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IMPURITY CONCENTRATIONS IN SEA ICE

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ABSTRACT. Three different types of saline ice were cut into sections a few millimeters thick along planes parallel to the surface. The resulting melts were analyzed quantitatively for chloride, sulphate, sodium, potassium, magnesium, and calcium. Two of the specimens were artificial sea ice, grown in the laboratory at ambient temperatures of −30°C and −15°C, respectively. A portion of the latter exhibited a clear, glassy, fresh-ice structure. The third was natural sea ice. The resulting ion concentration profiles and ion ratios are presented. For sections of widely varying salinity, the various ion ratios assumed values fairly close to those in natural sea-water.

RÉSUMÉ. *Concentration en impuretes dans la glace de mer.* Trois types différents de glace saline ont été coupés en lames de quelques millimètres d'épaisseur selon des plans parallèles à la surface. Les résultats de la fusion de ces lames ont été analysés quantitativement pour les chlorures, les sulfates, la natrium, le potassium, le magnésium et le calcium. Deux des échantillons étaient de la glace marine artificielle créée en laboratoire à des températures ambiantes de, respectivement, −30°C et −15°C. Une partie du dernier échantillon montrait une structure de glace fraîche, claire et lisse. Les troisième était de la glace de mer naturelle. On présente les profils des concentrations en ions et des rapports entre ions. Pour des sections de salinité très largement variables, les différentes valeurs trouvées pour les rapports entre ions concordaient bien avec ceux de l'eau de mer naturelle.

ZUSAMMENFASSUNG. *Die Konzentration von Verunreinigungen in Meereis.* Von drei verschiedenen Typen Salzwassereis wurden Schnitte von wenigen mm Dicke längs Ebenen parallel zur Oberfläche hergestellt. Nach Einschmelzung wurden sie quantitativ auf Chlor, Schwefel, Sodium, Potassium, Magnesium und Calcium untersucht. Zwei der Proben waren künstliches Meereis, das im Labor bei Umgebungstemperaturen von −30°C bzw. −15°C gewachsen war. Ein Teil dieser Proben zeigte eine klare, glasartige Frischeis-Struktur. Die dritte Probe war natürliches Meereis. Die ermittelten Profile der Ionen-Konzentration und die Ionenverhältnisse werden wiedergegeben. Für Schnitte mit sehr unterschiedlichem Salzgehalt nahmen die verschiedenen Ionenverhältnisse Werte an, die sehr nahe bei denen natürlichen Meerwassers liegen.

INTRODUCTION

Sea-water contains some 34‰ by weight of dissolved inorganic substances: this quantity (essentially) is known as its salinity (Sverdrup and others, 1942). While this parameter may vary from place to place, the ratios of the major ion concentrations stay reasonably constant at the values shown in Table I. Salinity is commonly established through the determination of one of these ions (often chloride). The same concepts are frequently extended to sea ice. It is less clear that this is justified: that is, we should be confident that the major ion ratios remain reasonably close to their sea-water values. The chemical analyses of Bennington (1963), on young Arctic sea and pack ice, do suggest that this is the case and that there is relatively little selective concentration of any particular ions with depth. The present paper reports the results of additional chemical analyses. It includes an investigation of natural sea ice by means of thinner sections than those employed by Bennington giving finer resolution with depth. Analyses are also reported upon artificial ice prepared from sea-water in the laboratory and upon the clear glassy ice which is sometimes obtained when brine is frozen slowly (Weeks and Lofgren, 1967). Little evidence of selective concentration was found in any region, and the results are, at least generally, in accord with those of Bennington.

TABLE I. CONCENTRATION OF THE MAJOR IONS IN NORMAL SEA-WATER

Ion	*Concentration* ‰	*Ratio*	*Ratio by weight*
Cl^-	19.000	—	—
Na^+	10.556	Na^+/Cl^-	0.556
$SO_4^{=}$	2.649	$SO_4^{=}/Na^+$	0.251
Mg^{++}	1.272	Mg^{++}/Cl^-	0.067
Ca^{++}	0.400	Ca^{++}/Cl^-	0.021
K^+	0.380	K^+/Cl^-	0.020
—	—	Mg^{++}/K^+	3.35

Sea ice is produced when sea-water freezes downward from the surface under unidirectional cooling. It is an inhomogeneous material which undergoes a complicated series of phase changes with decreasing temperature as various solid salts precipitate out from the entrapped liquid brine. In a well-known paper, Assur (1958) has analyzed the data of other workers to arrive at a postulated scheme of phase relationships. At about −1°C (relatively) pure ice crystals appear, thereby concentrating the brine in their immediate vicinity. At about −8°C the precipitation of solid $Na_2SO_4 \cdot 10H_2O$ commences and, at successively lower temperatures, other solid salts appear: $NaCl \cdot 2H_2O$ near −23°C, KCl near −37°C, and $MgCl_2 \cdot 12H_2O$ near −43°C. The latter four transitions have been indirectly observed by means of electrical measurements (Addison, 1969; Addison, 1975). Additional transitions were seen: an unidentified one at −47°C, that of (probably) $CaCl_2 \cdot 6H_2O$ near −53°C, and the probable ultimate solidus point of the system between −70 and −75°C. Assur, in addition, suggests the deposition of minor amounts of $CaCO_3 \cdot 6H_2O$ near −4°C and of $MgCl_2 \cdot 8H_2O$ near −20°C, although he mentions that the behaviour of both these salts may be somewhat erratic.

