SR 112



Special Report 112 UNDERSTANDING THE VARIATIONS OF THE PHYSICAL PROPERTIES OF SEA ICE

by W. F. Weeks

MAY 1967

U.S. ARMY MATERIEL COMMAND COLD REGIONS RESEARCH & ENGINEERING LABORATORY HANOVER, NEW HAMPSHIRE

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PREFACE

This paper is based on a talk given by Dr. W.F. Weeks, Geologist, Snow and Ice Branch, U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) at the Symposium on Antarctic Oceanography sponsored by the Scientific Committee on Antarctic Research (SCAR). The Symposium was held in September 1966 at Santiago, Chile.

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by

W.F. Weeks

During the winter, sea ice covers approximately 38×10^6 km² (7% of the earth's surface or 12% of the surface of the sea). Despite the tremendous area covered by this material, it has received little attention from scientific investigators. This is not too surprising inasmuch as sea ice is a rather unpleasant material to handle, it is not readily transportable, and most important it has been only recently that regular transportation to and from areas of active sea ice formation has become available during the winter months. The lack of investigators is, however, definitely not the result of any lack of problems.

This paper is limited to discussing a few problems associated with the rather unusual physical properties of sea ice. It therefore completely neglects the large scale geophysical problems associated with sea ice as a boundary layer between the ocean and the atmosphere.

Figure 1 shows the low temperature portion of the NaCl-H₂ O phase diagram which provides a great deal of information about sea ice. At equilibrium at a given temperature, <u>pure</u> ice coexists with brine of a specified composition; i.e., when sea water freezes, if the process can be approximated as a continuous series of equilibrium or near-equilibrium states, a sheet of lake ice containing no impurities should form. If this were to happen, all the salt initially in the volume occupied by the ice would be rejected back into the underlying sea water. However, this is not the case. A series of salinity profiles from young sea ice (Fig. 2) (Weeks and Lee, 1962) shows that (1) when sea ice first forms it is quite salty; (2) the salinity of a given segment of ice gradually decreases with time; and (3) the vertical salinity profile at any given time has a characteristic C shape.

To gain insight into why and how this salt is entrapped in the ice, it is necessary to examine a thin section of sea ice (Tabata and Ono, 1957; Weeks and Hamilton, 1962; Bennington, 1963). In Figure 3 areas having the same tone can be considered parts of a single crystal, and we note that each crystal possesses a characteristic platy substructure. Under greater magnification (see Fig. 14), it is seen that along these substructures are located the tiny liquid inclusions of brine (the so-called brine pockets) that contain the salt found in sea ice. One of the main prerequisites to understanding sea ice is to understand why this substructure forms and traps brine instead of rejecting all the salt back into the underlying sea water.

Fortunately, we do know something about this process. Figure 4a shows the buildup of salt ahead of an advancing planar solid-liquid interface. This buildup is produced by the partial rejection of salt by the growing ice. Through the phase relations this compositional profile uniquely fixes a freezing temperature profile (Fig. 4, T_e). The freezing temperature is, of course, lowest next to the growing interface where the water contains the most salt.

Consider two possible temperature gradients (G_1 and G_3) in the liquid ahead of the interface. With temperature gradient G_1 , the liquid ahead of the interface is always above the freezing temperature as specified by its composition. Therefore, if a protuberance were to form on the interface, it would protrude into a liquid that is above the freezing temperature. This is, of course, an unstable situation; the interface remains planar, all the salt is rejected back into the liquid and lake ice forms. However, with temperature gradient G_3 there is a zone ahead of the interface that is supercooled as a result of its composition. Once a nonplanar interface forms as a result of this so-called constitutional supercooling (Rutter and Chalmers, 1953; Tiller, 1963), brine is trapped and sea ice results.







Figure 2. Salinity profiles, young sea ice, Thule, Greenland (Weeks and Lee, 1962).



Figure 3. Photomicrograph of a thin section of sea ice, Point Barrow, Alaska. The grid is 1 cm on a side (Weeks and Hamilton, 1962).

Calculating the growth conditions under which each of these two interface morphologies is stable using the formal theory developed by Tiller, Jackson, Rutter and Chalmers (1953) and Smith, Tiller and Rutter (1955)*, we obtain the results shown in Figure 5. Here G is the temperature gradient in the liquid, v is the growth velocity, and k_0 is the equilibrium distribution coefficient between pure ice and sea water. If we assume that $k_0 \sim 10^{-4}$ (a maximum value; see Harrison and Tiller, 1963a, b; Weeks and Lofgren, 1966), we find that lake ice (water-salinity $\sim 10^{-2}$ %), which forms with a planar interface, falls well within the growth conditions that should specify a non-planar or sea ice interface. This is because the calculations assume that salt transfer in the liquid is transferred by a much more efficient process, convection. Therefore, the theory of constitutional supercooling should be revised to permit the treatment of both free convection (the fast ice situation) and forced convection (the pack ice situation) and the calculations compared with carefully controlled experiments.

