

## EFFECT OF GROWTH PARAMETERS ON SUBSTRUCTURE SPACING IN NaCl ICE CRYSTALS

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**ABSTRACT.** The effect of growth velocity  $v$  and solute concentration  $C$  on the cellular substructure that develops in NaCl ice is studied in the range  $3 \times 10^{-3}$  to  $10^{-5}$  cm s $^{-1}$  and 1 to 100‰ respectively. The substructure is the result of the formation of a constitutionally super-cooled zone in the liquid ahead of the advancing interface. Unidirectional freezing runs were made by placing a cold plate in contact with the "top" of the solution and using cold-plate temperatures of  $-20$  and  $-70^{\circ}\text{C}$ . The growth velocities were determined from a least-squares fit of the growth data to a power series. The average spacings between neighboring substructures  $\bar{a}_0$  were measured from photomicrographs of precisely located thin sections. Log-log plots of  $\bar{a}_0$  against  $v$  show that the slope  $n$  gradually changes as a function of  $v$ . In the run where no convection occurred,  $n$  changes from  $\frac{1}{2}$  to 1 as  $v$  decreases in agreement with the prediction of Bolling and Tiller. The results of Rohatgi and Adams are also shown to be in good agreement with this prediction. On the other hand when convection occurs,  $n$  changes from  $\frac{1}{2}$  to approximately 0 as  $v$  decreases. This is caused by convection reducing the effective value at  $C$  at the growing interface. The variation of  $\bar{a}_0$  with  $C$  is quite complex and shows a minimum in the composition range 9 to 25‰ NaCl.

**RÉSUMÉ.** Effet des paramètres de croissance sur l'espacement substructurel dans des cristaux de glace dopés de NaCl. L'effet de la vitesse de croissance  $v$  et de la concentration de la solution  $C$  sur la substructure cellulaire qui se développe dans la glace dopée de NaCl est étudié dans le domaine de  $3 \cdot 10^{-3}$  à  $10^{-5}$  et de 1 à 100‰ respectivement. La substructure est le résultat de la formation d'une zone constitutionnellement surfondue dans le liquide en avant de l'interface en croissance. Des cycles de congélation unidirectionnelle ont été réalisés en plaçant une plaque froide en contact avec le "sommets" de la solution et en usant d'une plaque froide de  $-20^{\circ}$  à  $-70^{\circ}\text{C}$ . Les vitesses de croissance ont été déterminées par la méthode des moindres carrés en exprimant les données de croissance par des séries de puissance. Les espacements moyens entre des substructures voisines  $\bar{a}_0$  ont été mesurés sur des microphotographies de coupes minces localisées avec précision. La courbe de  $\bar{a}_0$  en fonction de  $v$  sur graphique logarithmique montre que la pente  $n$  change graduellement en fonction de  $v$ . Dans le cycle où aucune convection n'avait lieu,  $n$  change de  $\frac{1}{2}$  à 1 lorsque  $v$  décroît, et cela en accord avec la prévision de Bolling et Tiller. Les résultats de Rohatgi et Adams sont aussi en bon accord avec cette prévision. D'autre part, lorsqu'il y a convection,  $n$  change de  $\frac{1}{2}$  à environ 0 lorsque  $v$  décroît. Ce fait est dû à la convection qui réduit la valeur effective de  $C$  à l'interface en croissance. La variation de  $\bar{a}_0$  avec  $C$  est plus complexe et montre un minimum dans l'intervalle de 9 à 25‰ NaCl.

**ZUSAMMENFASSUNG.** Der Einfluss von Wachstumsparametern auf die Feinstruktur von NaCl-Eiskristallen. Im Bereiche von  $3 \times 10^{-3}$  bis  $10^{-5}$  cm s $^{-1}$  bzw. 1 bis 100‰ wurde der Einfluss der Wachstumsgeschwindigkeit  $v$  und der Lösungskonzentration  $C$  auf die zelluläre Feinstruktur, die sich in NaCl-Eis bildet, untersucht. Die Feinstruktur ist die Folge des Auftretens einer natürlich unterkühlten Zone in der Flüssigkeit über der vorrückenden Grenzfläche. Durch Ansetzen einer Kälteplatte, deren Temperatur  $-20^{\circ}$  und  $-70^{\circ}\text{C}$  betrug, auf die Oberfläche der Lösung wurden einseitig ausgerichtete Gefrierbahnen erzeugt. Die Wachstumsgeschwindigkeiten wurden durch Ausgleichung der Wachstumsdaten nach einer Potenzreihe bestimmt. Die mittleren Abstände  $\bar{a}_0$  zwischen benachbarten Feinstrukturen wurden in Mikrophotographien von genau festgelegten Dünnschliffen gemessen. Log-Log-Diagramme von  $\bar{a}_0$  gegen  $v$  zeigen eine allmähliche Änderung der Neigung  $n$  als Funktion von  $v$ . Im konvektionsfreien Bereich ändert sich  $n$  von  $\frac{1}{2}$  in 1, während  $v$  in Übereinstimmung mit der Voraussage von Bolling und Tiller abnimmt. Für die Ergebnisse von Rohatgi und Adams ergibt sich ebenfalls gute Übereinstimmung mit dieser Voraussage. Andererseits ändert sich bei Konvektion  $n$  von  $\frac{1}{2}$  in annähernd Null bei abnehmendem  $v$ . Der Grund dafür liegt darin, dass die Konvektion den effektiven Wert von  $C$  an der wachsenden Grenzfläche herabsetzt. Die Variation von  $\bar{a}_0$  mit  $C$  ist sehr komplex und zeigt ein Minimum im Konzentrationsbereich von 9 bis 25‰ NaCl.