The structure and formation of sea ice have been frequently described (for example, Harrison and Tiller, 1963; Pounder, 1965; Weeks and Assur, 1968). The region just below the surface often arises from the solidification of frazil ice and consists of small ice crystals having random orientation of the (optic) *c*-axes, along with entrapped brine and solid salts. The body of the ice shows the well-known columnar structure where the crystal zones have predominantly horizontal *c*-axis orientations. This arises from the preferred growth of ice crystals, under a temperature gradient, in directions perpendicular to the optic axes (Perey and Pounder, 1958). A "transition layer", a few millimeters in thickness, lies between these two regions. It is created after the solidification of the frazil layer, when, of all those crystals nucleated, the ones most favourably oriented with respect to the temperature gradient grow preferentially. These overwhelm the others and establish the columnar structure. The transition layer is often found 5 to 25 cm below the surface. It is a region especially high in salt content. This arises partly because of its chaotic structure, and partly because of brine which drains from the more porous upper material and is retained by the less permeable material below.

New sea-ice salinities range from some 4‰ in regions well below the surface, to 10‰, or more, in the upper regions. In general, the faster the rate of freezing, the higher will be the salinity (Fertuck and others, 1972; Weeks and Lofgren, 1967). The salts are associated with liquid brine entrapped within the ice: either in rows of thread-like brine cells lying between the platelets of pure ice which make up a crystal zone, or at the inter-zone boundaries. The formation of these platelets has been described by Harrison and Tiller (1963) and the phenomenon has been considered, with some success, in terms of constitutional supercooling (for example, Milošević-Kvajić and others, 1973; Kvajić and others, 1973).

Once the ice has been formed however, the brine is not static. Various methods for the transport of brine have been suggested (for example by Kingery and Goodnow, 1963; Untersteiner, 1967; Lake and Lewis, 1970). These include drainage mechanisms, flushing by melt water, and expulsion through temperature cycling. Such processes are thought to account for a large part of the brine transport in natural sea ice.

A second, more microscopic, process also exists: the migration of closed liquid-brine inclusions (towards warmer regions) along a temperature gradient (see, for example: Pounder, 1965; Harrison, 1965; or Hoekstra and others, 1965). While accounting for a relatively small portion of the total brine movement, it seems to be the mechanism most likely to alter the ion ratios after the ice has formed. Specifically, the first solid salt to be deposited, $Na_2SO_4 \cdot 10H_2O$, could be left behind in such a migration and thereby appear somewhat displaced from the other impurities. Brine-cell migration is slow below −15°C.

The motion of a liquid inclusion under a temperature gradient has been the object of considerable study recently. Of interest is the observation of Jones (1973) that, depending on the shape of the inclusion, its path need not necessarily be parallel to the temperature, gradient, but may in fact lie at a considerable angle to it.

Artificial sea ice, frozen in the laboratory under conditions approximating unidirectional cooling, shows a structure which may be described as a "scale model" of the natural ice structure. There is no frazil-ice region. The transition layer, a millimeter or so in thickness, is found in the first centimeter beneath the surface. Below it, we again find the tendency towards vertical columnar crystal zones. These, however, are rather smaller than in natural sea ice: about 1 cm in diameter and, at most, 7 or 8 cm in length. By keeping the surface temperature approximately constant during freezing, we eliminate brine-transport mechanisms dependent upon temperature cycling and, in general, produce a material which has a simpler thermal history. Any selective concentration might be expected to show up more clearly in artificial ice.

THE PRESENT STUDY

Two samples of artificial ice and one of young sea ice (in the form of a 7.6 cm (3 inch) core, transported in dry ice from Fort Churchill, Manitoba, Canada) were sectioned along horizontal planes by means of a lathe with a milling device. The resulting "snow" was melted and the melts analyzed quantitatively for Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}, and K^+.

Artificial samples were prepared in a cold room by freezing 30 l of natural sea-water (salinity, 34.4‰; measured ion ratios similar to Table I) in a container about 40 cm in diameter by 65 cm deep. With the exception of the top, which was protected but not sealed, this vessel was completely insulated. Small weighted air bladders were placed on the bottom to relieve pressure during freezing. Examination of thin sections of the ice under crossed polaroids, showed that there was always a small central cylindrical volume, some 12 cm in diameter, at the top of the mass, where the temperature gradient had been essentially vertical during freezing. As this freezing system was closed, rejected ions accumulated in the underlying brine. Experience showed that some 15 cm of ice could form before effects of this enrichment were apparent. Consequently, the study was confined to the top 10 cm of ice. Freezing of the mass took approximately 6 weeks.

Two lots of artificial ice were produced: one at a constant ambient temperature of −30°C and the other at −15°C, a temperature chosen to effect the slow growth rates necessary for the production of glassy ice.

The natural sea ice was studied to a depth of 30 cm by means of sections approximately 5 mm thick. The −30°C artificial ice was shaved in 2 mm sections. Because of its extremely low salinity, the −15°C artificial ice was cut into 5 mm sections in an attempt to satisfy the requirements of chemical analysis.

