Research Report 195

EFFECT OF GROWTH PARAMETERS ON SUBSTRUCTURE SPACING IN NaCl ICE CRYSTALS

G. Lofgren and W.F. Weeks

January 1969

DA TASK 1T061102B52A02

U.S. ARMY MATERIEL COMMAND
TERRESTRIAL SCIENCES CENTER

COLD REGIONS RESEARCH & ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE
AND SALE; ITS DISTRIBUTION IS UNLIMITED.

PREFACE

This report was prepared by Dr. Gary Lofgren, Petrologist, Department of Earth Sciences, Dartmouth College, and Dr. W.F. Weeks, Research Glaciologist, Snow and Ice Branch, Cold Regions Research and Engineering Laboratory (CRREL), U.S. Army Terrestrial Sciences Center (USA TSC). This report was published under DA Task 1T061102B52A02, *Research in Earth Physics – Cold Regions and Related Environment*.

The present report is a condensation of a portion of Dr. Lofgren's M.S. thesis. Dr. Lofgren is currently with the Geology and Geochemistry Branch, National Aeronautics and Space Administration Manned Spacecraft Center, Houston, Texas 77058.

The authors wish to thank Mr. W.F. Reeves for assisting them during the experimental phase of the study and Drs. A. Assur, G.F. Bolling, J.B. Lyons, P.K. Rohatgi, and W.A. Tiller for their advice.

Citation of commercial products is for information only and does not constitute official endorsement or approval.

USA TSC is a research activity of the Army Materiel Command.

CONTENTS

	Page
Preface	ii
Abstract	iv
Introduction	1
Origin of the substructure	1
Previous work	3
Experimental procedures	5
Experimental results	8
Literature cited	12
Appendix A	15

ILLUSTRATIONS

Figure

1. A plot of the boundaries that for different k_o values separate growth conditions where a planar interface is stable and where it is unstable ..	2
2. Schematic comparison of the relations $a_o v = \text{const}$ and $a_o \sqrt{v} = \text{const}$ with the relations proposed by Bolling and Tiller, and Rohatgi and Adams	5
3. Schematic drawing of the freezing apparatus	6
4. Photomicrograph of thin section of NaCl ice showing substructure	7
5. Photomicrograph of thin section of NaCl ice showing substructure	7
6. Ice thickness vs elapsed time for some representative freezing runs	8
7. Plot of $(-\log \bar{a}_o)$ vs $(-\log v)$	9
8. Plot of $-\log(\bar{a}_o v)$ vs $\left(\log \frac{1}{v}\right)^2$	10
9. Plot of $\bar{a}_o$ vs $\sqrt{S_w}$	11

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 3×10^{-3} to 10^{-5} cm/sec and 1 to 100 %₀ respectively. The substructure is the result of the formation of a constitutionally supercooled 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°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 $\bar{a}_0$ vs v show that the slope n gradually changes as a function of v . In the run where no convection occurs, 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 of 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 %₀ NaCl.

EFFECT OF GROWTH PARAMETERS ON SUBSTRUCTURE SPACING IN NaCl ICE CRYSTALS

by

G. Lofgren and W.F. Weeks

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, therefore, that this cellular substructure is important in determining the mechanical properties of the resulting ice (Weeks and Assur, 1967). 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 (1962), Assur and Weeks (1963, 1964), and Rohatgi and Adams (1967a, b) 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 c-crystallographic 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' experiments, however, were not designed for studying the variation of plate width with the above parameters and their results only indicate that a general relationship does exist. Rohatgi and Adams' experiments, on the other hand, were designed to freeze the ice 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, density, and effective thermal conductivity of the sheet. Supercooling, if it exists, must be the result of the impurity buildup in the melt ahead of the interface. This phenomenon has been termed constitutional supercooling (hereafter referred to as C.S.) by metallurgists (Rutter and Chalmers, 1953). The critical growth conditions for the presence of C.S. under the conditions of no mixing in the liquid have been shown to occur (Tiller *et al.*, 1953) if

$$\frac{G}{v} < \frac{-m C_o (1 - k_o)}{D k_o} \quad (1)$$

where G is the temperature gradient in the liquid at the freezing interface; v the growth velocity; m the liquidus slope; C_o the initial concentration of NaCl in the solution; k_o 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 *et al.*, 1955). When eq 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/sec, $G \approx 1.00$ /cm, and $k_o = 10^{-4}$) the ratio $G/v = 10^6$. For this ratio C.S. should exist (Fig. 1) even for salinities representative of typical lake water (≈ 100 ppm or 0.1 ‰) much less the salt contents studied in this paper (1 ‰ and greater).