### INTRODUCTION

Single crystals of sea and NaCl ice have a characteristic cellular substructure consisting of evenly spaced ice platelets or cells separated by small-angle grain boundaries. Because ice exhibits only extremely limited solid solution with the salts in sea-water and because these ice platelets form regular protuberances on the ice-water interface during ice growth, the salt in sea ice is present as liquid inclusions trapped along these substructures. It is hardly surprising,

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therefore, that this cellular substructure is important in determining the mechanical properties of the resulting ice (Weeks and Assur, 1968). Changes in the platelet size and geometry during freezing should also influence the total amount of brine trapped in the ice.

Laboratory measurements by French (unpublished), Assur and Weeks (1963, 1964), and Rohatgi and Adams (1967 [b], [c]) show that in several salt-water systems the plate width  $a_0$  (the distance between the mid-points of the intercellular grooves measured parallel to the crystallographic  $c$ -axis) increases as the growth velocity of the ice decreases. Field measurements by Weeks and Hamilton (1962) and Tabata and Ono (1962) show a systematic increase in the average plate width  $\bar{a}_0$  with increasing depth in a sheet of sea ice. These results are in agreement because when sea ice forms, increased ice thickness invariably means decreased growth velocity. Rohatgi and Adams also show that the plate width increases as the solute content of the freezing solution increases. These two parameters, growth velocity  $v$  and solute concentration of the freezing solution  $C$ , are, therefore, the most obvious factors that influence  $\bar{a}_0$ . Only Assur and Weeks, and Rohatgi and Adams have examined the problem using unidirectional freezing which most closely approximates (natural) sea-ice growth conditions. Assur and Weeks's experiments were, however, not designed to study the variation of plate width with the above parameters and their results only indicate that a general relationship does exist. Rohatgi and Adams's experiments, on the other hand, were designed to freeze from the bottom up so that the problem of free convection, which occurs during the formation of natural sea ice, was not encountered.

#### ORIGIN OF THE SUBSTRUCTURE

Once a continuous skim of ice has formed across the upper surface of an aqueous NaCl solution, crystal growth due to purely thermal supercooling is no longer possible. The latent heat is extracted entirely through the ice sheet and the growth rate is determined by the temperature gradient in the sheet, its density, and effective thermal conductivity. Supercooling, if it exists, must be the result of the impurity build-up in the melt ahead of the interface. This phenomenon has been termed constitutional supercooling by metallurgists (Rutter and Chalmers, 1953). The critical growth conditions for the presence of constitutional supercooling under the conditions of no mixing in the liquid have been shown to occur (Tiller and others, 1953) if

$$\frac{G}{v} < -\frac{mC_0(1-k_0)}{Dk_0} \quad (1)$$

where  $G$  is the temperature gradient in the liquid at the freezing interface,  $v$  is the growth velocity,  $m$  the liquidus slope,  $C_0$  the initial concentration of NaCl in the solution,  $k_0$  the equilibrium partition coefficient, and  $D$  the diffusion coefficient of the solute in the melt. This relation has been found to be in good agreement with experimental observations in metal systems (Walton and others, 1955). When Equation (1) is applied to the freezing of both salt solutions and sea-water, it is found that even when optimum conditions for the maintenance of a planar interface occur ( $v \approx 10^{-6}$  cm/s,  $G \approx 1.0$  deg/cm, and  $k_0 = 10^{-4}$ ) the ratio  $G/v = 10^6$ . For this ratio constitutional supercooling should exist (Weeks, 1968, fig. 5) even for salinities representative of typical lake water ( $\approx 100$  p.p.m. or 0.1‰) much less the salt contents studied in this paper (1‰ and greater).

Although the existence of a constitutional supercooling layer ahead of the advancing solid-liquid interface is necessary for cell formation, it is not necessarily sufficient. In addition, there is considerable uncertainty in the preceding calculation as the result of possible variations in  $G$ . This difficulty can be avoided by calculating whether the growth conditions are such that the steep-walled cell boundary grooves associated with the entrapment of brine along plate boundaries are stable. The stability criterion for the formation of these grooves is (Tiller, 1962)

$$\frac{G_s}{v} < -\frac{mC_1(1-k_0)}{D} \quad (2)$$

where  $G_s$  is the temperature gradient in the solid and  $C_1$  is the composition of the liquid at the interface. If transfer in the liquid is by diffusion only,  $C_1 = C_0/k_0$  and Equation (2) becomes similar to Equation (1) with  $G_s$  substituted for  $G$ . Equation (2) is a more stringent criterion than (1) because for ice-solute systems  $G_s \gg G$ . Now if

