Quantitative Study of the Metamorphism of Snow Crystals by Sublimation

Yuki no kesshō no shōka henkei ni tsuite no teiryō-teki kosatsu

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I.

Snow crystals undergo metamorphism by sublimation even at temperatures below 0°C. The stages in this process of metamorphism have been investigated in detail by K. Kozima (1953). When snow crystals of the dendritic type are observed, moreover, it is found that the crystals, which initially form slender rectangular branches, are transformed into rounded rod-like forms (Fig. 1). Simultaneously, the "roots" of the branches become constricted and eventually the branches are severed at these points. The severed branches then gradually become spherical in shape. Crystalline metamorphism of this type undoubtedly is due to the fact that water vapor is generated in certain parts of the crystals, diffuses into the air surrounding the crystal, and condenses on other parts of the crystal. The following explanation of this type of water vapor formation and condensation on crystal surfaces is generally given.

Figure 1. Sublimation metamorphism of snow crystals.
From (a) to (b) at −5°C; thereafter at −0.1°C.
(From Kozima, 1953)
The curvature $K$ of the surface of a crystal varies from point to point on the surface. Let the radii of the two primary curves at a given point on the surface be $R_1$, $R_2$. Assuming that $R_1$ and $R_2$ are either positive or negative depending upon whether the center of the arcs described by the radii are inside or outside the surface, then the curvature $K$ of the surface at that point is given by

$$K = \frac{1}{R_1} + \frac{1}{R_2}. \quad (1)$$

Where the surface is flat, $K = 0$, and where it is convex, $K > 0$. Where the surface is concave, $K < 0$, but where, as in a saddle, the surface is concave in the front-to-rear direction and convex in the side-to-side direction, $K$ can be positive, negative, or even 0.

Where the surface of ice is convex, surface tension acts to compress the ice under the surface; where the surface is concave, surface tension acts to draw the ice outward. Hence, where the surface is convex, pressure in addition to the air pressure surrounding the crystal acts upon the ice under the surface. Where the surface is concave, additional negative pressure is brought to bear on the ice. This additional pressure, $\Delta F$, may be expressed generally by

$$\Delta P = aK. \quad (2)$$

Here $a$ refers to the surface tension of ice and, according to Hirobumi Oura (1952), is equivalent to 87 dyne/cm.

The free energy $F_v$ in 1 mol of water vapor in equilibrium with ice (i.e., water vapor having pressure equal to the vapor pressure of ice $p_v$) is given by

$$F_v = RT \log p_v + \text{const.} \quad (3)$$

Thermodynamic considerations require that this always be equal to the free energy $F_1$ of 1 mol of ice. (For convenience, the free energy $F_1$ per mol is considered here as chemical potential.) Substituting $p_v$, the vapor pressure of ice having a flat surface, i.e., where $K = 0$, of $F_v$ in eq 3, $F_v$ becomes $F_{v0}$, and the ice under the flat surface should have free energy $F_{v0}$ per mol equivalent to the value of $F_{v0}$. However, the free energy $F_1$ of ice varies as the pressure $P$ exerted on the ice changes. The relationship involved in this variation may be expressed by

$$\frac{\partial F_1}{\partial P} = V$$

where $V$ is the volume of 1 mol of ice. Hence, where $K = 0$ does not hold true, the free energy $F_1$ of the ice under the surface is, from eq 4 and 2, exactly

$$\Delta F_1 = V_aK \quad (5)$$

greater than $F_{v0}$. It follows that the $F_v$ of the water vapor in equilibrium with these surfaces, i.e., $F_v$ of the water vapor having a pressure equal to the vapor pressure of these surfaces, must be greater than $F_{v0}$ by $\Delta F_1$. Since we are assuming that the temperature $T$ is constant, it becomes clear that $p_v$ must increase by the increment

$$\Delta p_v = p_v \frac{\Delta F_1}{RT} = p_v \frac{V_a}{RT} aK \quad (6)$$

from eq 3. In other words, the vapor pressure on those parts of the surface where the curvature $K > 0^*$ is increased by the amount given by eq 6 as compared to the vapor pressure where $K = 0$. Where $K < 0$, there is a corresponding decrease.

If we assume that areas of high and low vapor pressures may be found on crystal surfaces, then water vapor will be generated from the former, diffuse through the air to the latter, and condense there. The fact that snow crystal branches, which initially have rectangular sections, gradually change to rounded sections is generally explained as follows. Since $K > 0$ at the edges of the rectangle, and $K = 0$ on the faces, the vapor pressure is high at the former and the water vapor evaporating from the edges condenses at the faces where the vapor pressure is low. From this point of view, the thinning process involving the roots of the branches must be explained by the fact that $K$ is greater at the roots than in other parts of the branches. However, the surface at the roots is precisely in the form of a saddle, and even if $K$ is positive, then negative, and then positive again, it cannot be immediately ascertained whether it is greater than the $K$ of other parts of the crystal.

II.