Although the existence of a C.S. 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 if 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 (Tiller, 1962) is

$$\frac{G_s}{v} < \frac{-m C_i (1 - k_o)}{D} \quad (2)$$

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

Figure 1. A plot of the boundaries that for different k_o values separate growth conditions where a planar interface is stable and where it is unstable. Solute transfer in the liquid is assumed to be by diffusion only.

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

(Carslaw and Jaeger, 1959) where t = time, ρ = density of the solid, L = latent heat of fusion, ΔT_o = difference between the solid surface (i.e., cold plate/ice) temperature and the freezing temperature of the solution, h = thickness of the solid, and κ = thermal conductivity of the solid, then

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

and

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

Therefore eq 2 becomes

$$\frac{\rho L}{\kappa} < \frac{-m C_o (1 - k_o)}{D k_o} \quad (6)$$

in which C_o is the only parameter under the control of the experimenter. Substitution of numerical values in eq 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_i to approach C_o . 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 C.S. 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). Undoubtedly, however, it will be possible to treat this problem using a numerical approach similar to that discussed by Oldfield *et al.* (1967). In existing attempts to theoretically relate the width of cell boundaries to growth conditions, it has been necessary to make a number of simplifications. Two different types of analyses have been utilized. The first analysis 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_o . The physical reasoning behind the Bolling and Tiller 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 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 it is 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 $x \approx \sqrt{Dt}$. Setting $x = a_o/2$, making several substitutions and solving the resulting equation as a quadratic, Bolling and Tiller (1960) obtain

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

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

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

where A is a constant, are 1 and $1/2$ respectively.

The alternative analysis currently available considers mass transport behind the macroscopic interface in a pool of liquid between two parallel dendritic plates. This analysis was initially developed for substructures in rapidly solidified alloys (Brown and Adams, 1960) and has been modified and applied to the freezing of salt solutions by French (1962) and Rohatgi and Adams (1967a, b). In the interdendritic pool model, the liquid ahead of a freezing interface is assumed to be capable of sustaining some critical amount of C.S. 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 buildup ahead of the interface will cause the C.S. 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 C.S. in the liquid. A convenient form in which to present the results of this theory is

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

where (df_s/dt) is the lateral freezing rate, ΔT is the supercooling, and the other parameters are as defined earlier. The terms on the right-hand side of eq 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 control the spacing of the cell tips at the advancing macroscopic interface. This is particularly true if changes in the value of a_o are produced by divergent plate growth as reported by Rohatgi and Adams (1967a). Provided the other parameters remain essentially constant, the effect of changes in the composition of the melt on a_o is quite clear in the interdendritic pool model: $a_o^2 \propto (1/C_o)$.

The only currently available measurements of changes in a_o with changes in growth parameters during the unidirectional freezing of salt solutions are those of Rohatgi and Adams (1967a, b). Their results clearly indicate that a_o increases as a linear function of solute concentration. This is in general agreement with eq 7 and in contradiction to eq 9 unless as suggested by Rohatgi (1964) the supercooling ΔT increases more rapidly than the concentration. Rohatgi and Adams also

Figure 2. Schematic comparison of the relations $a_0 v = \text{const}$ and $a_0 \sqrt{v} = \text{const}$ with the relations proposed by Bolling and Tiller (1960) and Rohatgi and Adams (1967a).