$$t = \frac{\rho L h^2}{2\lambda \Delta T_0} \quad (3)$$

(Carslaw and Jaeger, 1959) where  $t$  is the time,  $\rho$  the density of the solid,  $L$  the latent heat of fusion,  $\Delta T_0$  the difference between the solid surface (i.e. cold plate-ice) temperature and the freezing temperature of the solution,  $h$  the thickness of the solid, and  $\lambda$  the thermal conductivity of the solid, then

$$v = \frac{dh}{dt} = \frac{\lambda \Delta T_0}{\rho L h} \quad (4)$$

and 
$$G_s = \frac{\Delta T_0}{h}. \quad (5)$$

Therefore Equation (2) becomes

$$\frac{\rho L}{\lambda} < -\frac{mC_0(1-k_0)}{Dk_0} \quad (6)$$

in which  $C_0$  is the only parameter under the control of the experimenter. Substitution of numerical values in Equation (6) shows that for all NaCl concentrations used in this study, cell boundary grooves are stable if solute transfer in the liquid is by diffusion only. In actuality when ice freezes from the top down, the primary mechanism of solute transfer is free convection which causes  $C_1$  to approach  $C_0$ . This explains the observations of Weeks and Lofgren (1967) who recorded transitions from a non-planar to a planar interface during the freezing of 1‰ (unstirred) and 3‰ (stirred) NaCl solutions.

Once constitutional supercooling is established and a cell-boundary groove is stable, the planar ice-water interface breaks down into parallel rows of cellular projections within each grain (Harrison and Tiller, 1963). Concentrated brine is accumulated in the grooves that develop between the rows of cells and is eventually trapped when adjacent cells develop lateral connections. The entrapped brine leaves a permanent record of the positions of the intercellular grooves. It is the distance between the mid-points of these intercellular grooves that is termed the plate width as used in this paper.

#### PREVIOUS WORK

A rigorous solution of the simultaneous temperature and solute distribution ahead of a perturbed moving interface has proven to be quite difficult (Mullins and Sekerka, 1964) although it undoubtedly will be possible to treat this problem using a numerical approach similar to that discussed by Oldfield and others (1967). In existing attempts to relate the width of cells to growth conditions theoretically, it has been necessary to make a number of simplifications. Two different types of model have been utilized. The first considers rejection of salt into the bulk liquid around the cell tips and was developed by Bolling and Tiller (1960). Although the final form of this analysis is approximate, it compactly indicates the various factors controlling  $a_0$ . The physical reasoning behind their relation is quite clear and will be outlined here. The exact solution to the steady-state solute distribution in the liquid ahead of an advancing cell cap is known to consist of both plane-wave and non-plane-wave terms. These non-plane-wave terms cause lateral diffusion and can be considered to extend some

effective distance  $y$  into the liquid. Once lateral diffusion has started it continues until terminated by the advancing interface. The allowable time for diffusion is  $t = (y + y^*)/v$  where  $y^*$  is a function of interface shape. The distance  $x$  the solute can diffuse in this time is  $x \approx (Dt)^{\frac{1}{2}}$ . Setting  $x = a_0/2$ , making several substitutions and solving the resulting equation as a quadratic, Bolling and Tiller (1960) obtain

$$a_0 \approx \frac{D}{2\pi v} \left\{ 1 + \left[ 1 + \frac{16\pi^2 v}{D} \left( \frac{0.6\gamma}{\Delta S G'_0} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \right\} \quad (7)$$

where  $\gamma$  is the solid-liquid interfacial energy,  $\Delta S$  is the entropy of fusion per unit volume, and  $G'_0$  is the effective temperature gradient at the tip of the cell which is a function of the plate shape. This relation indicates that  $a_0$  increases with an increase in  $\gamma$  (observed in metal systems) and with an increase in  $C_0$  ( $G'_0$  decreases as  $C_0$  increases). The functional form of the relation between  $a_0$  and  $v$  is also clear for extreme growth velocities: for very small and very large values of  $v$ , the value of  $n$  in

$$a_0 v^n = A \quad (8)$$

where  $A$  is a constant, is 1 and  $\frac{1}{2}$  respectively.

The alternate analysis currently available considers mass transport behind the macroscopic interface in a pool of liquid between two parallel dendritic plates. This theory was initially developed to analyze substructures in rapidly solidified alloys (Brown and Adams, 1960) and has been modified and applied to the freezing of salt solutions by French (unpublished) and Rohatgi and Adams (1967[b], [c]). In the interdendritic pool model, the liquid ahead of a freezing interface is assumed to be capable of sustaining some critical amount of constitutional supercooling. This amount is believed to depend on the type of solute and the average concentration of the solution. If for a given plate width the interface moves too rapidly, the solute build-up ahead of the interface will cause the constitutional supercooling to exceed this critical value. The interface morphology will then adjust itself by decreasing the plate width so that less solute will be rejected per unit area of interface. The final plate width is assumed to be that which sustains just the critical constitutional supercooling in the liquid. A convenient form in which to present the results of this theory is

$$a_0^2 \left( \frac{df_s}{dt} \right) = \frac{8D\Delta T}{mC_0} \quad (9)$$

where  $(df_s/dt)$  is the lateral freezing rate,  $\Delta T$  the supercooling, and the other parameters are as defined earlier. The terms on the right-hand side of Equation (9) can be considered approximately constant. Although this type of model may well apply to growth conditions under which the side branching of dendrites occurs behind the macroscopic interface, the present authors find it difficult to visualize how details of the freezing process in the intercellular grooves can effect the spacing of the cell tips at the advancing macroscopic interface. This is particularly true if changes in the value of  $a_0$  are produced by divergent plate growth as reported by Rohatgi and Adams (1967[c]). The effect of changes in the composition of the melt on  $a_0$  is quite clear in the interdendritic pool model:  $a_0^2 \propto (1/C_0)$  providing the other parameters remain essentially constant.