In spite of the air bladders, a small quantity of brine was forced up along the sides of the freezing vessel on to the surface of the −30°C ice. This took place when the freezing was virtually complete, long after the upper ice had formed. The liquid was removed quickly and the ice was sectioned soon afterwards. The effects of this flooding were, therefore, confined to the surface itself and may be readily identified.

The thickness of the sections was usually chosen to yield about 10 ml of melt. Each sample was eventually diluted quantitatively by a factor of 20 to provide a suitable working volume. Analytical methods were chosen for simplicity and suitability, rather than for accuracy.

In any mixture of ions, some usually interfere in the determination of others. The sea-water group is especially troublesome in this regard. As a consequence, the anions and the cations were studied separately. Before the anion determinations, half of the sample was passed through an acidic cation exchange resin (to replace the cations by hydrogen) and the pH adjusted to neutrality. Similarly, before the cation determinations, the remaining half was subjected to an anion exchange resin to replace these ions by Cl^-.

The chloride ion was determined by the well-known silver nitrate (Mohr) titration (Kolthoff and Sandell, 1952). At lower concentrations, the end-point was somewhat subjective, but little real difficulty was encountered. Sulphate was measured colorimetrically with barium chloranilate at 330 nm (Bertolacini and Barney, 1957, 1958).

Na^+, K^+, and Ca^{++} were determined by flame photometry at 589 nm, 768 nm, and 554 nm, respectively (Burriel-Marti and Ramirez-Muñoz, 1957). These ions interfere mutually in the flame in a rather complex manner (Kuemmel and Karl, 1954; Broderick and Zack, 1951). A method was devised to obviate this difficulty (at least partially). When potassium was being determined, an amount of sodium equal to the average amount of this ion present in the particular group of samples under study was added to the potassium standards. Similarly, average amounts of both sodium and potassium were added to the calcium standards during the determination of this ion. Magnesium was measured colorimetrically at 435 nm by means of the dye titan yellow (Sandell, 1959).

It is felt that this scheme generally served to determine these ions to within ±5%, or better, with the exception of calcium, where the error might be as high as ±8%. Analyses of typical synthetic mixtures of known concentrations confirmed these estimates. (An additional check (of a sort) was also carried out. For each sample, the ion concentrations were converted to normalities and the positive and negative sums compared. Usually, these sums "balanced" to within ±4%, or better.) For the extremely dilute solutions from the −15°C artificial ice the errors were sometimes greater. A number of these samples were not measurable and, for some of the others, the methods were pushed to the limits of usefulness.

DISCUSSION

The concentration profiles for the −30°C and −15°C artificial ices and the natural sea ice are shown, respectively, in Figures 1, 3, and 5; and the resulting ion concentration ratios

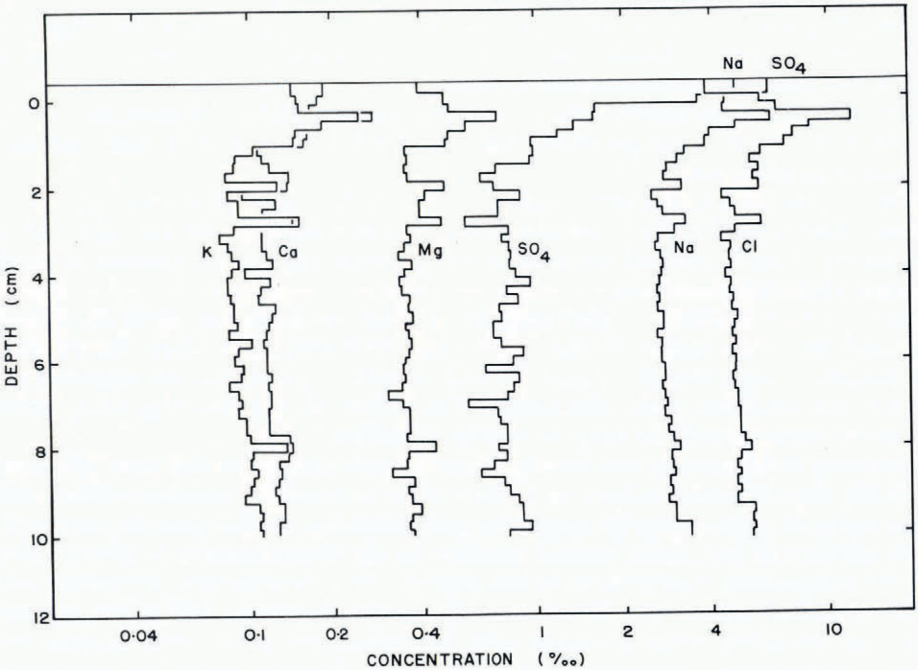


Fig. 1. Ion concentration profiles for saline ice grown at −30°C. (Zero depth indicates the true surface of the ice.)

in Figures 2, 4, and 6. In each of the latter, vertical lines indicate the values of these ratios in sea-water.

With some exceptions, the ion ratios show a tendency to remain fairly near the sea-water values. This suggests that the application of the concept of salinity to sea ice, at least to bulk samples, is reasonable. There is little evidence of selective ion concentration.

