}{\delta_p} + \frac{1}{\rho_b} \right) [Cl] \Delta([Cl]_b^{-1}),$$

where

$$\Delta([Cl]_b^{-1}) = \left(\frac{1}{[Cl]_b} \right)_0 - \left(\frac{1}{[Cl]_b} \right)_2. \tag{47}$$

Because $\delta_p \approx 0.92 \text{ Mg m}^{-3}$ and $\rho \approx 1.10 \text{ Mg m}^{-3}$ we can write

$$v_{2c} = 2.00[Cl] \Delta([Cl]_b^{-1}). \tag{48}$$

Exogenetic processes

Of the two exogenetic processes we mentioned earlier, no way has been found to develop a quantitative formulation of process 3a, therefore we will only discuss process 3b.

Process 3b which is concerned with the migration of air inclusions across the snow-ice interface can be investigated using a theoretical relation developed by Kheysin and Cherepanov (1969). In considering the rate of migration ($d\zeta/dt$) of spherical air bubbles through ice they obtained

$$\frac{d\zeta}{dt} = \frac{2k_i D}{k_a + 2k_i + \lambda \delta} \frac{1}{\delta} \frac{\partial \gamma}{\partial \theta} \frac{\partial \theta}{\partial z}, \tag{49}$$

where k_i and k_a are the thermal conductivities of ice and air, D is the diffusion coefficient for water vapour in air, and γ is the density of saturated water vapour. According to Kheysin and Cherepanov the values of these parameters when applied to Equation (49) are $k_i = 54 \times 10^{-4} \text{ cal g}^{-1} \text{ cm}^{-1} \text{ s}^{-1}$, $k_a = 5.84 \times 10^{-3} \text{ cal g}^{-1} \text{ cm}^{-1} \text{ s}^{-1}$, $D = 22 \text{ cm}^2 \text{ s}^{-1}$ and $\delta = 0.9 \text{ g cm}^{-3}$. If the snow is quite fresh we can consider that $\lambda = 80 \text{ cal g}^{-1}$ and we can obtain values for $\partial \gamma / \partial \theta$ from table 132 in Zubov (1957). In Table III we have calculated the migration rate of air bubbles as a function of temperature for a constant temperature gradient $\partial \theta / \partial z$ of 1 deg/cm. For comparison the migration rate of the air bubbles is two orders of magnitude smaller than for brine pockets (values also given in Table III). Hence the motion of air inclusions from snow into ice, although possible, is clearly not of major importance.

TABLE III. THE RATE OF MIGRATION OF AIR BUBBLES AND BRINE POCKETS IN THE ICE WITH THE TEMPERATURE GRADIENT 1/deg cm⁻¹.

θ °C	$d\zeta/dt$ air nm h ⁻¹	$d\zeta/dt$ brine nm h ⁻¹	θ °C	$d\zeta/dt$ air nm h ⁻¹	$d\zeta/dt$ brine nm h ⁻¹
-1	1.01	320	-8	0.36	29
-2	0.85	100	-9	0.30	26
-3	0.75	70	-10	0.26	23
-4	0.66	52	-11	0.22	20
-5	0.56	44	-12	0.19	18
-6	0.44	39	-13	0.16	16
-7	0.41	34	-14	0.13	14

CALCULATIONS OF POSSIBLE GAS POROSITY IN SEA ICE

Let us consider young ice about 8 cm thick having a temperature of -10°C at its upper surface and -1.9°C (i.e. the freezing point of sea-water) at its lower surface. If this temperature gradient were to remain unchanged it would take 5.5 months for an air bubble 1 mm in diameter to move entirely from the snow cover into the ice. In fact the process would occur even slower than this in as much as typical temperature gradients encountered in real sea ice are usually appreciably lower than this. Therefore the displacement of air inclusions from the snow into sea ice can only occur within a very thin layer with a thickness of less than a millimetre occurring at the upper ice surface. Also the shorter the ice growth season the thinner the layer.