The heavy line schematically represents the relation suggested by Bolling and Tiller (eq 7) which is transitional between the limiting cases of $a_0 v = \text{const}$ and $a_0 \sqrt{v} = \text{const}$ at low and high values of v respectively. The experimental relation (eq 11) determined by Rohatgi and Adams is in good agreement with eq 7 throughout all but the high velocity portion of Figure 2. In this range, $1/a_0 \rightarrow \text{const}$ as $v \rightarrow \infty$ and eq 11 starts to predict a value of a_0 that is significantly larger than predicted by eq 7. Over an appreciable velocity range, eq 11, however, should be a quite satisfactory approximation to the relation suggested by Bolling and Tiller.

observed that a_0 consistently increases 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, 1967c, their Fig. 4), we may substitute for h from eq 4 giving

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

where $c_2 = (c_1 \kappa \Delta T_0)/(\rho L)$. This expresses a_0 in terms of the velocity of the macroscopic interface and allows Rohatgi and Adams' results to be compared with eq 7. The results of such a comparison are shown in Figure 2.

EXPERIMENTAL PROCEDURES

The apparatus used (Fig. 3) 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 or -70°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 hours) before the specified cold-plate temperature was reached because of the initial rapid heat flow into the plate. Runs lasted 48 to 110 hours during which elapsed 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 ($^\circ\text{oo}$) of the freezing solution and the letter the general temperature of the cold plate ($a = -20^\circ\text{C}$, $c = -70^\circ\text{C}$). A summary of data describing the different freezing runs is given in Table AI (p. 15).

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°C by cutting precisely located slabs of ice perpendicular to the growth direction.

Figure 3. Schematic drawing of the freezing apparatus.

The thin sections were then photographed. The average plate width $\bar{a}_0$ was determined for each section by marking several lines on the photograph normal to the (0001) planes of different crystals. The length of the lines and the number of substructure boundaries intersected by each line were then measured. This procedure determines $\bar{a}_1, n_1; \bar{a}_2, n_2; \dots \bar{a}_k, n_k$ where $\bar{a}_k$ is the average plate width for the k^{th} grain in the section and n_k is the number of plates counted in determining this average. A weighted average for the whole thin section was then computed using

$$\bar{a}_0 = \frac{n_1 \bar{a}_1 + n_2 \bar{a}_2 + \dots + n_k \bar{a}_k}{n_1 + n_2 + \dots + n_k}. \quad (12)$$

Figures 4 and 5 are typical thin-section photomicrographs showing the change in a_0 in a given run

The growth velocities were obtained by fitting by least-squares an empirical equation of the form

$$t = \alpha_1 h + \alpha_2 h^2 + \alpha_3 h^3 + \alpha_4 h^4 \quad (13)$$

to the time (t) vs ice thickness (h) data. A tabulation of the correlation and regression coefficients for the different freezing runs is given in Table AII. Equation 13 was then differentiated to obtain an estimate of v at any position in the ice sheet. The first two terms of eq 13 have theoretical justification. When convective heat transfer at the ice-air interface is taken into account, the fresh-ice growth equation (Neumann, 1949; Adams *et al.*, 1960) becomes

$$t = \frac{\rho L h}{\Delta T_a} \left(\frac{1}{e} + \frac{h}{2\kappa} \right) \quad (14)$$

where ΔT_a is the difference between the ambient temperature (i.e., temperature of the circulating coolant) and the freezing temperature of the water and e is the overall coefficient of surface heat transfer. If we ignore slight complications in the definitions of L and κ as applied to NaCl ice, we can rewrite eq 14 as

$$t = \left(\frac{\rho L}{e \Delta T_a} \right) h + \left(\frac{\rho L}{2\kappa \Delta T_a} \right) h^2. \quad (15)$$

If ΔT_a is held constant, eq 15 is of the same form as eq 13 if only the first two terms of eq 13 are considered. If the ice surface temperature T_o is always the same as the air (coolant) temperature T_a (i.e., the surface heat transfer coefficient is considered to be infinite), eq 15 becomes identical with eq 3, which is the classic form of the ice growth equation first suggested by Stefan (Carslaw and Jaeger, 1959). The h^3 and h^4 terms of eq 13 are needed because it was not possible to maintain the coolant circulating through the freezing plate at a constant temperature during the initial

Figure 4. Photomicrograph of thin section of NaCl ice showing substructure;
Run 3a, $v = 1.8 \times 10^{-4}$ cm/sec, distance from cold plate 5.88 cm.