Differences in curvature $K$ are used very commonly to explain not only the change of snow crystals from a rectangular to a circular shape but also the fact that the branches which are cut off at the roots assume the shape of a sphere. These, however, are all qualitative explanations; quantitative research to determine, for example, whether the theoretically determined velocity of change agrees with the actual velocity of change has not been carried out as yet. Even if a qualitative explanation has been agreed upon, it cannot be considered correct if it does not accord with quantitative findings. For example, it was long explained qualitatively that the reason for the low friction of skates sliding over ice was that the melting point of ice was lowered by the pressure of the skates, causing formation of water which acted as a lubricating agent. Considered quantitatively, however, this explanation is open to grave doubt (Bell, 1948).

Sections III-VII are concerned with a theoretical treatment of the phenomenon observed in dendritic snow crystals which, after attaining a circular cross-sectional shape, undergo a thinning process at the roots. This phenomenon has been regarded as due to differences in the curvature $K$ of the crystal surfaces. The theory rests on various assumptions and is admittedly imperfect; as a result, there is quantitatively excessive vari-

* We have supplied "> 0" which is missing in the Japanese text. The previous sentence, it may be noted, also contains misprints—Translator's note.
ance with the facts. Hence, one cannot help wondering whether the surface-curvature theory is applicable to the thinning of the roots of the branches. At the same time, doubt arises as to the correctness of the generally accepted explanations, based on surface curvature, of various other metamorphoses.

After discovering the inadequacy of the curvature theory in describing the thinning process of the branch roots, another explanation was sought (see section VIII). This was based on the idea that the weight of the branch itself must subject the root to considerable elastic stress; that the free energy $F_1$ of the ice is increased because of this elastic stress; and that as a result the vapor pressure rises and this part evaporates. Where $S$ is the strain on the ice, $t$ is stress, $V$ is the volume of 1 mol of ice, we obtain as an expression corresponding to eq 4:

$$\frac{\delta F_1}{\delta S} = V \epsilon$$

(7)

Hence, the free energy of the ice under strain, as compared to the state where strain is lacking, is greater by

$$\Delta F_1 = V E \epsilon^2$$

(8)

Equation (8) may also be obtained by defining, in reversible isothermal changes, work done externally as free energy. The $E$ in this equation is the modulus of elasticity ($S = E \epsilon$). The vapor pressure of the ice will rise by

$$\Delta p_\epsilon = p_\epsilon \frac{V E \epsilon^2}{RT}$$

(9)

because of this increase in $F_1$.

As we shall make clear in section VIII, however, it is impossible to explain the thinning of the branch roots quantitatively by this line of reasoning, as was the case with the curvature theory.

III.

In order to investigate the theory that thinning of the roots of dendritic snow crystals is due to differences in curvature $K$, the following preparatory steps must be taken.

Consider an infinitely long cylinder of ice with radius $a$; and let the vapor pressure of the water in the air surrounding the cylinder correspond to the curvature $K = 1/a$ of the cylindrical surface, i.e. pressure $p_\epsilon = p_\epsilon + p_a (V_a/RT_a)$. In this situation, the shape of the ice cylinder can be maintained without change. However, if a small change occurs on the cylindrical surface for any reason, resulting changes in the curvature $K$ will initiate evaporation and condensation; so that further deformation can readily take place.

Figure 2 illustrates a horizontal section of a specimen of ice which, after the passage of time $t$, has changed from a cylinder with a uniform radius $a$ to one with generating line SSS. The shape of the surface changes symmetrically along the axis of the cylinder. Let $x$ be the coordinate along the center line of the cylinder, and $y$ be the distance from the axis to the surface. With $t = a - y$, we will consider a case where $t$ is very small as compared to $a$.

Since the two primary curves $(1/R_{1})$, $(1/R_{2})$ on the surface of the $x$ coordinate can be expressed by

$$\frac{1}{R_{1}} = \frac{1}{y}, \quad \frac{1}{R_{2}} = \frac{3y}{a x^2}$$

when $t \ll a$, curvature becomes

$$K = \frac{1}{y} \frac{3y}{a x^2}$$

Hence, the vapor pressure of the ice here is greater than $p_\epsilon$ by

$$\Delta p = \frac{V_a}{RT} p_\epsilon \left( \frac{1}{y} \frac{3y}{a x^2} - \frac{1}{a} \right)$$

This equation may be rewritten

$$\Delta p = \frac{V_a}{RT} p_\epsilon \left( \frac{2t}{ax^2} + \frac{t}{a^2} \right)$$

(10)

Evaporation occurs where $\Delta p > 0$, while condensation occurs where $\Delta p < 0$. Here it is assumed that the evaporation-condensation velocity is proportional to $\Delta p$. This assumption appears natural from the standpoint of physics. Thus, $\xi$ increases with evaporation and decreases with condensation, and $d \xi/dt$ is proportional to the evaporation-condensation velocity. Hence the relationship

$$\frac{d \xi}{dt} = \lambda \left( \frac{2t}{ax^2} + \frac{t}{a^2} \right), \quad \lambda > 0$$

(11)

is established. The proportionality constant $\lambda$ is determined not only by the properties of the substance, but also by the quantity related to the shape of the surface. This value will be determined later. As one solution to (11)

$$\xi = \xi_0 \exp \left( \frac{4 \pi^2 t}{k^2} \right) - \frac{2t}{a x^2} - \frac{t}{a^2}$$

is obtained. Here $k$ is a real number constant which can be selected arbitrarily. If $t = 0$,

$$\xi = \xi_0 \cos \sqrt{\frac{4 \pi^2 t}{k^2}} - \frac{2t}{a x^2} - \frac{t}{a^2}$$

Figure 2.