The ion profiles of the −30°C ice (Fig. 1) contain few surprising features. As a consequence of some visible condensation, and the previously mentioned flooding during freezing, the natural surface of this ice (as revealed by sections) lay somewhat lower than the apparent surface. The zero level in Figures 1 and 2 indicates this natural surface. (The erratic behaviour of some of the ions in the first one or two sections is a consequence of the flooding.)

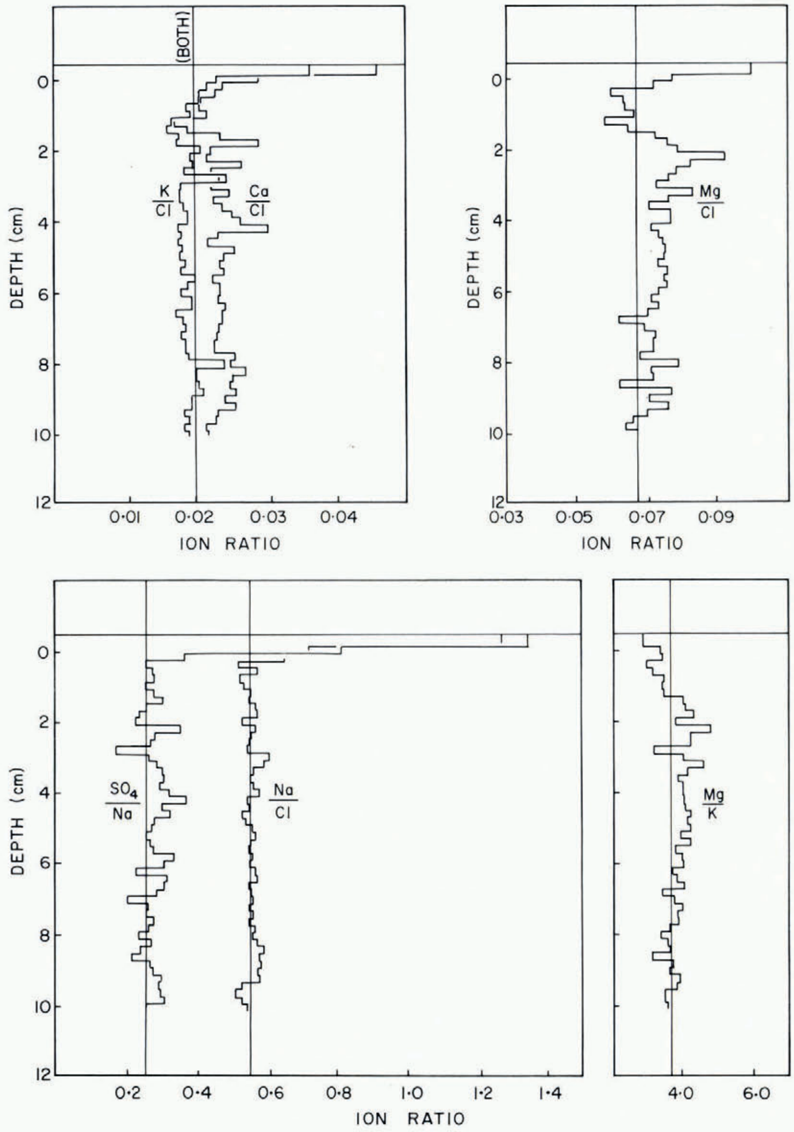
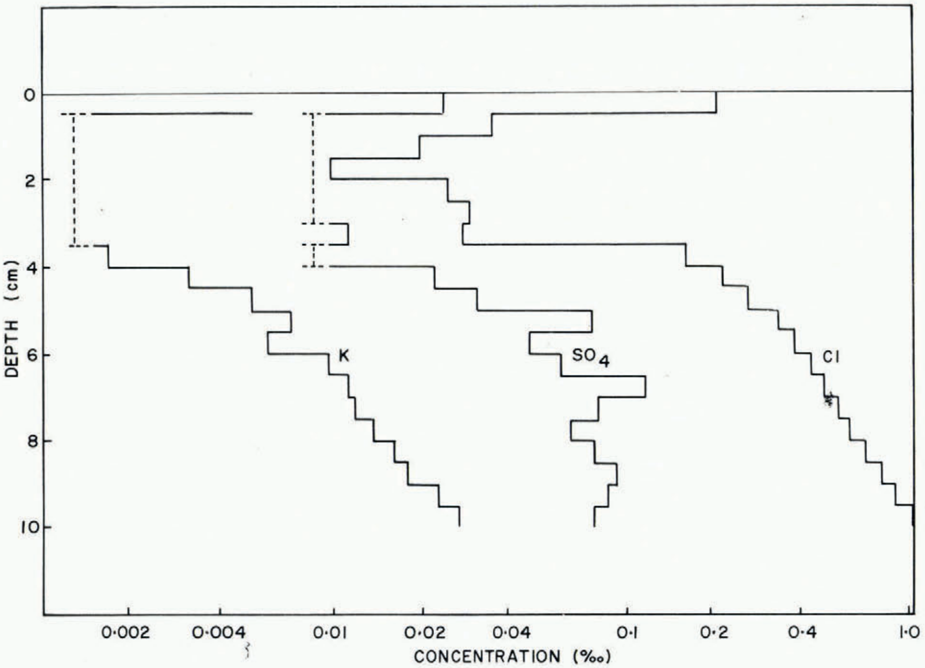


Fig. 2. Ion ratios for saline ice grown at −30°C.