Figure 5. Photomicrograph of thin section of NaCl ice showing substructure;
Run 3a, $v = 2.39 \times 10^{-5}$ cm/sec, distance from cold plate 23.18 cm.

Figure 6. Ice thickness vs elapsed time for some representative freezing runs.

stages of ice growth. Also the rejection of salt by the ice depressed the freezing temperature of the underlying solution.

For most freezing runs eq 13 gives an excellent fit throughout the complete range of the growth data. Representative plots of ice thickness vs elapsed time and the fitted least-squares curves are shown in Figure 6. However, in runs 3a, 15a and 100c, negative growth velocities were obtained for ice thicknesses of less than 3 cm. This was undoubtedly the result of rapid changes in the temperature of the circulating coolant. To eliminate these negative velocities, the data were fitted to eq 13 with the first term deleted. The data and both empirical equations were then plotted and a breakoff point between the two equations was determined. The growth velocities given in Table AIII are the result of this compromise.

EXPERIMENTAL RESULTS

Figure 7 shows the experimental results plotted as $(-\log \bar{a}_0)$ vs $(-\log v)$. Table AIII gives a complete listing of the data. If an equation with the general form of eq 8 applies, the plot should be linear with a slope of $-n$ since

$$\log \bar{a}_0 = \log A - n \log v. \quad (16)$$

As Figure 7 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

$$\bar{a}_0 = \frac{A}{v} \cdot f(v) \quad (17)$$

or

Figure 7. Plot of $(-\log \bar{a}_0)$ vs $(-\log v)$. The curve is a least-squares fit of eq 19.

$$\log(a_0 v) = \log A + f(v) \quad (18)$$

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 $[\log(1/v)]^2$, the resulting relation

$$\log(\bar{a}_0 v) = \log A + n_1 \left(\log \frac{1}{v} \right)^2 \quad (19)$$

is surprisingly linear. The data and the least-squares fitted line are plotted in this form in Figure 8 ($\log A = -4.069$, $n_1 = -0.093$). The curve in Figure 7 shows eq 19 plotted on a $(-\log \bar{a}_0)$ vs $(-\log v)$ graph. The correlation coefficient obtained for eq 19 is 0.97.

An interesting aspect of Figure 7 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 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 ≈ 50 cm in a growing season of ≈ 10 months giving an average velocity of $\approx 10^{-6}$ cm/sec. Such values do not contradict the results shown in Figure 7.

The obvious question posed by Figure 7 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 (1960)? The answer becomes apparent by examining the paths of individual freezing runs as shown on Figure 7. 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°C , the values of v are sufficiently large that

Figure 8. Plot of $-\log(\bar{a}_0 v)$ vs $\left(\log \frac{1}{v}\right)^2$.

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 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_i , the solute concentration at the interface, causing C_i 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_i produced by the convective process, would be expected to cause a_0 to decrease, as observed. Presumably the value of n in Figure 7 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_i .

The effects of convection also appear in Figure 9, which is a plot of $\bar{a}_0$ vs 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 eq 19 to determine a_0 values for a fixed set of velocities for each run. In the S_w range 1 to 10 ‰, the plate width decreases as the 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, we can make a few observations. The minimum in Figure 9 is clearly not the eutectic composition (233 ‰) 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 buildup 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

Figure 9. Plot of $\bar{a}_0$ vs $\sqrt{S_w}$. The symbols are those used in Figures 7 and 8.

shown in Figure 9 is strikingly different from the results of Rohatgi and Adams (1967a, their Fig. 14), who found a simple linear increase in a_0 of 0.06 mm as C increased from 0 to 100 ‰. In Figure 9 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 *et al.*, 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, 1967a, 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.