Axis

$S$
this is the deformation initially imparted to the surface for any reason whatever. We are considering a case where, with this beginning, the deformation gradually increases, and eq 12 shows that the absolute values of $\xi$ and time $t$ increase together.

IV.

Let us next consider the movement of water vapor in the air surrounding the ice cylinder. On the surface where $\Delta p > 0$, the vapor pressure $p$ of water in the air is higher than $p_c$; where $\Delta p < 0$, $p$ is lower than $p_c$. Hence, water vapor diffuses through the air from the former to the latter.

Let $r$ be the distance to any point in the air from the axis of the ice cylinder. Then

$$u = p - p_a$$

is a function of $r, x, t$. This $u$ is clearly zero when $r = \infty$, and on the surface of the cylinder must coincide with $\Delta p$. That is, the condition

$$u_{r=a} = \Delta p$$

must be satisfied. But where $\xi << a$, this condition is approximated by

$$u_{r=a} = \Delta p.$$ (13)

The amount of water vapor flowing by diffusion outwardly from the surface of the cylinder is expressed by

$$-\beta D \frac{\partial u}{\partial r} \bigg|_{r=a} \xi$$

per unit area and per unit time. $D$ refers to the diffusion coefficient of water vapor in air, while $\beta$ is the ratio between the density and pressure of water vapor. This quantity should be equivalent to the amount of ice evaporated, and may be given by

$$\rho \frac{\partial u}{\partial t} = -\beta D \frac{\partial u}{\partial r} \bigg|_{r=a}$$ (14)

once more according to the condition $\xi << a$.

With regard to the diffusion of water vapor in air, which is regarded as quasi-stationary, we have the differential equation

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial z^2} = 0$$ (15)

disregarding the term $\partial u/\partial t$. In solving this differential equation, we first determine the function $u$ which will satisfy the conditions of eq 13 and 14. The $\Delta p$ of eq 13 is obtained by introducing the $t$ of eq 12 into eq 10. Thus

$$\Delta p = \frac{V_s}{RT} \xi_0 p_c k^2 \exp(\lambda k^2 t) \cos x \sqrt{(1/a)^2 - k^2}$$ (16)

and the $\partial u/\partial t$ of eq 14 is obtained from eq 12 as

$$\frac{\partial u}{\partial t} = \xi_0 \lambda k^2 \exp(\lambda k^2 t) \cos x \sqrt{(1/a)^2 - k^2}.$$ (17)

In the solution of eq 15, $r = \infty$; where $r = 0$, we have

$$u = u_0 \frac{iH_{1,0}(i\xi_0)}{iH_{1,0}(i\xi_0)} \cos (\xi_0).$$ (18)

$H$ refers to Hankel's cylindrical function, while $\xi_0$ is a constant which can be selected arbitrarily. Also, $\xi_0$ equals $\sqrt{-1}$. Differentiating (18) with respect to $r$, we obtain

$$\frac{\partial u}{\partial r} = -u_0 \frac{\omega}{iH_{1,0}(i\xi_0)} \cos (\xi_0).$$ (19)

Here, if

$$f = \sqrt{(1/a)^2 - k^2}$$ (20)

$$u_0 = \frac{\alpha V}{RT} p_c k^2 \exp(\lambda k^2)$$ (21)

$$\lambda = \frac{\alpha \beta D p_0}{\rho R T a} - (\xi_0) \frac{H_{1,0}(i\xi_0)}{H_{1,0}(i\xi_0)}$$ (22)

it is clear that the $u$ of eq 18 satisfies the conditions of (13), (14), (16) and (17). The desired function $u$ is obtained in this manner.

V.

The fact that a function $u$ which will satisfy all conditions has been determined indicates that changes in the form of the surface, such as given by

$$t = t_0 \exp(\lambda k^2 t) \cos x \sqrt{(1/a)^2 - k^2}$$ (12)

can actually occur in ice cylinders. As a result of this deformation, a section of the ice cylinder will actually occur in ice cylinders. As a result of changes in the form of the surface, such as given by eq 20, the determination of one results in the determination of the other. However, since $\xi$ must be a real number, the value of $\lambda$ must fall in the range

$$0 < k < \frac{1}{a}.$$ (23)

The value of $f$ is restricted to the same range. Eq 12 is written

$$t = t_0 \exp(\lambda k^2 t) \cos x \xi.$$ (23)

This indicates that the generating line of the surface of a deformed cylinder is a cosine curve, with the length $L$ between peaks or valleys being equal to

$$L = \frac{2\pi}{f}.$$ (23)

Since the maximum value of $f$ is $1/a$, the minimum value of $L$ is $2\pi$. That is to say, the distance between peaks cannot be less than 3 times (to be precise, $\pi$ times) the diameter of the cylinder.

Here, $L = 2\pi$ corresponds to the case where $k = 0$. In this instance, $\exp(\lambda k^2 t) = 1$, and $\xi$ does not change with time. That is to say, the initial deformation, $\xi_0 \cos (x/a)$, is retained without change. Even if this kind of deformation is actually imparted, the curvature of the surface at all points is equal to $1/a$, as is clear from the $K$ equations in section III, the curvature being the same as that of a cylindrical surface with radius $a$.