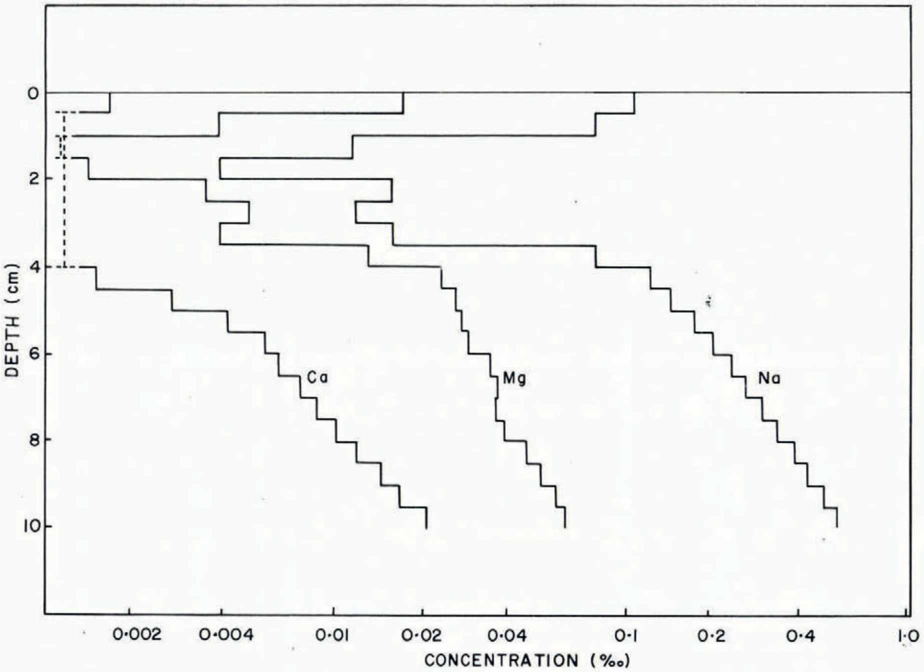


Fig. 3. Ion concentration profiles for saline ice grown at −15°C. (The top 4 cm showed the clear, glassy structure of fresh ice.)

The apparent transition layer, with enriched salt content, is clearly indicated about 5 mm below the true surface. The section corresponding to the peak in concentration, and the three directly below it, form a pattern which is reproduced in all of the profiles except that of sulphate. This ion does not, on first glance, appear to show a transition-layer peak. However, it seems probable that this feature is present in the sulphate profile at a level one or two sections higher and that the peak has merged with the high spurious concentration of this ion at the surface. If so, it suggests that the transition-layer process took place about 2 mm closer to the surface than the other profiles indicate, and that the liquid brine migrated downwards leaving the sulphate behind. The behaviour of the Na^+/Cl^- ratio at this level is consistent with this speculation. The ion ratios suggest a slight enrichment of magnesium in all but the top 2 cm.