LITERATURE CITED

- Adams, C.M.; French, D.N. and Kingery, W.D. (1960) Solidification of sea ice. *Journal of Glaciology*, vol. 3, p. 745-760.
- Assur, A. and Weeks, W.F. (1963) Growth, structure and strength of sea ice. International Union of Geodesy and Geophysics. International Association of Scientific Hydrology. General Assembly of Berkeley, 19-31 Sept 1963, Publication No. 61, p. 95-108.
- _____ (1964) Growth, structure and strength of sea ice. U.S. Army Cold Regions Research and Engineering Laboratory (USA CRREL) Research Report 135.
- Bolling, G.F. and Tiller, W.A. (1960) Growth from the melt, II. Cellular interface morphology. *Journal of Applied Physics*, vol. 31, no. 11, p. 2040-2045.
- _____ (1961) Growth from the melt, III. Dendritic growth. *Journal of Applied Physics*, vol. 32, no. 12, p. 2587-2605.
- Brown, P.E. and Adams, C.M. (1960) Fusion zone structures and properties in aluminum alloys. *Welding Journal*, vol. 39, no. 12, *Welding Research Supplement*, p. 520S-524S.
- Carslaw, H.S. and Jaeger, J.C. (1959) *Conduction of heat in solids*. London: Oxford University Press.
- Cole, G.S. (1967) Temperature measurements and fluid flow distributions ahead of solid-liquid interfaces. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 239, no. 9, p. 1287-1295.
- _____ and Bolling, G.F. (1965) The importance of natural convection in casting. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 233, no. 8, p. 1568-1572.
- _____ (1966) Augmented natural convection and equiaxed grain structure in casting. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 236, no. 9, p. 1366-1368.
- _____ (1967a) Enforced fluid motion and the control of grain structures in metal castings. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 239, no. 11, p. 1824-1835.
- _____ (1967b) Visual observations of crystallization from aqueous solution under enforced fluid motion. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 239, no. 11, p. 1860-1861.
- French, D.N. (Unpublished) Solidification of aqueous solutions. M.I.T. Sc. D. Thesis, 1962.
- Harrison, J.D. and Tiller, W.A. (1963) Controlled freezing of water. In *Ice and snow: properties, processes, and applications: Proceedings of a conference held at the Massachusetts Institute of Technology, 12-16 February 1962* (W.D. Kingery, Ed.). Cambridge: The M.I.T. Press, p. 215-225.
- James, D.W. (1966) On the nature of the solid/liquid interface transition at the onset of constitutional cooling. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 236, no. 6, p. 936.
- Mullins, W.W. and Sekerka, R.F. (1964) Stability of a planar interface during solidification of a dilute binary alloy. *Journal of Applied Physics*, vol. 35, no. 2, p. 444-451.
- Neumann, K. (1949) Die Wachstumsgeschwindigkeit von Eisdecken in Abhängigkeit von Lufttemperatur und Windgeschwindigkeit (The growth velocity of ice sheets as a function of air temperature and wind velocity). *Annalen der Meteorologie*, vol. 2, p. 144-155 (text in German).