We will now consider the possible contributions of processes 1b, 2b, and 2c. Suppose that a new ice layer 10 cm thick has grown under a 20 cm thick ice cover. Let the chlorinity and salinity of this layer be 3.85‰ and 6.93‰ respectively. In addition let the same parameters for the sea-water under the ice be 13.00‰ and 23.48‰ and also assume that the total gas content of the water is $C_{\Sigma\text{W}} = 0.027$ and that the ice temperature profile is linear, changing from -10°C on the upper ice surface to the freezing point on the lower. If after the formation of the new ice layer in question, its temperature rises by an average of 0.5°C , then $v_{1\text{b}} = 0.067$, $v_{2\text{b}} = 0.020$, $v_{2\text{c}} = 0.110$ and $v_{1\text{b}} + v_{2\text{b}} + v_{2\text{c}} = 0.197$ (or expressed in percent $34 + 10 + 56 = 100$).

Under the same conditions, except for the chlorinity and the salinity of the sea-water which are now taken as 19.30‰ and 35.00‰ respectively, and with a proportional increase for the salinity of the ice, we have $v_{1\text{b}} = 0.091$ (59%), $v_{2\text{b}} = 0.005$ (3%), $v_{2\text{c}} = 0.058$ (38%) and $v_{1\text{b}} + v_{2\text{b}} + v_{2\text{c}} = 0.154$.

As can be seen from these examples, the porosity values are large: 15 to 20% of the total ice volume. Nevertheless they appear possible in as much as we have observed ice porosities of 17% on the Caspian Sea. The above calculations indicate that the main contributions to the formation of the gas content of the ice come from the release of gases from the water and the generation of water-vapour-filled pores. The effect of the release of gases from the brine is relatively small. However, these apparently small values may be caused by our limited knowledge of the solubility of gas in brine. Only in the case of the release of gas from the brine will the porosity depend inversely on the composition of the sea ice. In the other processes the porosity will increase if the salinity increases. Our observations on the White and Caspian Seas show that changes of porosity and composition can occur with both the same and the opposite signs.

It is difficult to estimate porosity values resulting from the release of gases from the bottom because of the lack of knowledge of the rate of release of such gas. According to our determinations on Ozero Baykal, $v_{1\text{c}}$ varies between 0.088 and 0.180. These are probably not extreme values.

Let us now consider the possible porosity values which can be attributed to effect 2a, the substitution of a part of the brine by air. Tsurikov (1976) has shown that the strength of sea ice will become equal to zero if the volume of brine or gas inclusions exceeds 0.9 (90%) of the total volume of sea ice, while the minimum value of $v_{2\text{a}}$ is certainly zero. According to Equation (37) these values of $v_{2\text{a}}$ correspond to brine volumes $v_{\text{b}} = 0.374$ and 0.631 respectively. Hence Equation (37) can only be used within these limits until the part above sea-level has replaced brine by air. Although $v_{\text{b}} = 0.374$ is a large value, it is a most probable one because of the internal melting of ice that takes place in the course of the rise in the ice temperature in the spring and summer. Judging from the data of Tsurikov (1976), the relative brine volume of 0.374 at a temperature of -0.2°C corresponds to an ice salinity of only 1.38‰.

THE GAS COMPOSITION OF SEA ICE

Among investigators who study sea ice there is no common opinion what to call the gaseous phase of sea ice. Kheysin and Cherepanov (1969), Weeks and Assur (1968, 1972), and Bari and Hallett (1974) call it air; Zubov (1945), Savel'yev (1963), and Matsuo and Miyake (1966) are more careful in calling it gas, a more general term. We can appraise the applicability of the first term by examining the limited results that are available concerning the composition of the gas in sea ice. Analyses of the composition of such gases have been performed by Bruns (1937) and by Matsuo and Miyake (1966) and are presented in Table IV. As can be seen, the composition of the gas in sea ice can differ significantly from that in the atmosphere ($O_2/N_2 = 0.27$) with the ice sometimes being deficient in oxygen (to $O_2/N_2 = 0.19$) and sometimes enriched (to $O_2/N_2 = 0.46$). However the content of oxygen in the ice never reaches the value that would correspond to the saturation values of these gases in sea-water at its freezing temperature ($O_2/N_2 = 0.54$). This is presumably the result of oxygen being depleted because of the oxidation of organic matter and the respiration of marine organisms living below the ice at a rate higher than it can be produced in the course of photosynthesis. This latter process is, of course, greatly slowed by the photo-insulating action of the ice. This argument is supported by the high CO_2 content of some samples of sea and pond ice (24.3% and 24.8% respectively). Savel'yev (1963) has suggested that the lower O_2 content and the higher CO_2 content in the ice as compared with that in the water is the result of the activity of organisms living within the ice. We consider this explanation doubtful in as much as if it were true microscopic animals would be expected to develop rapidly within the ice. However, this is not the case since according to Buynitskiy (1973) the rapid development of algae was observed instead.