The only currently available measurements of changes in  $a_0$  with changes in growth parameters during the unidirectional freezing of salt solutions are those of Rohatgi and Adams (1967[b], [c]). Their results clearly indicate that  $a_0$  increases as a linear function of solute concentration. This is in general agreement with Equation (7) and in contradiction to Equation (9) unless, as suggested by Rohatgi (unpublished), the supercooling  $\Delta T$  increases more rapidly than the concentration. Rohatgi and Adams also observed that  $a_0$  consistently increased as a linear function of the distance  $x$  from the constant-temperature chill. Now if the value of  $a_0$  is in some way related to the velocity of the macroscopic interface,  $h$  may be substituted for  $x$  giving

$$a_0 = c_0 + c_1 h. \quad (10)$$

Because their experimental conditions ideally correspond to the case of parabolic ice growth with a constant surface temperature (Rohatgi and Adams, 1967[a], figure 4), we may substitute for  $h$  from Equation (4) giving

$$a_0 = c_0 + \frac{c_2}{v} \quad (11)$$

where  $c_2 = (c_1 \lambda \Delta T_0) / (\rho L)$ . This expresses  $a_0$  in terms of the velocity of the macroscopic interface and allows Rohatgi and Adams's results to be compared with Equation (7). The results of such a comparison are shown in Figure 1. The heavy line schematically represents the relation suggested by Bolling and Tiller (Equation (7)) which is transitional between the limiting cases of  $a_0 v = \text{const}$  and  $a_0 v^{1/2} = \text{const}$  at low and high values of  $v$  respectively. The experimental relation (Equation (11)) determined by Rohatgi and Adams is in good agreement with Equation (7) throughout all but the high-velocity portion of Figure 1. In this range,  $1/a_0 \rightarrow \text{const}$  as  $v \rightarrow \infty$  and Equation (11) starts to predict a value of  $a_0$  that is significantly larger than predicted by Equation (7). Over an appreciable velocity range, Equation (11) should, however, be quite a satisfactory approximation to the relation suggested by Bolling and Tiller.

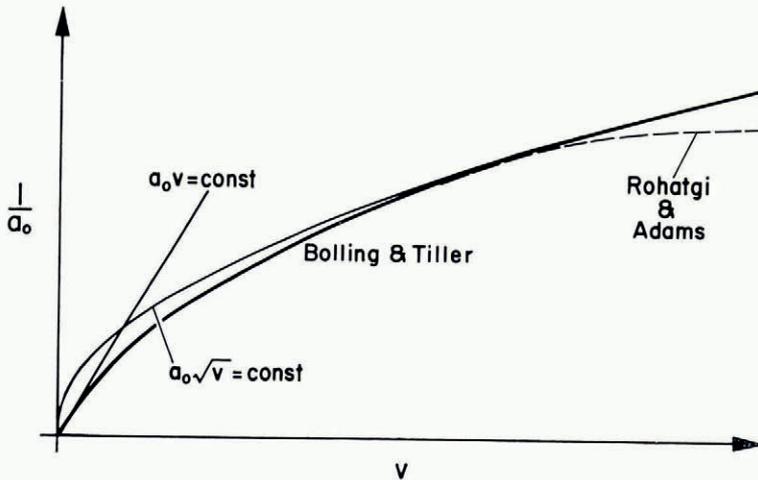


Fig. 1. Schematic comparison of the relations  $a_0 v = \text{constant}$  and  $a_0 v^{1/2} = \text{const}$ . with the relations proposed by Bolling and Tiller (1960) and Rohatgi and Adams (1967[c]).

#### EXPERIMENTAL PROCEDURES

The apparatus used (Fig. 2) to attain unidirectional freezing consisted of a lucite tube 14 cm in diameter and 62 cm long. A copper cold plate was set on top of the tube in contact with the solution. Interface temperatures were measured by a thermistor imbedded in the cold plate at the interface. A coolant was then circulated through the cold plate at a specified temperature (usually either  $-20^\circ$  or  $-70^\circ\text{C}$ ). The time at which the initial ice skim formed on the cold plate was noted as time zero. There was necessarily a time lag (on the average 3.6 h) before the specified cold-plate temperature was reached because of the initial rapid heat flow into the plate. Runs lasted 48 to 110 h during which time, ice thickness, temperature and conductivity cell readings were made. The runs are designated by a number followed by either the letter a or c. The number indicates the approximate starting salinity ( $\text{‰}$ ) of the freezing solution and the letter the general temperature of the cold plate (a =  $-20^\circ$ , c =  $-70^\circ\text{C}$ ).