However, when $L$ is greater than $2\pi$ and $k$ is not equal to 0, the initial deformation is prolonged, the speed of the deformation process increasing with $\lambda k^2$.

Using the function $u$...
the deformation velocity drops quite low. This is due to the fact that, as the deformation velocity reaches a maximum when $L = 0$. As $f(a)$ nears 0, $f(f(a))$ also approaches 0, and the deformation velocity drops quite low. This is due to the fact that, as $L$ increases, the peaks and valleys of $\xi$ become smoothed out.

The diagram for $f(f(a))$ is shown in Figure 3, the maximum occurs when $f(a) = 0.5$. That is, the deformation velocity reaches a maximum when $L = 4\pi a$. When $f(a) = 1$, $f(f(a)) = 0$, and this corresponds to the case, previously mentioned, where $k = 0$. As $f(a)$ nears 0, $f(f(a))$ also approaches 0. Thus, the deformation velocity drops quite low. This is due to the fact that, as $L$ increases, the peaks and valleys of $\xi$ become smoothed out.

![Figure 3](image)

**Figure 3.**

**VI.**

In this section we will try to apply the above results to branches of dendritic snow crystals which have reached the rod state and have thinned out at the roots. Snow-crystal branches are not infinite in length; moreover, the deformation does not occur in the direction of the axis in a periodic fashion. However, we should be able to take one interval of deformation occurring in the infinitely long ice cylinder above (i.e., that interval lying within the length $L$ in the direction of the axis and centering on $x = 0$) and consider it as corresponding to the thinning of the crystal roots.

**VII.**

In addition to the fact that the theoretical and actual velocities of the thinning process in dendritic snow crystals simply do not agree, theoretical and actual lengths* of the thinned parts also do not agree. According to the above theory, the length* of the thinned part should correspond to the distance $L$ between the peaks on the generating line on the surface of the ice crystal. $L$ should be at least 3 times (or to be more precise $\pi$ times) the diameter of the cylinder. According to Figure 1, however, the actual length* of the thinned part is roughly equivalent to, or at most twice the diameter of the branch.

In the above theory, only the case where $L > 2\pi a$ was considered, but what of the case where $L < 2\pi a$? In the above discussion, eq 12 was used as a solution to differential equation 11, but there is also the solution

$$t = \xi \exp (-\lambda k^2 t) \cos x \sqrt{(1/a)^2 + k^2} . \quad (26)$$

Here $L$ is clearly smaller than $2\pi a$. If the calculations previously made are now carried out based on eq 26, we obtain absolutely the same value of $\alpha$ as that of eq 22. Eq 26 expresses changes in $\xi$ when the initial deformation is

$$\xi \cos x \sqrt{(1/a)^2 + k^2} .$$

This deformation, because of the factor $\exp (-\lambda k^2 t)$, decreases as time $t$ increases. Hence, the deformation described by $L < 2\pi a$ gradually ceases regardless of the causative factor and the shape of the snow crystal. 

*Japanese text gives "width", but "length" seems more appropriate - Translator's note
ice cylinder returns to its original form. In other words, the cylindrical surface of an ice column is stable against minute deformations of the order of \( L < 2a \), and is unstable against gross deformations of the order \( L > 2a \). The fact that \( \varepsilon \) decreases after slight deformation, i.e. that condensation of water vapor occurs at the thinned parts, is due to the fact, according to the above theory, that the curvature \( K \) there becomes negative. With slight deformation, the negative curves on the generating line on the surface of the ice cylinder, i.e. \( 1/R \), of section III, increase in strength, withstand the positive curves \( 1/R \), on the circumference of the cross section of the cylinder, and cause the curvature \( K \) on the surface to become negative.

Thus far we have confined our discussion to cases where \( \varepsilon < a \), i.e., cases of initial deformations. This is sufficient if we are only concerned with the possibility or impossibility of thinning, since results which are not satisfactory in the initial period will not lead to meaningful results later. We will briefly consider the case where, under certain conditions, considerable thinning has taken place.

According to the above theory, when \( L = 2a \), curvature \( K \) on the surface of the ice cylinder is equivalent to the curvature \( 1/a \) of a cylindrical surface. Such uniformly curved surfaces have great significance as surfaces corresponding to boundaries of deformation increase or decrease. The shape of soap bubbles has long been studied as a general case of uniformly curved surfaces. Since the internal air pressure of a soap bubble is higher than the external air pressure by a fixed value \( \Pi \), there must exist the relationship

\[
\Pi = 2aK
\]

between \( \Pi \) and the surface curvature \( K \) of the soap bubble. (The coefficient 2 is introduced because of the effect of the inner surface tension of soap bubble films.) As a result, the surface curvature \( K \) of soap bubbles is of equivalent value everywhere. Figure 4 shows a uniformly curved surface called an unduloid (see Lamb, 1924, p. 284). When thinning attains these proportions, the length \( L \) of the thinned part is 1.6 times the diameter \( 2a \) of the thinnest part. If thinning of the unduloid type were to occur on an ice cylinder, the thinning would be maintained without change; and for thinning of this magnitude to increase, the condition \( L > \pi (2a) \). However, even if thinning which satisfies this condition occurred, there would probably be no agreement between theory and fact as regards the rate of increase.