TABLE IV. GAS COMPOSITION IN SEA AND POND ICE

No. of sample	Porosity	Gases composition, % by volume					O_2/N_2
		<i>N₂ and rare gases</i>	<i>O₂</i>	<i>Ar and heavy gases</i>	<i>CO₂</i>		
Sea ice from Antarctic (lat. 66° 15' to 69° 25' S., long. 36° 02' to 40° 30' E.) (Matsuo and Miyake, 1966)							
1	0.076	76.8	21.3	0.93	0.98	0.27	
2	0.020	54.2	20.6	0.99	24.3	0.38	
3	0.163	69.3	29.0	1.1	0.53	0.42	
4	0.155	71.4	26.5	1.1	1.0	0.37	
						Average 0.36	
Sea ice from the Sea of Okhotsk near the north coast of Hokkaido (Matsuo and Miyake, 1966)							
5	0.090	69.5	29.0	0.97	0.60	0.42	
6	0.123	67.7	31.0	0.94	0.41	0.46	
7	0.125	74.3	23.8	1.1	0.84	0.32	
8	0.154	72.5	25.4	1.1	0.93	0.35	
						Average 0.39	
Sea ice from the Barents Sea (September 1934) (Bruns, 1937)							
1	—	81.7	18.3	0.92	—	0.22	
2	—	83.5	15.9	0.90	0.6	0.19	
3	—	83.0	16.5	0.88	0.5	0.19	
4	—	81.4	18.5	0.94	0.4	0.22	
						Average 0.21	
Pond ice (Matsuo and Miyake, 1966)							
1	0.007	52.2	22.0	1.0	24.8	0.42	

During process 1a gas is captured from both the atmosphere and the water. Therefore the composition of the resulting gas should be different from that in the atmosphere alone. This difference should be more the calmer the sea because the presence of waves promotes the capture of gas from the air in the upper part of the water column. In process 1b, however, which is concerned with the separation of gases from solution within sea-water, the composition of the resulting gas should approach the composition of the gas in the sea-water. In all probability the composition of gases rising up from the sea bottom will be different from those in the atmosphere or in the ocean. For instance, Zubov (1945) has pointed out that the pores from some samples collected in the Laptev Sea were filled with methane.

In the course of the substitution of air for a part of the brine (via process 2a), the pores are filled with gases of atmospheric composition. However this substitution only affects the layers of the ice cover that are located above sea-level. In the parts below sea-level any loss of brine would be replaced by sea-water. The composition of the gases released from the brine (in process 2b) must be close to the gas content of sea-water because the brine originates from this water, process 2c would lead to the formation of pores filled mainly with water vapour. If the gas in the pores results from photosynthetic processes carried out by algae within the ice, it would be rich in oxygen (process 2d).

The composition of gas in infiltration ice (process 3a) will be similar to that in the atmosphere. However this process can only affect the composition of the upper layers of the ice cover. The same can be said about process 3b, but in this case the penetration of air is so slight to be of little practical importance.

CONCLUSIONS

The problem of the formation of the gaseous porosity of sea ice is clearly in need of investigation both in the field and in the laboratory. As the first step it would be desirable to determine the solubility of oxygen and nitrogen in sea-water brines of different compositions.

From the analysis of the gas compositions in sea ice it is possible to conclude that this composition differs quite clearly from gas in the atmosphere in all but the very uppermost layers of the ice.

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