- Oldfield, W.; Geering, G.T. and Tiller, W.A. (1967) The evolution of crystal shape: a computer model. *Materials Science and Engineering*, vol. 2, no. 2, p. 91-106.
- Plaskett, T.S. and Winegard, W.C. (1960) Cell to dendrite transition in tin base alloys. *Canadian Journal of Physics*, vol. 38, no. 8, p. 1077-1088.
- Rohatgi, P.K. (Unpublished) Dendritic solidification of aqueous solutions. M.I.T. Sc.D. Thesis, 1964.
- Rohatgi, P.K. and Adams, C.M. (1967a) Ice-brine dendritic aggregate formed on freezing of aqueous solutions. *Journal of Glaciology*, vol. 6, no. 47, p. 663-679.
- _____ (1967b) Freezing rate distributions during unidirectional solidification of solutions. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 239, no. 6, p. 850-857.
- _____ (1967c) Effect of freezing rates on dendritic solidification of ice from aqueous solutions. *Transactions of the Metallurgical Society of the American Institute of Mining and Metallurgical Engineers*, vol. 239, no. 11, p. 1729-1736.
- Rutter, J.W. and Chalmers, B. (1953) A prismatic substructure formed during solidification of metals. *Canadian Journal of Physics*, vol. 31, no. 1, p. 15-39.
- Schwarzacher, W. (1959) Pack-ice studies in the Arctic Ocean. *Journal of Geophysical Research*, vol. 64, no. 12, p. 2357-2367.
- Tabata, T. and Ono, N. (1962) On the crystallographic study of several kinds of ice. *Low Temperature Science*, vol. A-20, p. 199-214 (text in Japanese).
- Tiller, W.A. (1962) Effect of grain boundaries on solute partitioning during progressive solidification. *Journal of Applied Physics*, vol. 33, no. 10, p. 3106-3107.
- _____ ; Jackson, K.A.; Rutter, J.W. and Chalmers, B. (1953) The redistribution of solute atoms during the solidification of metals. *Acta Metallurgica*, vol. 1, no. 4, p. 428-437.
- Walton, D.; Tiller, W.A.; Rutter, J.W. and Winegard, W.C. (1955) Instability of a smooth solid-liquid interface during solidification. *Journal of Metals*, vol. 7, p. 1023-1026.
- Weeks, W.F. and Assur, A. (1967) The mechanical properties of sea ice. USA CRREL Cold Regions Science and Engineering Monograph II-C3.
- Weeks, W.F. and Hamilton, W.L. (1962) Petrographic characteristics of young sea ice, Point Barrow, Alaska. *American Mineralogist*, vol. 47, no. 7. and 8, p. 945-961.
- Weeks, W.F. and Lofgren, G. (1967) The effective solute distribution coefficient during the freezing of NaCl solutions. *Proceedings of the International Conference on Low Temperature Science*, Hokkaido University, vol. 1, no. 1, p. 579-597.

APPENDIX A

Table AI. Descriptive data on the different freezing runs.

Run	Initial salinity (‰)	Approximate cold-plate temperatures (°C)	Final ice thickness (cm)	Total time t (hr)
1a*	1.05	-20	19.00	47.16
3a	3.10	-20	24.10	99.58
5a	5.00	-20	15.60	53.96
5c	5.13	-70	12.15	4.88
15a	15.05	-20	14.20	99.80
25a	25.50	-20	11.30	82.13
30a	30.00	-20	13.20	29.78
30c	28.70	-70	12.65	5.34
50a	48.50	-20	16.35	50.86
100a	99.00	-20	10.55	50.91
100c	95.50	-70	10.45	4.91

* Run numbers indicate approximate initial water salinities in ‰ and the letters indicate cold-plate temperatures: a is -20C and c is -70C.

Table AII. Tabulation of correlation and regression coefficients.

$t = a_1h + a_2h^2 + a_3h^3 + a_4h^4$						
Run	Data points	a_1	a_2	a_3	a_4	Correlation coefficient
1a	25	0.0657	0.1277	-0.0029	0.0001	0.9999
1b	17	0.4567	0.1983	-0.0054	0.0002	0.9999
3a	23	-0.3057	0.2378	-0.0124	0.0004	0.9998
3s*	22	-0.7594	0.8521	-0.1368	0.0084	0.9987
5a	20	0.0021	0.2274	-0.0148	0.0009	0.9995
5b	13	0.7113	0.1726	-0.0026	0.0001	0.9999
15a	20	-0.4297	0.4578	-0.0076	0.0008	0.9991
25a	23	0.0570	0.9755	-0.2266	0.0175	0.9997
30a	17	0.2777	-0.0733	0.0304	-0.0010	0.9997
50a	18	1.2923	0.0835	-0.0071	0.0005	0.9999
100a	13	2.6970	-0.2230	-0.0015	0.0039	0.9996
5c	36	0.0362	0.0124	0.0026	-0.0001	0.9999
30c	39	-0.0219	0.0474	-0.0010	0.0000	0.9999
100c	29	-0.0688	0.0831	-0.0021	-0.0001	0.9998
$t = a_2h^2 + a_3h^3 + a_4h^4$						
3a	23		0.1736	-0.0083	0.0003	0.9998
3s*	22		0.5411	-0.0994	0.0070	0.9986
15a	20		0.2796	0.0139	0.0000	0.9991
100c	29		0.0467	0.0035	-0.0004	0.9997

* Stirred.