![Figure 4](image)

**Figure 4.**

### VIII.

In theories which consider curvature of ice surfaces as a causative factor, the problem arises that, when the length* of the thinned part of crystal branches is small, the thinning should disappear. In fact, the length* of thinned parts is quite small. The question arises whether or not conditions exist which prolong the thinning process in short thinned parts. Increases in vapor pressure due to elastic stress certainly fall into this category, as discussed in section III. In all cases, the greater the thinning process in the thinned parts the greater is the elastic stress found there. Moreover, when the length* of the thinned part is small, and thinned areas are close to those which have not thinned, water vapor dispersion occurs speedily, and the thinning is readily maintained.

In this section the thinning process is discussed in terms of this kind of elastic stress, although the results, as noted previously, do not quantitatively accord with the facts. In addition, the effect of curvature is completely disregarded in the discussion in this section.

First of all, consider an infinitely long ice cylinder with radius \( a \), subjected throughout to a uniform bending moment \( G \). The cylinder will then bend uniformly, and the center line will assume a circular form. The \( x \)-coordinate is taken along the axis, with the \( y \)-axis vertical to the \( x \)-axis and facing outward from the surface subjected to \( G \) (Fig. 5). The strain produced in the ice cylinder is then given by

\[
\epsilon = \left( \frac{4G}{\pi E a^2} \right) \frac{y}{a}.
\]

The modulus of elasticity \( E \) in this case corresponds to Young's modulus for ice. Then, according to eq 8 in section II, the free energy \( F \), of ice increases by

\[
\Delta F = \left( \frac{8G^2}{\pi E a^2} \right) \frac{y^2}{a^2}
\]

while the vapor pressure, according to eq 9, increases by

\[
\Delta p = p_0 \left( \frac{8VG^2}{\pi RTE} \right) \frac{y^2}{a^2}.
\]

\( \Delta p \) is a function of \( y \), and its value changes according to the position above the surface. In terms of Figure 5, \( \Delta p \) is highest at points \( A, A \), and decreases along the surface toward points \( O, O \). Hence, water vapor moves from the vicinity of points \( A \), toward points \( O, O \), the shape of the cylinder changing probably from circular to elliptical. If this factor is taken into consideration, however,
the situation becomes extremely complex. Let us consider the case therefore where the mean value of $\Delta p$ is taken as

$$\Delta p = p_0 \left( \frac{4VG^2}{\pi^2RTE} \right) \left( \frac{1}{a^6} \right)$$

and it is assumed that the vapor pressure on the surface of the ice cylinder has risen by this amount uniformly along the entire body of the cylinder. In short, we assume symmetry with respect to the $x$-axis. In addition, it is assumed that the water vapor in the air surrounding the cylinder has a pressure of $p_0 + \Delta p$ and is in equilibrium with the cylinder under stress.

Thus if the radius is decreased by $t$ ($<a$) at a certain place on the ice cylinder, a pressure rise occurs inversely proportional to the 6th power of the radius, according to eq 29. The pressure rises here in comparison to other places on the cylinder. If this pressure rise is calculated in terms of a mean value taken around the circumference of the cylinder, it becomes, according to eq 29:

$$\Delta p = p_0 \left( \frac{4VG^2}{\pi^2RTE} \right) \left[ \frac{1}{(a-t)^6} - \frac{1}{a^6} \right]$$

This is proportional to $t$. Assuming once more that the evaporation-condensation velocity of the water vapor is proportional to $t$, we obtain

$$\frac{\partial t}{\partial t} = \lambda t$$

with $\lambda$ as a proportional constant. As a solution

$$t(x) = \xi \cos(tx)$$

is obtained. The term $t(x)$ refers to the initial deformation due to any factor whatever.

Eq 31, 32 correspond to eq 11, 12 in section III, and the discussion can be advanced along the same lines as the curvature theory. Thus, for the terms $t(x)$, $\lambda$ in eq 32:

$$\xi(x) = \xi_0 \cos(\xi x)$$

are obtained. Here $t$ is a positive real number which can be arbitrarily selected, with no limit imposed on the range of its value. In the equation for $\lambda$, the part that is a function of $(l)\alpha$ can be expressed approximately as $0.5 + (l)\alpha$, and it increases with $(l)\alpha$. Hence with larger $l$, i.e., smaller $L = 2\pi/l$, $\lambda$ becomes larger. Moreover, as is clear from eq 32, $t$ increases more rapidly with larger $\lambda$. In this case, unlike the curvature theory, $t$ increases whatever the value of $L$, and the smaller $L$ is, the greater the rate of increase of $t$.

As with the curvature theory, we shall regard the thinning at the roots of a snow crystal branch as being the same as a single thinning occurring periodically in an ice cylinder. In addition, it will be assumed that the length of the thinning is equal to the diameter $2a$ of the cylinder, in order to consider $\lambda$ as a numerical value. That is, let $fa = 2\pi$.

As the bending moment $G$, $3.5 \times 10^3 \text{ dyne-cm}$ is used, the weight of a bar of ice of 0.1 mm diam and 1 mm length. The value of $10^3\text{dyne/cm}^2$ will be used as Young's modulus $E$ for ice. Using the values employed previously for the other factors, we obtain

$$\lambda = 5 \times 10^{-17}/\text{sec} = 4.3 \times 10^{-7}/\text{day}.$$  

Thus the time required for $t$ to double is 500,000 years. This result indicates that elastic stress has entirely no effect on the metamorphism.