Once a non-planar interface has developed, it can assume a variety of shapes (Harrison and Tiller, 1963a, b; James, 1966). The interface shown in Figure 6 is composed of a series of parabolic platelets; brine can easily become trapped between these plates producing the characteristic brine pockets associated with sea ice. If it were possible to precisely specify the interface geometry as a function of growth conditions, it is quite possible that some simple geometrical models could be developed that would permit the calculation of the amount of brine entrapment. This approach appears particularly appealing inasmuch as some recent studies have shown that the amount of brine entrapment is directly controlled by the growth conditions (Tsurikov, 1965; Weeks and Lofgren, 1966).

In Figure 7, k (the salinity of the ice divided by the salinity of the water at the time the ice formed) is plotted as $\ln (1/k - 1)vs$ the growth velocity v. Some theoretical work on the solidification of metal systems has suggested that such a plot should be linear as indeed it is for sea ice (Weeks and Lofgren, 1966). This indicates that k is a smooth function of v provided the mixing conditions in the liquid are relatively constant (Fig. 8). This relation, of course, breaks down once we begin to approach growth conditions where a planar interface becomes stable: notice the consistent "tailing off" to high $\ln (1/k - 1)$ values at low values of v in Figure 7. This trend is clearly shown in Figure 9 which plots freezing runs that went through the sea ice \rightleftharpoons lake ice transition. Here the k values show significant deviations from k values determined from samples showing the sea ice substructure. These deviations appear well before the gross sea ice substructure disappears.

Once an equation is available relating k to growth conditions, initial salinity profiles can be calculated in terms of the factors that control the growth rate (that is, the meteorology). Figure 10 shows several such salinity profiles calculated for different air temperatures. It is encouraging to note that the upper parts of these profiles are in good agreement with observed salinity profiles. Unfortunately, this agreement completely disappears in the lower parts of the profiles; the bottom parts of the C-shaped profiles shown in Figure 2 are completely missing in Figure 10, presumably because we have neglected the fact that in general the salinity of any given layer of sea ice decreases with time. The mechanism of this brine drainage is not known. There are no detailed field or experimental data on the subject. It is even difficult to find a simple series of salinity profiles on the same ice during its initial year of formation. Some recent model calculations by Untersteiner (1966) have, however, shown that brine pocket migration as visualized by Whitman (1926) is far too slow to account for any

*See also Mullins and Sekerka (1964).







Figure 5. A plot of the boundaries for different k_0 values that separate growth conditions where a planar interface is stable from growth conditions where it is unstable. Solute transfer in the liquid is assumed to be by diffusion only.



Figure 6. Schematic drawing of the solid-liquid interface for sea ice.



Figure 7. Plot of ln (1/k - 1) vs v for samples with a fully developed sea ice substructure (Weeks and Lofgren, 1966).



Figure 5. Ine distribution coefficient k vs the normalized growth velocity, $\delta v/D$, where δ is the thickness of the laminar boundary layer, D is the diffusion coefficient of salt in water and v is the growth velocity (Weeks and Lofgren, 1966).

significant decrease in the salinity of the ice. Untersteiner was able to obtain a steady-state salinity profile similar to that observed in old multi-year pack ice by using a "flushing" and a brine pocket "expulsion" mechanism (Fig. 11). However, as he points out, this general agreement in no way proves that his postulated mechanisms are the dominant ones. More field work and experimentation are clearly needed.

In dealing with problems such as brine drainage, it is necessary to know the brine volume at different positions in the ice as a function of time. A phase diagram for sea water at sub-freezing temperatures is required to obtain brine volume values from the temperature and salinity values. Figure 12 (Assur, 1958) is calculated from the studies of Ringer (1906), Nelson (1953) and Nelson and Thompson (1954). It shows the different temperatures of crystallization of some solid salts and the amount of brine and ice in the system at any given temperature. It has been known for some time that there were significant discrepancies between the results of these authors at temperatures below -25C. However, because natural sea ice rarely becomes this cold, this was not considered too critical.