Salinity samples were taken immediately upon terminating a run. The samples, each representing 1 cm of vertical growth, were allowed to melt and the salinities determined with a conductivity bridge. The water salinities corresponding to the time of growth of each sample were then calculated using the relations given in Weeks and Lofgren (1967). Thin sections were prepared in a cold room at  $-34^{\circ}\text{C}$  by cutting precisely located slabs of ice perpendicular to the growth direction. The thin sections were then photographed and the average plate width  $\bar{a}_0$  was determined from measurements on the photographs. Figures 3 and 4 are typical thin-section photographs showing the change in  $a_0$  in a given run. The growth velocity was

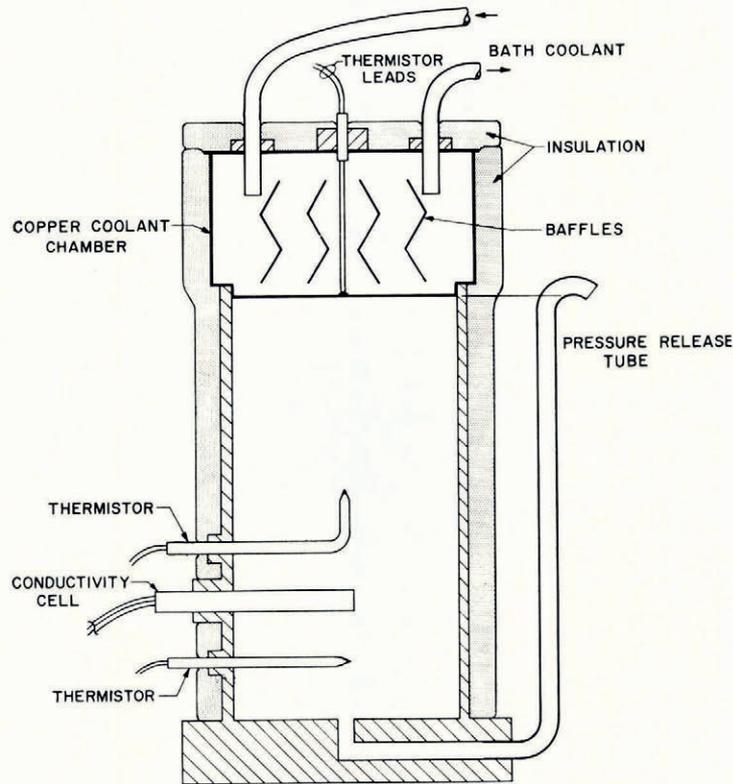


Fig. 2. Schematic drawing of the freezing apparatus.

obtained by fitting for each freezing run a 4th degree polynomial to the graph of time against ice thickness measurements. Representative plots of ice thickness against time and the fitted least-squares curves are shown in Figure 5. This relation was then differentiated to obtain an estimate of  $v$  at any position in that ice sheet. A complete tabulation of the results is contained in *U.S. Cold Regions Research and Engineering Laboratory. Research Report 195* which can be obtained from the authors.

#### EXPERIMENTAL RESULTS

Figure 6 shows the experimental results plotted as  $(-\log \bar{a}_0)$  against  $(-\log v)$ . If an equation with the general form of Equation (8) applies, the plot should be linear with a slope of  $-n$ , since

$$\log \bar{a}_0 = \log A - n \log v. \quad (12)$$

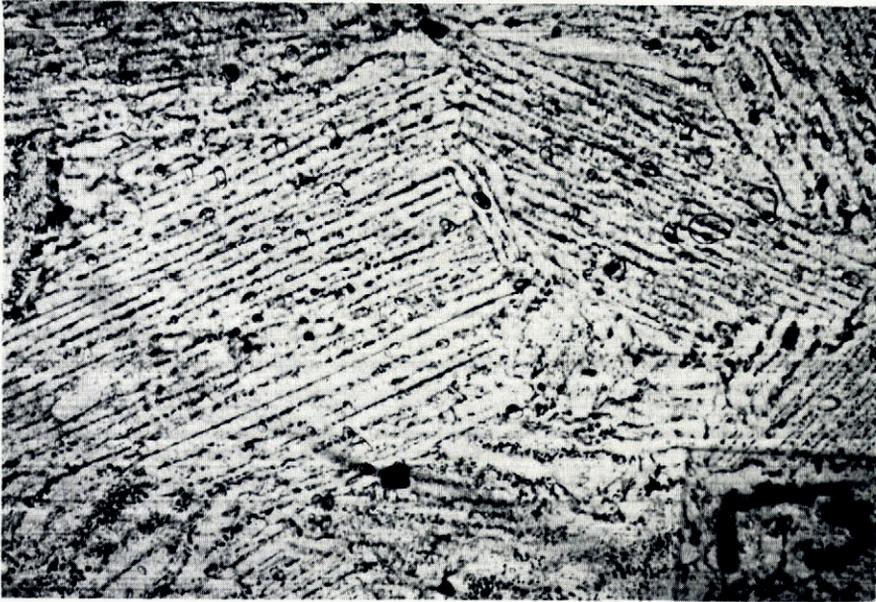


Fig. 3. Photomicrograph of thin section of NaCl ice showing substructure: Run 3a,  $v = 1.8 \times 10^{-4} \text{ cm s}^{-1}$ , distance from cold-plate 5.88 cm.