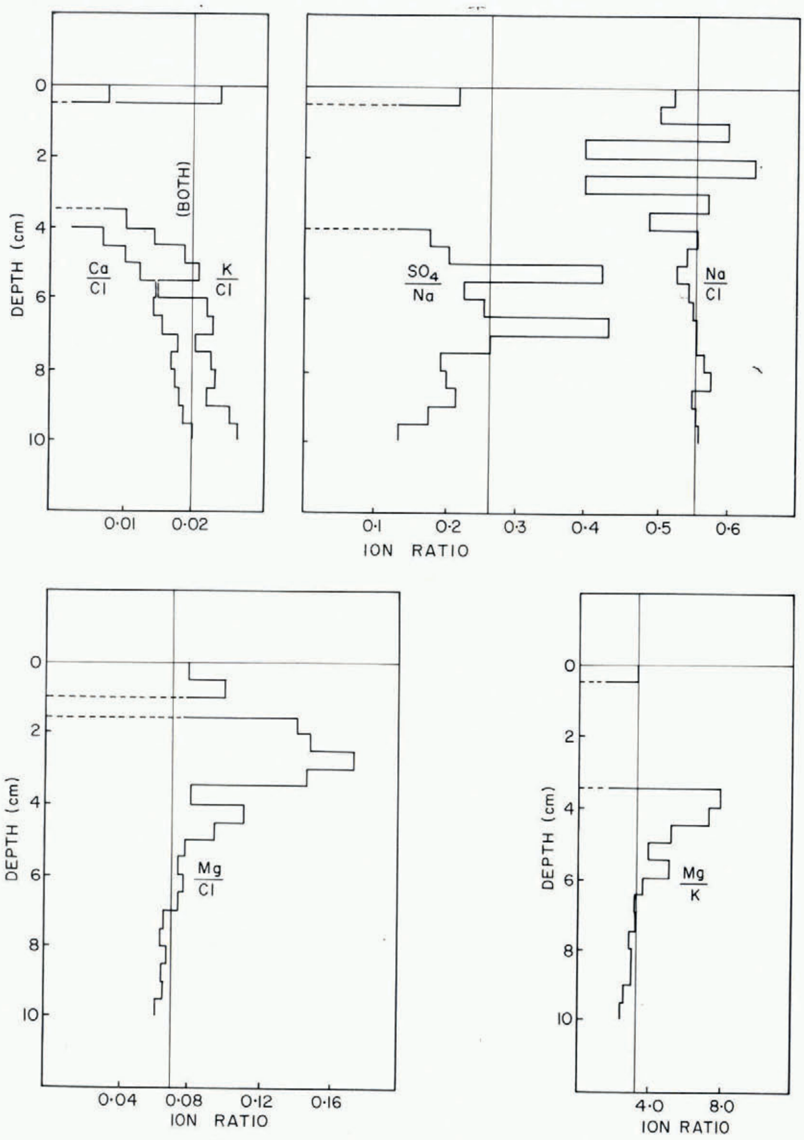


Fig. 4. Ion ratios for saline ice grown at −15° *C.*

The −15°C ice contained a layer which was very similar in appearance to fresh ice. Except at the very surface, the top 3.5 cm were absolutely clear and glass-like. The usual columnar structure became established only below 6 cm. Analysis confirmed that the clear ice had rejected virtually all of the impurities. Several of the ions could not be determined here. (The vertical dotted bars in Figure 3 provide visual continuity and are not meant as detection limits.) Below this layer, the salinity increases just about monotonically with depth. There was no visual sign of a transition layer, nor are there concentration peaks to indicate the presence of one. (The peaks on the sulphate profile are attributed to experimental error at these low concentrations.) It is interesting to note that the ion ratios of Figure 4, where experimental error permits them to have meaning, are, even here, reasonably close to the sea-water values.

Figure 5 shows the results obtained for the natural sea-ice sample. The top 7 cm have the expected high salt content. At the bottom of this region, small peaks coinciding with the transition region are seen in the Na^+, Cl^-, and SO_4^{2-} curves. Below this, the salinity falls off as the structure became more regular. It then rises again, possibly because of faster freezing due to increasingly cold winter weather at the surface. The sulphate profile is again somewhat different from the others. The zone of decreased salinity between 7 and 15 cm, and the differing behaviour of the sulphate curve, undoubtedly arise, at least in part, from downward brine transport. For example, the rather high values of the SO_4^{2-}/Na^+ ratio (Fig. 6), at (and above) the transition layer, suggest that solid sodium sulphate was left behind in a region which consequently suffered a depletion of brine through drainage and migration.

The K^+/Cl^- and (especially) the Ca^{2+}/Cl^- ratios are smaller than the expected values. For our other samples, more reasonable concentrations of these ions were found, with one ion or the other showing a slight preponderance. This suggests the possibility of some systematic error in the Ca^{2+} determination. However, for just this reason, known control samples

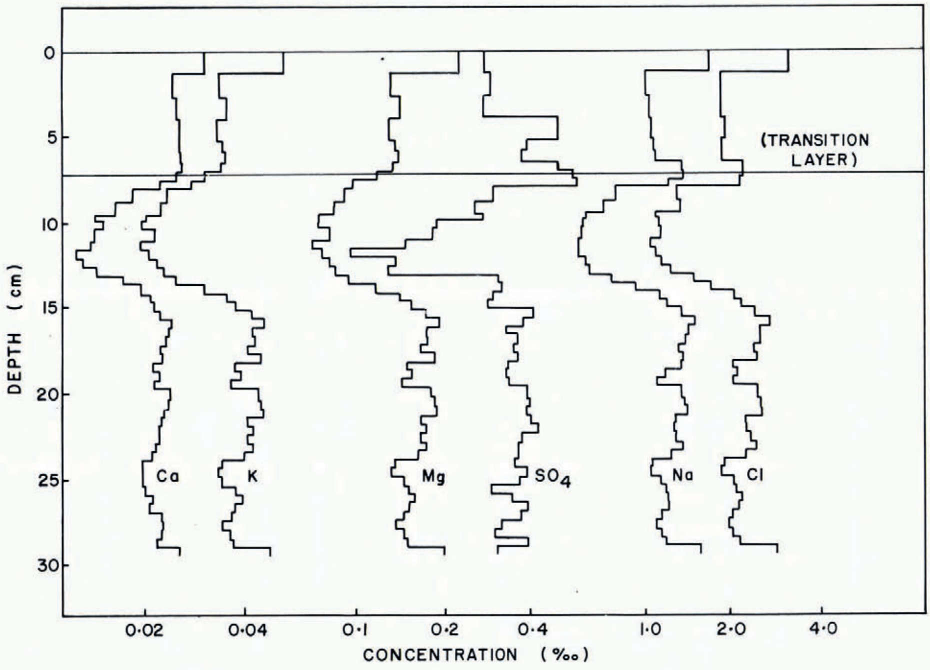


Fig. 5. Ion concentration profiles for natural sea ice.