**IX.**

In the preceding sections we have seen that, from the quantitative point of view, it is erroneous to explain the thinning by sublimation of the roots of dendritic snow crystals in terms of differences in curvature of crystal surfaces. Moreover, one cannot but harbor doubts about the surface curvature theory with regard to other forms of metamorphism of snow crystals. An attempt to explain the thinning in terms of elastic stress set up by the weight of the branches themselves was also a complete failure. In view of these considerations, it would appear that the cause of sublimation metamorphism of snow crystals is to be found in the internal structure of the ice crystal itself. Since the snow crystal is formed with great rapidity, undoubtably it will contain many internal faults. It is to be presumed, moreover, that the properties and quantity of these faults will vary from region to region in the crystal. If this is true, then it follows that different places on the surface of the crystal should also have different vapor pressures.

**X.**

The elastic stress theory of the thinning of crystal branches cannot be applied to single isolated snow crystals. In the case of snow crystals in snow deposits, however, the effect of elastic stress on sublimation can reach considerable proportions because of the magnitude of the stress produced. The following case may be considered as an example.

Consider a layer of snow $2H$ in thickness projecting a distance of $2L$ from the edge of a stand (Fig. 6a). Taking the $x$ and $y$ coordinates as shown in the diagram, consider the situation in the vicinity of the vertical plane where $x = 0$. For simplicity, it is assumed that the projecting part is subjected to a force $Mg$ equal to the weight of this part (where $M$ is the mass of a unit length of the snow layer in direction $z$) at the point $x = L$ in a downward vertical direction. It is also assumed that the
snow itself is a substance without mass and possessing only elasticity. Even under such conditions, actual and theoretical results agree with respect to elastic relationships in the vicinity of \( x = 0 \). Thus, when determining the stress component at \( x = 0 \), we obtain

\[
\begin{align*}
X_x &= -\frac{3L Mg}{2H^3}, \\
Y_y &= -X_x = \frac{3M g}{4H^2}(H^2 - y^2)
\end{align*}
\]

(35)

(see, for example, Matsuzawa, 1929, p. 80).

The value for \( X_y \) at the center of the snow sheet is 0; it reaches maxima at the upper and lower surfaces. The value for \( X_x \) reaches a maximum in the center and becomes 0 at the upper and lower surfaces. That is to say, in terms of the stress at work in the \( x \) and \( y \) planes, we find, near the upper and lower surfaces, only the forces of tension and compression at work in the \( x \) direction; while, at the center, we find only shearing force at work. Thus, we shall consider only the center where \( y = 0 \) and the two surfaces, i.e., where \( y = \pm H \).

For simplicity the structure of deposited snow may be depicted (Fig. 6b) in terms of ice rods arranged parallel to axes \( x, y, z \) at \( l \) intervals. In short, the structure consisting of ice bridges with length \( l \) connected in \( x, y, z \) directions. Where \( y = 0 \), shearing force

\[
(X_y)_o = \frac{3M g}{4H}
\]

(36)

works along the \( x \) and \( y \) planes. Therefore, if we let \( N \) be the number of ice bridges present in a unit area vertical to the ice bridge, i.e., let \( N = 1/F \), then the force

\[
f = \frac{(X_y)_o}{N}
\]

(37)

acting in the horizontal direction at both roots of the vertical ice bridges comes into play, while the same force acts vertically at the roots of the ice bridges lying parallel to the \( x \) direction. Also, in both cases, the force seeks to rotate the ice bridges at the moment \( fL \). As a result, the bending moment

\[
G = \frac{ffL}{2}
\]

(38)

due to elasticity appears at the roots of the ice bridges. The bending moment of the ice bridges takes the higher of the maximum values at the roots of both ends, becoming 0 at the center of the bridge. Hence, the situation is exactly the same as that considered in the preceding section where the roots of the branches of snow crystals are thinned because of the weight of the branches themselves. Thus, let us interpolate the value for \( G \) obtained here with the results shown in the preceding section.

Let the density of a layer of deposited snow projecting beyond the edge of a stand be \( 0.3 \text{ g/cm}^3 \), \( L = 25 \text{ cm} \), and \( H = 20 \text{ cm} \). Then \( Mg = 5.9 \times 10^5 \text{ dyne/cm}, \) and \( (X_y)_o = 2.2 \times 10^4 \text{ dyne/cm}^2 \). If the length \( l \) of the ice bridge is 1 mm, then \( N = 100/\text{cm}^2 \), and using these values,

\[
f = 2.2 \times 10^2 \text{ dyne}, \ G = 11 \text{ dyne} - \text{cm}.
\]

In the preceding section, \( \lambda = 5 \times 10^{-15/\text{sec}} \) was obtained using \( G = 3.5 \times 10^4 \text{ dyne} - \text{cm} \). Since \( \lambda \) is proportional to \( G^2 \), and the present \( G \) is \( 3.14 \times 10^4 \text{ times} \) the \( G \) of the preceding section, then \( \lambda \) increases by \( 10^4 \text{ times} \), giving

\[
\lambda = 5 \times 10^{-15/\text{sec}} = 1.8/\text{hr}.
\]