Table AIII. Tabulation of measured substructure spacings and associated growth and compositional parameters.

z is the position of thin section measured from the ice-cold plate interface; a is the average observed plate width; n is the number of plates measured; v is the growth velocity (computed); and S_w is the water salinity at z .

$z(\text{cm})$	$a(\text{cm})$	n	$v(\text{cm/sec})$	$S_w(\text{‰})$
Run 1a				
0.17	1.01×10^{-2}	50	2.55×10^{-3}	1.04
1.38	1.61×10^{-2}	315	6.88×10^{-4}	1.05
2.33	1.86×10^{-2}	269	4.46×10^{-4}	1.06
3.93	2.43×10^{-2}	237	2.85×10^{-4}	1.07
5.83	2.88×10^{-2}	212	2.00×10^{-4}	1.09
7.97	3.29×10^{-2}	125	1.49×10^{-4}	1.13
9.93	4.05×10^{-2}	68	1.18×10^{-4}	1.17
11.93	5.50×10^{-2}	29	9.53×10^{-5}	1.21
Run 3a				
0.17	9.72×10^{-3}	85	4.76×10^{-3}	3.11
1.38	1.76×10^{-2}	296	6.38×10^{-4}	3.13
2.23	1.94×10^{-2}	302	4.17×10^{-4}	3.13
3.73	2.27×10^{-2}	253	2.68×10^{-4}	3.16
5.88	2.54×10^{-2}	205	1.80×10^{-4}	3.22
8.68	3.02×10^{-2}	248	1.32×10^{-4}	3.31
11.98	3.50×10^{-2}	143	9.48×10^{-5}	3.44
15.78	4.03×10^{-2}	137	6.14×10^{-5}	3.63
19.03	4.74×10^{-2}	134	4.06×10^{-5}	3.83
23.18	5.36×10^{-2}	249	2.39×10^{-5}	4.16
Run 5a				
1.53	1.36×10^{-2}	184	4.58×10^{-4}	5.06
2.43	1.42×10^{-2}	300	3.10×10^{-4}	5.09
3.83	1.60×10^{-2}	364	2.14×10^{-4}	5.16
5.78	2.19×10^{-2}	301	1.49×10^{-4}	5.25
8.83	2.78×10^{-2}	272	8.97×10^{-5}	5.42
11.88	2.69×10^{-2}	105	5.21×10^{-5}	5.65
14.68	3.03×10^{-2}	207	3.16×10^{-5}	5.95
Run 5c				
1.15	4.18×10^{-3}	444	3.74×10^{-3}	5.13
2.05	6.34×10^{-3}	377	2.38×10^{-3}	5.13
3.75	1.06×10^{-2}	254	1.26×10^{-3}	5.14
5.8	1.13×10^{-2}	176	7.47×10^{-4}	5.14
8.7	1.38×10^{-2}	164	4.59×10^{-4}	5.16
11.8	2.19×10^{-2}	123	3.37×10^{-4}	5.23
Run 15a				
1.28	1.39×10^{-2}	66	3.54×10^{-4}	15.21
2.08	1.50×10^{-2}	161	2.06×10^{-4}	15.31
3.73	2.07×10^{-2}	155	9.78×10^{-5}	15.52
5.73	2.50×10^{-2}	270	5.93×10^{-5}	15.87
7.83	2.68×10^{-2}	224	4.40×10^{-5}	16.35
9.83	2.93×10^{-2}	203	2.93×10^{-5}	16.78
13.08	3.17×10^{-2}	303	1.85×10^{-5}	17.61