Figure 9. A plot of $\ln (1/k - 1) vs v$ for freezing runs showing the sea ice \rightarrow lake ice transition: solid black symbols indicate saltice, open symbols indicate lake ice, eq 9 represents the least-squares line through the data shown in Figure 7 (Weeks and Lofgren, 1966).



Figure 10. Salinity profiles calculated for different values of $\Delta \theta$, the temperature difference between the freezing temperature of sea water and the ambient air temperature (Weeks and Lofgren, 1966).







Figure 12. Phase relations for sea ice (Assur, 1958).

No one had ever positively identified, either optically or by X-rays, the different solid salts that crystallize from the brine at low temperatures. The chance for severe errors in the diagram became apparent when the work of the Russian chemist Gitterman became available (Savel'ev, 1963). Gitterman claims that CaSO₄ precipitates in significant quantities. This is a solid salt that does not even appear in Assur's diagram. Gitterman's results also suggest that some of the early formed salts partially rereact with the brine at lower temperatures and go back into solution. These reactions result in a final solidification of the brine at -36C as compared with the value of -54C as determined by Ringer. I am skeptical of Gitterman's results; needless to say they must be carefully checked. There is also the recent interesting suggestion of Tsurikov (1965) that certain effects attributed to the precipitation of $CaCO_3$. $6H_2$ O are actually the result of the adsorption of the calcium ion on ice. Also, we are not even certain that the ionic ratios in sea ice brine are identical with those in normal sea water.

Figure 13 shows the peculiar effects that the changes in brine volume and the precipitation of solid salts have on a non-structurally sensitive property, the density of sea ice (Anderson, 1960). Note the minimum in the density in the low salinity range and the pronounced discontinuity when NaCl. 2H₂ O precipitates.

It is, however, in the structurally sensitive properties that the extremely interesting changes occur. For example consider the tensile strength of sea ice. A relatively cold specimen of sea ice is shown in Figure 14. Note that the brine pockets are small. If we consider any possible failure plane in this specimen, we find that an appreciable percentage of this plane is ice. Therefore, this specimen would be expected to have a significant tensile strength. The specimen shown in Figure 15, on the other hand, contained a large volume of brine at the time the thin section was prepared. (Unfortunately, because these brine passages were interconnected, this brine is no longer in the specimen. It is quite clear, however, where it was,) A plane can be passed through this sample without ever encountering



Figure 13. Sea ice density at different salinities as a function of temperature (Anderson, 1960).

an ice-ice bond. Therefore, this specimen would be expected to have a tensile strength close to zero even though it contains an appreciable amount of ice. In Figure 16 the tensile strength of NaCl ice with a structure identical to sea ice (Weeks, 1962) varies from a σ axis intercept (σ_0) of roughly 25 kg/cm² at low temperatures (low brine volumes) to a strength of zero kg/cm² at a $v^{1/2}$ axis intercept (vo) of 0.48 (vo = 230%). Similar results have been obtained for natural sea ice by Assur (1958), Hendrickson and Rowland (1965) and Frankenstein (1966). Rubbings have also shown (Anderson and Weeks, 1958; Tabata, 1960) that the fracture surface does indeed follow the planes of weakness as specified by the substructure. It is, therefore, possible to construct some simple geometrical models to explain the variation in the strength of sea ice. This has been done by Anderson and Weeks (1958), Assur (1958), and Tsurikov (1947a, b) and the results were quite successful in predicting variations in sea ice strength until recently when a large amount of information on the strength of warm, high brine volume sea ice became available (Frankenstein, 1966). These results (Fig. 17) show that in the high brine volume

range, strength becomes independent of brine volume. It is quite possible that this is the result of some change in the growth pattern of the brine pockets. There is, however, no direct proof of this at the present.

Assur (1958) has suggested that the precipitation of solid salts causes significant strengthening of sea ice, even to the point of making it stronger than lake ice. Graystone and Langleben (1963), Tabata (1966) and Weeks (1962) showed that there was no experimental justification for this suggestion. Nor does there appear to be any indication of Na₂ SO₄. 10H₂ O strengthening in the results of either Frankenstein (Fig. 17) or Hendrickson and Rowland (1965). However, Peyton (1966) has revived the idea. Unfortunately, in his figure that supposedly demonstrates the effect he does not differentiate specimens that contain solid Na2 SO4.10H2 O from those that do not. Therefore, it is still difficult to decide whether the effect is real. It is also possible that the effect only appears when certain types of test procedures are used. However, let us assume that Assur and Peyton are correct: they then suggest several strengthening models that purportedly explain the experimental results. Unfortunately, in the current literature there are no observations on either the precipitation patterns of salt in brine pockets or on the failure mechanisms in sea ice with or without solid salts.