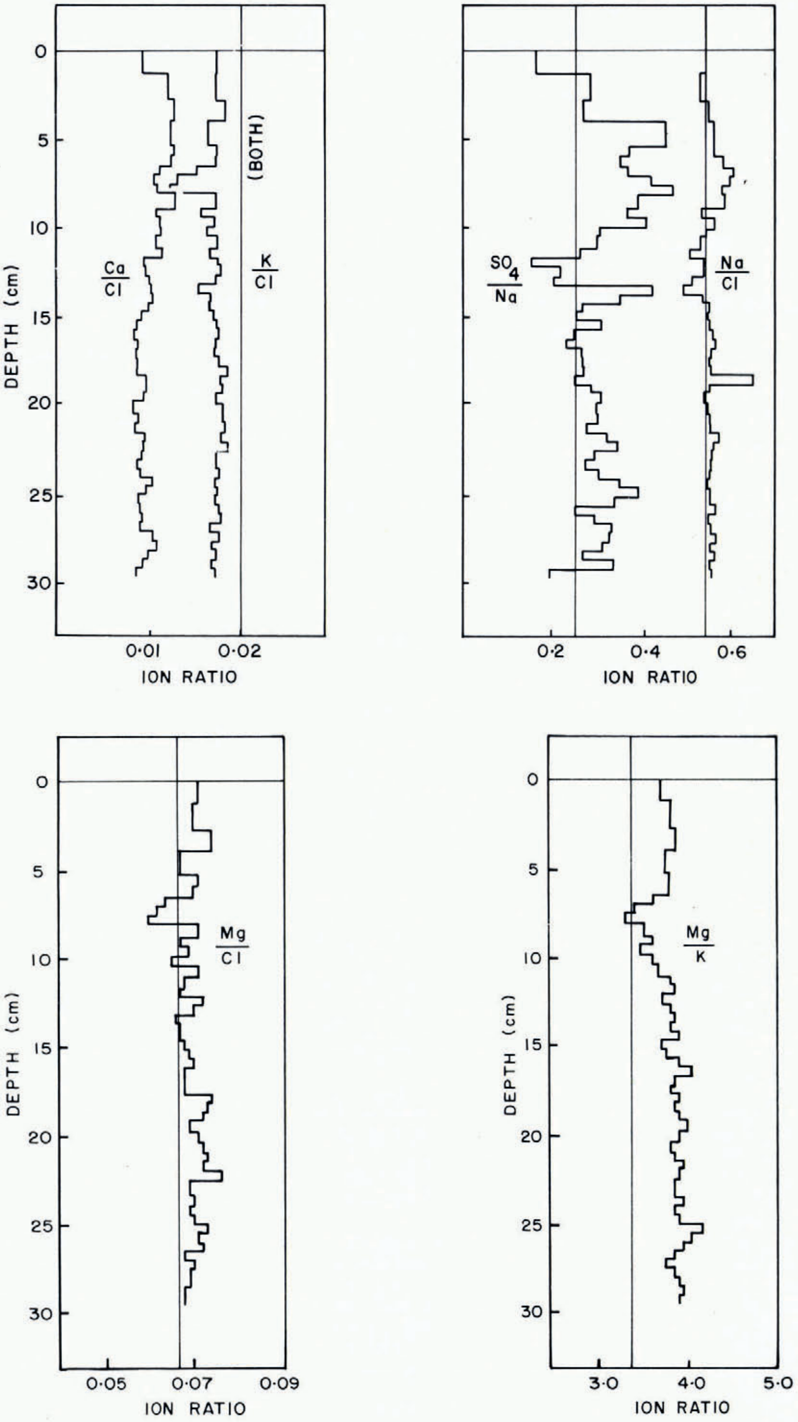


Fig. 6. Ion ratios for natural sea ice.

were included with each batch of samples during analysis. It is hoped that the probability of such an error having escaped detection is not high. In any case, the concentrations of these ions are small and they make only a small contribution to the salinity calculation. (Unfortunately, a sample of sea-water from the site was not available.)

Our profiles for natural sea ice may be compared with those of Bennington (in particular, with his figures 4 and 7). The comparison must be rather indirect since the 30 cm depth of the present study corresponds to just two of his thicker sections. Our curves show larger variations than do his: this is reasonable since his measurements were averaged over much larger samples. Within these limitations, there seem to be few significant differences between the two studies, especially when we take into account the wide variability of this natural material. Bennington's K^+/Cl^- and Ca^{2+}/Cl^- ratios were similar both to each other and to the sea-water values. Depending on his particular sample, either ion might show a slight excess in concentration over the other. In general, all of his ion ratios exhibited smaller departures from the sea-water values than were observed in the present case.

On the basis of these two investigations, we may conclude, with a fair degree of generality, that the impurity ratios in sea ice remain encouragingly similar to those in sea-water. The results of the present work are largely corroborative. In view of the large expenditures of time and effort demanded by the chemical analyses, the project was not pressed further.

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REFERENCES

Addison, J. R. 1969. Electrical properties of saline ice. *Journal of Applied Physics*, Vol. 40, No. 8, p. 3105–14.

Addison, J. R. 1975. Electrical properties of saline ice at 1 kHz down to −150°C. *Journal of Applied Physics*, Vol. 46, No. 2, p. 513–22.

Assur, A. 1958. Composition of sea ice and its tensile strength. (*In Arctic sea ice*. Washington, D.C., National Academy of Sciences—National Research Council, p. 105–38. (Publication 598.))

Bennington, K. O. 1963. Some chemical composition studies on Arctic sea ice. (*In* Kingery, W. D., *ed. Ice and snow; properties, processes and applications: proceedings of a conference held at the Massachusetts Institute of Technology, February 12–16, 1962*. Cambridge, Mass., M.I.T. Press. p. 248–57.)