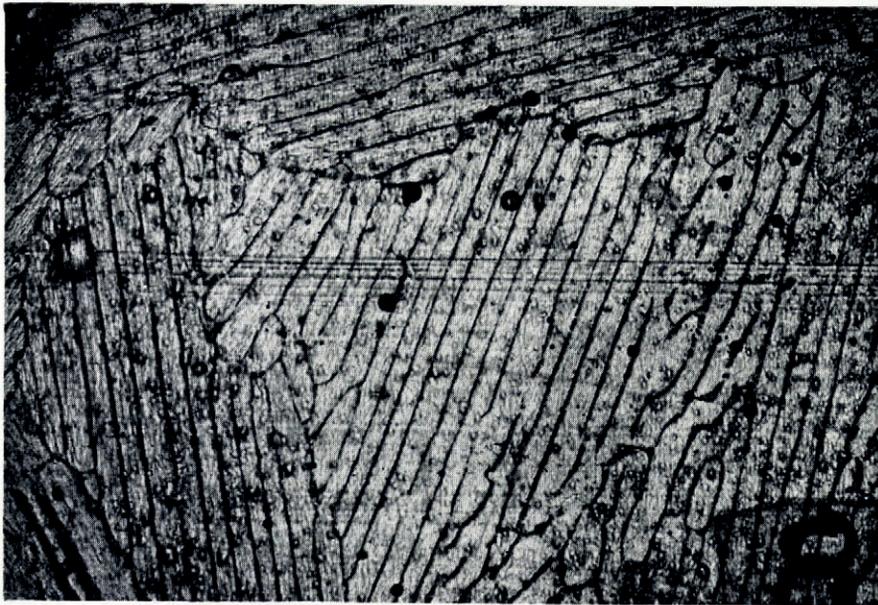


Fig. 4. Photomicrograph of thin section of NaCl ice showing substructure: Run 3a,  $v = 2.39 \times 10^{-5} \text{ cm s}^{-1}$ , distance from cold-plate 23.18 cm.

As Figure 6 clearly shows, the data do not fall on a straight line and  $n$  appears to be some smooth function of  $v$ . As  $v$  becomes large,  $n$  approaches a value of  $\frac{1}{2}$  while at low values of  $v$ ,  $n$  approaches zero. Equation (7) which may be expressed as

$$\bar{a}_0 = \frac{A}{v} f(v), \quad (13)$$

or 
$$\log(\bar{a}_0 v) = \log A + f(v), \quad (14)$$

suggests a convenient form for presenting these results within the range of the data. By trial we have found that when  $f(v)$  is represented by  $\left(\log \frac{1}{v}\right)^2$ , the resulting relation

$$\log(\bar{a}_0 v) = \log A + n_1 \left(\log \frac{1}{v}\right)^2 \quad (15)$$

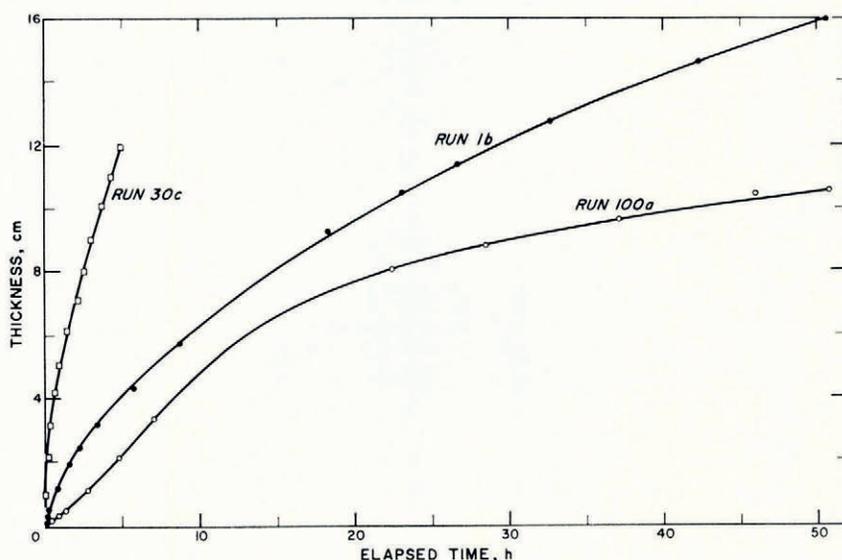


Fig. 5. Ice thickness versus elapsed time for some representative freezing runs.

is surprisingly linear. The data and the least-squares fitted line are plotted in this form in Figure 7 ( $\log A = -4.069$ ,  $n_1 = -0.093$ ). The curve in Figure 6 shows Equation (15) plotted on a graph of  $(-\log \bar{a}_0)$  against  $(-\log v)$ . The correlation coefficient obtained for Equation (15) is 0.97.

An interesting aspect of Figure 6 is the suggestion that at small growth velocities  $\bar{a}_0$  becomes relatively independent of  $v$ . Some evidence in support of such a suggestion has been obtained from the study of thick perennial polar floes. Both Schwarzacher (1959) and A. Assur (personal communication) have noted that plate widths found in such sea ice are remarkably constant with an average value of approximately 1 mm. Although no detailed growth velocity measurements are available for this type of ice, a rough estimate may be obtained by noting that the ice grows  $\approx 50$  cm in a growing season of  $\approx 10$  months giving an average velocity  $\approx 10^{-6}$  cm/sec. Such values do not contradict the results shown in Figure 6.