Figure 18 shows that in NaCl ice, v_0 (the brine volume necessary to cause the ice to have zero tensile strength) is a function of position in the ice sheet (Weeks and Assur, 1963). This means that if ice near the top of the sheet has the same brine volume as ice near the bottom of the sheet, it still will not have the same physical properties. This, of course, introduces an extreme difficulty in discussing structurally sensitive physical properties. We first must correct the measured values to a constant vertical location in a given ice sheet before we can begin to make significant comparisons. But to make this correction, it is necessary to understand the structural basis for the physical property change. We



Figure 14. Photomicrograph of sea ice at low temperatures (-19C, Thule, Greenland).



Figure 15. Photomicrograph of sea ice at a temperature only slightly below the freezing temperature (-3C, Thule, Greenland).



Figure 16. Average ring-tensile strength vs average brine volume v 1/2, NaCl ice, ice temperature warmer than -21.2C (Weeks, 1962).

know a little about the controlling factors. The spacing between the brine layers is a function of the freezing velocity (v) when that particular layer of ice formed. Assur and Weeks (1963) assumed the relation $\bar{a} v^{1/2}$ = constant where \bar{a} is the distance between the brine layers based on experimental results from the freezing of metals and limited data on NaCl ice. Using this relation they were able to explain a number of peculiarities in the vertical profile of sea ice properties. However, when Lofgren and Weeks (unpublished) performed a series of experiments to see if the assumed relation was correct, they found that the power of v, instead of having a constant value of 1/2, had a power that varied from 1 at high values of v to almost 0 at low values. This is probably the result of convection instead of diffusion in controlling the solute transfer in the liquid. If so, we should obtain the $\frac{1}{2} = \frac{1}{2}$ constant relation when we freeze from the bottom up so that salt transfer is diffusion limited. Unfortunately, this experiment has not been performed.

There are other structural parameters that vary with position in the ice sheet. Grain size increases with depth (Fig. 19) and basic brine pocket spacing probably varies with depth also. In short, we are currently blaming all the vertical variation on differences in the spacing of the brine layers. The need for more studies on the interrelations between structural parameters and growth conditions is obvious.

Another presumably structurally sensitive parameter which has just begun to be investigated is the dielectric constant of sea ice. There are three recent papers on this subject: Wentworth and Cohn (1964), Addison and Pounder (1966) and Fujino (1966). Fujino's results show pronounced changes in the slopes of both the isofrequency dielectric constant and conductivity curves as plotted as a function of temperature. These slope changes occur at roughly -22 and -52C. The -22C change obviously correlates with the precipitation of NaCl. 2H2 O and the -52C change with the final disappearance of liquid brine. The change of slope at -52C should not be very encouraging to Gitterman who claimed that the last of the brine disappeared at -36C. All of these authors have found extremely high dielectric values in the low frequency range, presumably as the result of polarization of the brine cells to form macroscopic dipoles. It will be interesting to see some theoretical treatments of this phenomenon. In the high frequency range ($\gtrsim 1$ megacycle/sec) the effects of polarization decline and it should be possible to apply a modified mixing formula to obtain information on the temperature dependence of the geometry of the brine pockets. This, unfortunately, has not been attempted. If, however, we replot Wentworth and Cohn's data at 3 mc/sec versus brine volume instead of versus temperature and salinity, some very interesting relations appear. Figure 20 shows a simple linear dependence of the dielectric constant on the brine volume. Slush ice, which is quite structurally different, lies on a separate curve as should be expected if sea ice is considered as a simple mixture of ice and brine. Fujino's results cannot be used because his work was limited to the frequency range below 100 kilocycles/second. Although there have been a large number of studies on the dielectric characteristics of pure ice (Evans, 1965).



Figure 17. Ring tensile strength, σ , vs (brine volume, ν)^{1/2}, sea ice (Frankenstein, 1966).



Figure 18. Brine volume necessary to cause the ice to have zero tensile strength (ν_0) vs position in the ice sheet (z) (Weeks and Assur, 1963).







Figure 20. Dielectric constant ε_r vs brine volume ν , 3 mc/sec (data of Wentworth and Cohn, 1964).

there are apparently no measurements of the dielectric properties of sea ice brine. It should be possible to make significant progress in this area in the near future.

I hope that in this short paper I have been able to give some general impression of the field referred to as sea ice physics. The fascinating thing about the subject is the interrelations between meteorology, growth conditions, structural details in the ice, and physical properties. Unfortunately, we are just beginning to appreciate how complex these interrelations are.

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