The time \( \tau \) required for \( \xi \) to double is the short period of 23 minutes. Since the value for \( \tau \) for isolated snow crystals is several days, in comparison the time is very short. Hence, in this case, it must be said that the effect of elastic strain is exceedingly important. However, it cannot be said that the roots of all the ice bridges undergo the thinning process at this speed. For snow deposits of 0.3 g/cm\(^3\) density, presently being considered, the structure shown in Figure 6 gives between 0.3 and 0.4 mm as the diameter of ice bridges. The value for \( \tau \) obtained above was for bridges of 0.1 mm diameter and, since \( \tau \) is proportional to the 8th power of the diameter, it increases very abruptly by 256 and 6500 times when the diameter increases by 2 or 3. However, the structure of actual snow deposits is exceedingly complex, and, even where a structure such as that in Figure 6b is assumed, the existence of small and large bridges of varying diameters must be taken into consideration. Moreover, the value for \( G \) obtained above is a mean value, while actual values for \( G \) vary from ice bridge to ice bridge. Hence, it follows that small ice bridges can have large \( G \) values. The above calculations were for small ice bridges where a mean value for \( G \) was produced. Although large \( G \) values can occur for small ice bridges, there are limits here, since the ice bridge crumbles when \( G \) is large. A force of \( f = 2.2 \times 10^5 \text{ dyne} \), obtained above, applied to ice bridges of 0.1 mm diameter, gives a shearing force of 2.8 kg/cm\(^2\). This is close to the shearing force which destroys ice.

Tension is at work near the top surface of a snow layer, while compression is at work near the bottom surface. In terms of the absolute values of stress, however, the values are the same for both the top and bottom surfaces. Accordingly, the top and bottom surfaces are the same insofar as the effect of elastic stress on sublimation is concerned. Thus, calculating the absolute value of \( X_x \) by means of eq 35 gives

\[
(X_x)_n = 9 \times 10^4 \text{ dyne/cm}^2
\]

while the tension (or pressure) \( f \) on a single horizontal ice bridge is given by

\[
f = 9 \times 10^4 \text{ dyne}.
\]
The identical treatment can be applied in the case of thinning when a force $f$ is applied in the direction of the axis of an ice cylinder, with the result that

$$t = t_o \exp \left( \frac{2 \beta_D V P_o}{\rho R T a^3} \left( \frac{-(\alpha f)H_{11}}{iH_{11}(\alpha f)} \right) \right)$$

are obtained. When a force $f$ with the above value acts on a cylinder with a diameter of 0.1 mm, then

$$\lambda = 6.8 \times 10^{-4} \text{ sec}^{-1} = 2.4 \text{ hr}^{-1}$$

and $\tau = 17$ minutes. Hence, elastic stress has a very great effect here. However, it cannot be said that all the ice bridges undergo the thinning process at this rate of speed.

The actual structure of deposited snow is extraordinarily complex. The ice bridges comprising the deposit are extremely varied in size, even within a short range. It follows that the application of a force to a deposit of snow results in areas of varying elastic stress adjacent to each other. Water vapor moves from areas of high stress to areas of lower stress, and this should cause changes in the structure of the deposit. Moreover, it can be imagined that the rate of this development will be quite high on the basis of the above example.

In conclusion, I wish to express my profound gratitude to Dr. M. Sugita, whose advice greatly aided me in the writing of this paper.

This study was conducted under a research grant from the Ministry of Education.

**SUMMARY**

The cause of metamorphism by sublimation of snow crystal below the melting point of ice is commonly believed to be the non-uniformity of curvature of the crystal surface. At those parts of the surface, such as points or edges of the crystal, which have positive curvatures, the vapor pressure of the crystal surface is higher than at ditches or pits engraved on the snow crystal surface which have negative curvatures. The tension of the surface in conjunction with positive curvature brings about a local pressure on the ice lying under the surface in addition to the atmospheric pressure acting uniformly on the whole surface of the crystal. This local additional pressure causes an increase in the chemical potential (free energy per gram molecule) of the ice lying under the surface, which in turn increases the vapor pressure of that part of the surface by an amount proportional to the increase in chemical potential. In the same way negative curvature of the surface brings about a decrease in the vapor pressure. Water vapor then evaporates from those parts of the snow crystal surface where the curvature is positive, diffuses through the air surrounding the crystal, and condenses on those parts where the curvature is negative. Such a transfer of water vapor evidently makes the surface of the crystal smooth. This concept seems to accord with the mode of metamorphism observed in an actual snow crystal.

The smoothing of the surface of the crystal is not the only process observed to occur during metamorphism; the branches and twigs of the dendritic type crystal become thin at their roots and finally are cut off there. Usually the branches and twigs begin to thin at their roots when they have changed to rod-like pieces with smooth surfaces. The author made a mathematical study on this thinning process of the roots under the assumption that the phenomenon is due to the curvature of those thinning parts of the crystal.

Let a long circular cylinder of ice with radius $a$ be in equilibrium with water vapor having a pressure corresponding to the curvature of the cylindrical surface and let the radius be slightly changed by any cause to $a - \ell_o \cos \ell_o$.