Bertolacini, R. J., *and* Barney, J. E. 1957. Colorimetric determination of sulphate with barium chloranilate. *Analytical Chemistry*, Vol. 29, No. 2, p. 281–83.

Bertolacini, R. J., *and* Barney, J. E. 1958. Ultraviolet spectrophotometric determination of $SO_4^=$, Cl^-, and F^- with chloranilic acid. *Analytical Chemistry*, Vol. 30, No. 2, p. 202–05.

Broderick, E. J., *and* Zack, P. G. 1951. Flame spectroscopy for the determination of sodium, potassium and lithium in glass. *Analytical Chemistry*, Vol. 23, No. 10, p. 1455–58.

Burriel-Marti, F., *and* Ramirez-Munoz, J. 1957. *Flame photometry*. New York, Elsevier.

Fertuck, L., *and others*. 1972. Computing salinity profiles in ice, [by] L. Fertuck, J. W. Spyker and W. H. W. Husband. *Canadian Journal of Physics*, Vol. 50, No. 3, p. 264–67.

Harrison, J. D. 1965. Measurement of brine droplet migration in ice. *Journal of Applied Physics*, Vol. 36, No. 12, p. 3811–15.

Harrison, J. D., *and* Tiller, W. A. 1963. Controlled freezing of water. (*In* Kingery, W. D., *ed. Ice and snow; properties, processes and applications: proceedings of a conference held at the Massachusetts Institute of Technology, February 12–16, 1962*. Cambridge, Mass., M.I.T. Press. p. 215–25.)

Hoekstra, P., *and others*. 1965. The migration of liquid inclusions in single ice crystals, [by] P. Hoekstra, T. E. Osterkamp and W. F. Weeks. *Journal of Geophysical Research*, Vol. 70, No. 20, p. 5035–41.

Jones, D. R. H. 1973. The temperature-gradient migration of liquid droplets through ice. *Journal of Crystal Growth*, Vol. 20, No. 2, p. 145–51.

Kingery, W. D., *and* Goodnow, W. H. 1963. Brine migration in salt ice. (*In* Kingery, W. D., *ed. Ice and snow; properties, processes and applications: proceedings of a conference held at the Massachusetts Institute of Technology, February 12–16, 1962*. Cambridge, Mass., M.I.T. Press. p. 237–47.)

Kolthoff, I. M., *and* Sandell, E. B. 1952. *Textbook of quantitative inorganic analysis*. New York, MacMillan.

Kuemmel, D. F., *and* Karl, H. L. 1954. The flame photometric determination of alkali and alkaline earth elements in cast iron. *Analytical Chemistry*, Vol. 26, No. 2, p. 386–91.

Kvajić, G., *and others*. 1973. Selective growth of ice crystals from dilute water solution, [by] G. Kvajić and V. Brajović, M. Milošević-Kvajić and E. R. Pounder. (*In* Whalley, E., *and others, ed. Physics and chemistry of ice: papers presented at the Symposium on the Physics and Chemistry of Ice, held in Ottawa, Canada, 14–18 August 1972. Edited by E. Whalley, S. J. Jones, L. W. Gold*. Ottawa, Royal Society of Canada. p. 251–55.)

Lake, R. A., *and* Lewis, E. L. 1970. Salt rejection by sea ice during growth. *Journal of Geophysical Research*, Vol. 75, No. 3, p. 583–97.

Milošević-Kvajić, M., *and others*. 1973. Freezing parameters for ice single crystals and the separation of basal platelets, by M. Milošević-Kvajić and G. Kvajić and V. Brajović. *Canadian Journal of Physics*, Vol. 51, No. 8, p. 837–42.

Perey, F. G. J., *and* Pounder, E. R. 1958. Crystal orientation in ice sheets. *Canadian Journal of Physics*, Vol. 36, No. 4, p. 494–502.

Pounder, E. R. 1965. *The physics of ice*. Oxford, etc., Pergamon Press. (The Commonwealth and International Library. Geophysics Division.)

Sandell, E. B. 1959. *Colorimetric determination of traces of metals*. New York, Interscience.

Sverdrup, H. U., *and others*. 1942. *The oceans: their physics, chemistry and general biology, by H. U. Sverdrup, M. W. Johnson and R. H. Fleming*. New York, Prentice-Hall.

Untersteiner, N. 1967. Natural desalination and equilibrium salinity profile of old sea ice. (*In* Ōura, H., *ed. Physics of snow and ice: international conference on low temperature science. . . . 1966 . . . .* *Proceedings*, Vol. 1, Pt. 1. [Sapporo], Institute of Low Temperature Science, Hokkaido University, p. 569–77.)

Weeks, W. F., *and* Assur, A. 1968. The mechanical properties of sea ice. *Canada. National Research Council. Associate Committee on Geotechnical Research. Technical Memorandum* No. 92, p. 25–78.

Weeks, W. F., *and* Lofgren, G. 1967. The effective solute distribution coefficient during the freezing of NaCl solutions. (*In* Ōura, H., *ed. Physics of snow and ice: international conference on low temperature science. . . . 1966 . . . .* *Proceedings*, Vol. 1, Pt. 1. [Sapporo], Institute of Low Temperature Science, Hokkaido University, p. 579–97.)