$z(\text{cm})$	$a(\text{cm})$	n	$v(\text{cm}/\text{sec})$	$S_w(^{\circ}/_{00})$
Run 25a				
1.38	1.48×10^{-2}	33	1.70×10^{-4}	25.75
2.38	1.82×10^{-2}	183	1.55×10^{-4}	25.89
3.88	2.19×10^{-2}	204	1.88×10^{-4}	26.16
5.78	2.56×10^{-2}	209	1.31×10^{-4}	26.66
7.83	2.66×10^{-2}	257	3.85×10^{-5}	27.32
10.33	3.12×10^{-2}	209	1.12×10^{-5}	28.36
Run 30a				
0.27	8.96×10^{-3}	29	1.14×10^{-3}	Not meas- ured
1.38	1.88×10^{-2}	245	1.17×10^{-3}	
2.38	2.09×10^{-2}	294	7.11×10^{-4}	
4.38	2.38×10^{-2}	186	2.66×10^{-4}	
7.03	2.52×10^{-2}	341	1.18×10^{-4}	
9.43	2.79×10^{-2}	335	7.70×10^{-5}	
11.53	2.90×10^{-2}	299	3.17×10^{-5}	
Run 30c				
1.15	5.89×10^{-3}	340	3.34×10^{-3}	28.73
2.35	9.93×10^{-3}	293	1.51×10^{-3}	28.75
3.8	1.22×10^{-2}	260	9.42×10^{-4}	28.80
6.33	1.40×10^{-2}	248	6.04×10^{-4}	28.95
9.75	1.98×10^{-2}	111	4.93×10^{-4}	29.36
Run 50a				
1.38	1.71×10^{-2}	247	1.87×10^{-4}	49.1
2.28	2.10×10^{-2}	222	1.75×10^{-4}	49.43
3.88	2.46×10^{-2}	246	1.59×10^{-4}	50.1
5.88	2.87×10^{-2}	189	1.41×10^{-4}	51.13
8.83	3.11×10^{-2}	256	1.08×10^{-4}	52.9
11.83	3.25×10^{-2}	279	7.26×10^{-5}	55.1
14.83	3.65×10^{-2}	220	4.58×10^{-5}	57.3
Run 100a				
1.28	2.04×10^{-2}	166	1.29×10^{-4}	100.45
2.38	2.41×10^{-2}	239	1.53×10^{-4}	101.46
3.93	2.48×10^{-2}	286	1.53×10^{-4}	103.22
5.88	2.73×10^{-2}	227	9.07×10^{-5}	105.7
7.73	3.22×10^{-2}	142	4.54×10^{-5}	108.05
9.63	3.54×10^{-2}	255	2.36×10^{-5}	110.35
10.23	3.70×10^{-2}	228	1.95×10^{-5}	111.05
Run 100c				
2.25	9.49×10^{-3}	124	1.03×10^{-3}	95.62
3.65	1.34×10^{-2}	236	6.38×10^{-4}	95.80
6.30	1.65×10^{-2}	202	4.37×10^{-4}	96.45
9.80	2.45×10^{-2}	105	4.52×10^{-4}	98.20

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Cold Regions Research and Engineering Laboratory U.S. Army Terrestrial Sciences Center Hanover, New Hampshire		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE EFFECT OF GROWTH PARAMETERS ON SUBSTRUCTURE SPACING IN NaCl ICE CRYSTALS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Research Report			
5. AUTHOR(S) (First name, middle initial, last name) G. Lofgren and W.F. Weeks			
6. REPORT DATE January 1969		7a. TOTAL NO. OF PAGES 20	7b. NO. OF REFS 32
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) Research Report 195	
b. PROJECT NO.			
c. DA Task 1T061102B52A02		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Cold Regions Research and Engineering Laboratory U.S. Army Terrestrial Sciences Center Hanover, New Hampshire	
13. 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 3×10^{-3} to 10^{-5} cm/sec and 1 to 100 %/100 respectively. The substructure is the result of the formation of a constitutionally supercooled 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 -70C. 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 $\bar{a}_0$ vs v show that the slope n gradually changes as a function of v . In the run where no convection occurs, 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 of 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 %/100 NaCl.			

DD FORM 1473
1 NOV 65

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS
OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ice Freezing Sea ice NaCl ice Ice crystal						