The smoothing of the surface

$$t = t_o \exp \left( \frac{2 \beta_D V P_o}{\rho R T a^3} \left( \frac{-(\alpha f)H_{11}}{iH_{11}(\alpha f)} \right) \right)$$

in the case when the condition

$$\alpha f < 1$$

is satisfied, that is, the period $L = 2 \pi f$ of the change in radius along the axis of the cylinder is greater than $\pi$ times the diameter $2a$ of the cylinder.

$$\lambda \frac{\alpha f}{\rho R T} \frac{V}{a^3} \left\{ 1 - \frac{(\alpha f)}{iH_{11}(\alpha f)} \right\}$$

where

- $\alpha$ = surface tension of ice
- $\beta$ = ratio of density and pressure of water vapor
- $D$ = diffusion coefficient of water vapor through air
- $V$ = volume of one gram molecule of ice
- $\rho$ = density of ice
- $R$ = universal gas constant
- $T$ = absolute temperature
- $P_o$ = vapor pressure of ice at temperature $T$
- $H_{11}$ = Hankel's cylindrical function
- $i$ = imaginary unit $\sqrt{-1}$

The change $\ell$ takes its maximum value when $(\alpha f) = 0.5$, that is, when the period $L$ is $2 \pi$ times as large as the diameter $2a$ of the cylinder.

One periodical length of the cylinder between $x = -(L/2)$ and $x = + (L/2)$ is assumed to correspond to the thinning parts at the roots of branches and twigs of snow crystal. Then the decrease of radius at the center of the thinning part of the crystal is given by

$$t = t_o \exp (\lambda \ell t)$$

which means that $t$ is multiplied by the same amount for each definite increase of time $t$. The time necessary for $t$ to double is given by

$$\tau = (\log 2) / \lambda \ell^2$$

and numerical calculation yields, for the case

$2a = 0.1 \text{ mm}$ and $L = 2\pi (2a)$

$\tau = 6$ years,

while $\tau$ was experimentally observed by K. Kozima.

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*Original English summary with minor revisions. Editor's note.
to be not more than several days in metamorphism of the actual snow crystal.

Discrepancy between theory and experiment is found not only in the rate of change of $\xi$ but also in the length $L$ of thinning part. As described above, $\xi$ can increase only when $L > \pi (2a)$, but it was shown by experiments that $L$ was less than twice the diameter $2a$. The theory gives

$$\xi = \xi_0 \exp (-\lambda k^2 t) \cos \lambda x$$

in the case when $L$ is smaller than $\pi (2a)$, with the same formula for $\lambda k^2$ as above, showing that $\xi$ must be decreased as time goes on. In the case of $L = \pi (2a)$, $\lambda k^2$ vanishes and $\xi$ does not change.

The author considers that these discrepancies between theory and experiment are enough to prove wrong the assumption that thinning of the roots of branches is caused by the curvature of the crystal surface. Furthermore he is doubtful that the smoothing of snow crystal surface is due to its curvature.

If elastic stress $S$, such as tensile stress or shear stress, is produced in ice, its chemical potential is raised by

$$S^2 / 2E$$

and its vapor pressure is increased by the amount

$$p_v = \frac{V}{RT} \cdot \frac{S^2}{2E}.$$

The branches and twigs of snow crystal are striving to bend themselves by their own weight and the bending moment $G$ is greatest at their roots. A small change $\xi \cos (\lambda x)$ produced by any cause in the radius of a long circular cylinder of ice bent uniformly by a constant bending moment $G$ is promoted by water vapor transfer; the change $\xi$ in radius at time $t$ is given by

$$\xi = \xi_0 \exp (\lambda t) \cos \lambda x$$

$$\lambda = \frac{24DVG^2}{\pi^2 TE} \cdot \frac{P_v}{H_{1,1}(ifa)}$$

with no restriction on the value of $\xi$. $E$ is here the Young's modulus of ice. The larger $\lambda$ becomes, the larger is $fa$, that is, the smaller is the period $L$, contrary to the former case of $\lambda k^2$. This result was applied to the case of the root of a branch of snow crystal with diameter of 0.1 mm and length of 1 mm in the same way as before. The weight of the branch produces at its root a bending moment $G$ of the value $3.5 \times 10^4$ dyne/cm and the time $\tau = (\log 2) / \lambda$ turns out to be one half million years for the case $L = 2a$, which shows that elastic stress has entirely no effect upon the metamorphism.

Although elastic stress has no effect on the metamorphism of a single independent snow crystal, large stresses appearing in a deposited snow layer, such as one hanging over the edge of a terrace or roof, are expected to be sufficiently effective to promote the metamorphism of ice grains in the snow layer. In the case of a sheet of deposited snow of density $0.3$ g/cm$^3$ and thickness $40$ cm, projecting out $50$ cm horizontally over an edge, calculation gave less than 1 hr for $\tau$ for a rod-like ice grain of diameter $0.1$ mm on the vertical plane standing on the edge. Here the snow layer was considered to consist of rod-like grains of length $1$ mm and of various diameters whose mean value was about $0.35$ mm. Elastic stress is effective only on those grains of small diameter since its effect is reduced very rapidly with increasing diameter as shown by the fact that $\tau$ is proportional to the 8th power of the radius $a$.

REFERENCES