The obvious question posed by Figure 6 is: why does the value of  $n$  appear to approach zero at low values of  $v$  instead of a value of 1 as predicted by Bolling and Tiller? The answer becomes apparent by examining the paths of individual freezing runs as shown on Figure 6.

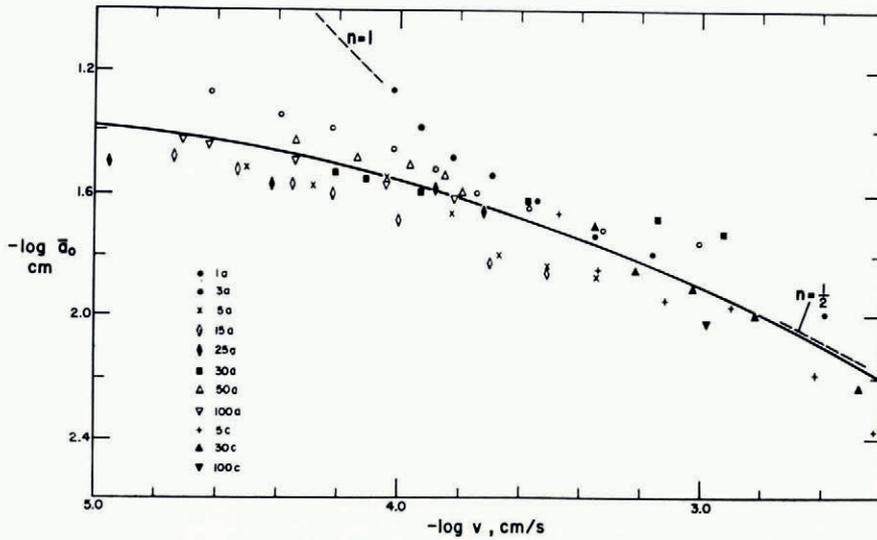


Fig. 6. Plot of  $(-\log \bar{a}_0)$  versus  $(-\log v)$ . The curve is a least-squares fit of Equation (15).

Only four runs (1a, 5c, 30c and 100c) have average  $n$  values close to or greater than 0.5. Run 1a is in exact agreement with the predictions of Bolling and Tiller with  $n$  changing from  $\frac{1}{2}$  to 1 as  $v$  decreases. This run also has the lowest initial salinity of any of the freezing runs. In the  $c$ -runs, which were made with an interface temperature of  $-70^\circ\text{C}$ , the values of  $v$  are sufficiently large that the transition of  $n$  from  $\frac{1}{2}$  to 1 might not occur. In addition, because of these large growth rates, essentially all the salt was trapped in the growing solid (Weeks and Lofgren, 1967). Therefore, these four runs have one principal thing in common: a minimal chance for appreciable convective overturn in the liquid ahead of the advancing interface. In run 1a the impurity concentration is sufficiently small that the density increase due to the rejected salt is not sufficient to counteract the density decrease as a result of the temperature

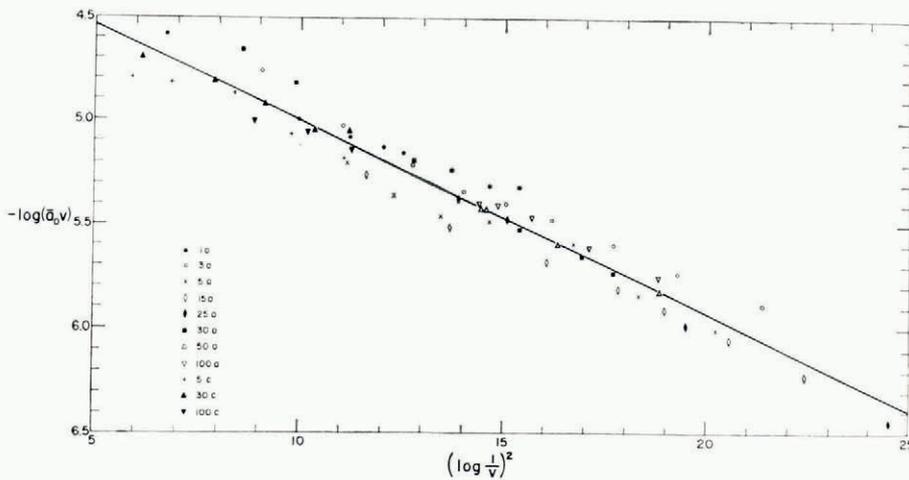


Fig. 7. Plot of  $\log(\bar{a}_0 v)$  versus  $(\log 1/v)^2$ .

drop near the interface. In runs 5c, 30c and 100c there is no convection because all the impurity is trapped in the ice. Freezing runs with initial salinities greater than 15‰ all show a general decrease in  $n$  in the low velocity range while run 3a shows a behavior intermediate between this group and run 1a. The effects of convection will be most pronounced at low growth velocities and produce a decrease in  $C_1$ , the solute concentration at the interface, causing  $C_1$  to approach  $C_0$ . As indicated by the experimental results of Rohatgi and Adams,  $a_0$  increases as  $C$  increases. Therefore, the decrease in  $C_1$  produced by the convective process, would be expected to cause  $a_0$  to decrease, as observed. Presumably the value of  $n$  in Figure 6 approaches zero at small growth velocities because the increase in  $a_0$  produced by the decrease in  $v$  is balanced by the decrease in  $a_0$  caused by the decrease in  $C_1$ .

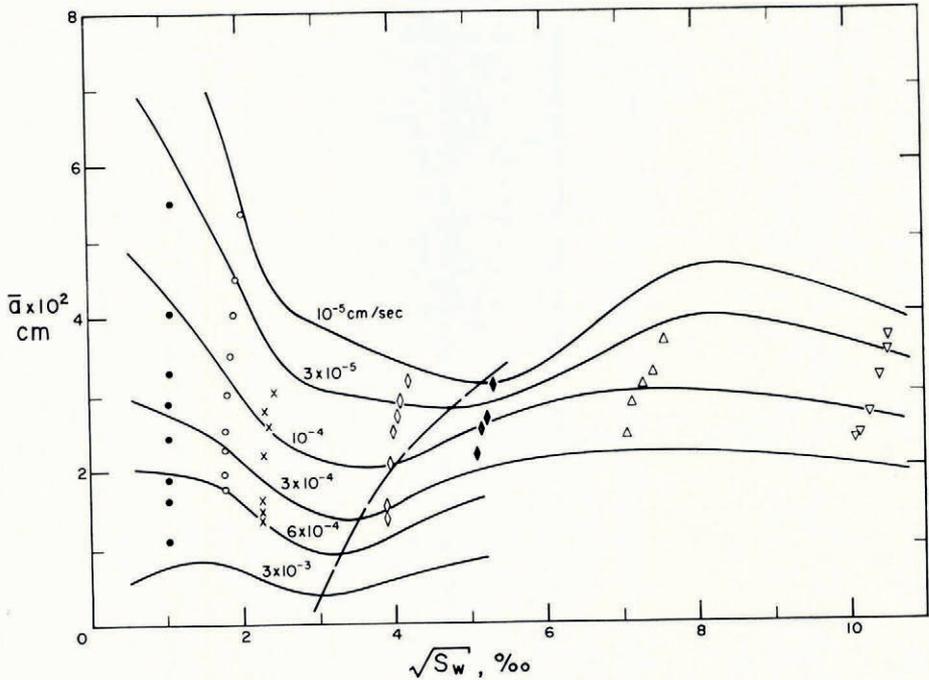


Fig. 8. Plot of  $\bar{a}_0$  versus  $S_w^{1/2}$ . The symbols are those used in Figures 6 and 7.

The effects of convection also appear in Figure 8 which is a plot of  $\bar{a}_0$  against the square root of the calculated water salinity from which each measured set of platelets grew. The lines represent constant growth velocities which were obtained by using Equation (15) to determine  $a_0$  values for a fixed set of velocities for each individual run. In the  $S_w$  range 1 to 10‰, the plate width decreases as the solute concentration increases. A minimum indicated by the dashed line occurs in the range 10 to 25‰ and appears to depend on the growth velocity. At  $S_w$  values greater than 25‰ there is initially an increase in  $a_0$  and then a slight decrease. Although we currently do not understand the details of this complex pattern, a few observations can be made. The minimum in Figure 8 is clearly not the eutectic composition (23.3‰) and occurs close to the composition where the maximum density of the solution is at its freezing point (24.7‰). As the growth velocity increases, increased solute build-up would cause convection to start at lower bulk solute concentrations. This agrees with the observed decrease in the salinity of the minimum with an increase in  $v$ . The behavior shown in Figure 8 is strikingly different from the results of Rohatgi and Adams (1967[c], fig. 14) who

found a simple linear increase in  $a_0$  of 0.06 mm as  $C$  increased from 0 to 100%. In Figure 8 this effect appears to be masked by the variation in  $a_0$  produced by convection. Further experimental studies are clearly needed.

It also should be remembered that overall interface morphology changes as a function of  $v$ . At high growth velocities the shapes of the platelet or cell "caps" should, to a good approximation, be parabolic (Bolling and Tiller, 1961; Harrison and Tiller, 1963). As the velocities become slower the cell caps become broader (Bolling and Tiller, 1960) presumably becoming almost rectangular at very low growth rates. The transition between these different morphologies is apparently gradual (Walton and others, 1955; Plaskett and Winegard, 1960; James, 1966). These changes will also presumably be part of any complete understanding of the variation in  $a_0$  with growth parameters.

This study appears to have produced more problems than it has solved. During the formation of natural sea ice, convection occurs continuously. Therefore, it is imperative that its effect on the sea-ice substructure be taken into account. We feel that these results should also be of interest to metallurgists. Attention has recently been focused on the effect of convective processes in influencing the columnar-to-equiaxed transition during the solidification of ingots by the studies of Cole and Bolling (1965, 1966, 1967[a], [b]) and Cole (1967). The present paper suggests the importance of similar convective processes in controlling the size of intracrystalline substructures during the solidification of metals.

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