A Water-Like Film Produced by Pressure on the Surface of Ice Crystals*

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Abstract

A glass plate was pressed against both a hemisphere of polycrystalline ice and a column of single crystal of ice, and the contact area between the ice and the glass plate was observed through a microscope during the compression. In the case of a single crystal, the crystallographic *c*-axis of the crystal lay either parallel or perpendicular to the axis of the column. A thin water-like film was seen to appear between the surfaces of the glass plate and the ice even at temperatures as low as −30°C. The film was stable during the compression. Temperatures of the film were thirty times lower than those predicted by Clausius-Clapeyron's equation.

I. Introduction

A few years ago, the present author began an experiment on the friction between ice and other materials. He placed a movable glass plate on a hemisphere of ice with the intent of conducting microscopic observations as to what would happen at both contact surfaces. But, before moving the glass plate, he found that a closed dark line expanded or contracted on the contact surface as the glass plate was pressed down or released. He concluded that the closed dark line was the margin of a water film or a water-like film which was produced on the surface of ice by the pressure of the plate.

It is well known that the melting point T_m of ice is lowered when ice and water in contact with each other are both subjected to a hydrostatic pressure P. The Clausius-Clapeyron's equation

$$dP/dT_m = -L/(v_i - v_w)\,T_m\,, \tag{1}$$

gives the relationship between T_m and P, if latent heat of fusion of ice, specific volumes of ice and water are denoted by L, v_i and v_w respectively. But the present experiment showed that the water-like film appeared at pressures much smaller than that which is given by formula (1) for the temperature of the experiment.

Although the melting point T_m of ice is reduced by pressure, the reduction does not proceed without a limit. When T_m is brought down to −22°C by the pressure of 2 100 kg-wt/cm^2, ice changes its crystal lattice and T_m begins to rise as pressure increasing. But the water-like film was still observed between the ice and the glass plate at temperatures as low as around −30°C.

Telford and Turner (1963) measured the advancing speed of a thin steel wire which

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was forced to penetrate into ice laterally. They found that the speed suddenly slowed down to 1/200 when the temperature of ice was decreased to the lower limit T_m of pressure melting, that is to say, to the temperature given by formula (1) for the pressure exerted on the ice by the penetrating steel wire. Telford and Turner attributed this very slow penetration without pressure melting to a liquid-like film which was assumed by some authors to be invariably present on the surface of ice, independently of whether it is subjected to a pressure or not.

Although much more work will be needed for complete verification of the existence of the water-like film between the ice and the glass plate, the experimental results obtained hitherto by the author will be presented in the following sections. Though not due to the phenomenon of pressure melting in the ordinary sense, the water-like film here seems to be still produced mainly by pressure, unlike the film suggested by the above authors.

II. Experiments on Polycrystalline Ice

The device used for the experiments on polycrystalline ice is shown in Fig. 1. A hemisphere H of polycrystalline ice frozen from water is fixed to a plate A of methacrylate resin which is placed on another plate N of the same material with some clearance between. The plate N is pushed up by two springs S placed on the stage T of a microscope. The hemispherical ice is pressed at its top against a glass plate G which is supported by four rollers R's and can be moved freely in a horizontal direction. The contact surface at the top of the hemispherical ice with the glass plate is observed through the microscope M. Force F with which the two springs S push up the plate N is determined from the distance between plates N and T by the use of the force constant of the springs. Pressure P at the contact surface between the ice and the glass plate is equal to F/A, where A is the area of the contact surface which can be determined by microscopic observation.

The experiment was carried out in a cold room of −15°C. The above mentioned exprimental device was placed in a box in which any desired temperature between −3

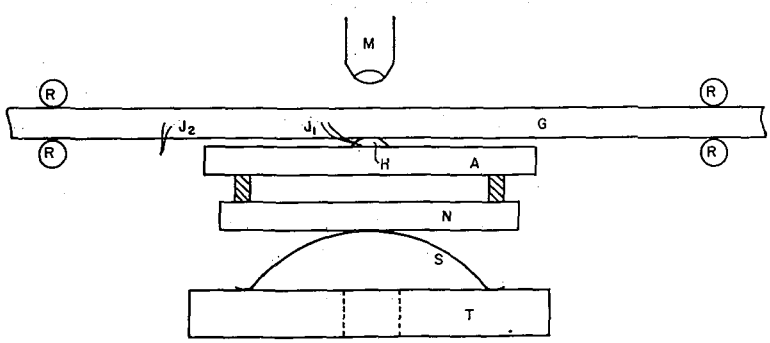

Fig. 1. Schematic diagram of the experimental apparatus for polycrystalline ice
H, hemispherical polycrystalline ice; A, N, methacrylate resin plates; S, spring; T, stage of microscope; G, glass plate; R, rollers for supporting the glass plate; M, microscope; J_1, J_2, thermocouples

and $-15°C$ could be maintained internally. Temperatures of the ice and the air in the box were recorded on an automatic balancing recorder by the use of two thermocouples J_1 and J_2. Absolutely no difference was found between the two temperatures.

III. Results of the Experiments on Polycrystalline Ice

At first the top of the hemispherical ice touched the glass plate at a point, and in one or two hours the contact surface between the two expanded to an area of a few mm^2. The higher the temperature was, the faster the contact surface expanded. The contact surface could be distinguished clearly from the free surface of the hemispherical ice, because a thin but distinct dark line outlined the contact surface as illustrated in Fig. 5 b. Figure 5 a shows the top surface of the ice before it touched the glass plates. For the sake of brevity, the above dark line will be called the "margin line".

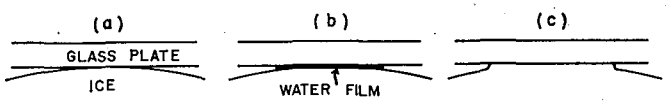

Fig. 2. Explanation of appearance of margin line
a: Margin line is not seen. b, c: Margin line can be seen

If the hemispherical ice touched the glass plate simply with a flattened top as shown in Fig. 2 a, such a dark line would not have appeared, because no abrupt change would occur in the refraction of light rays at the margin of the contact surface. The margin line suggests that there is a water film, one or more wave lengths of light thick, between the glass plate and the flat top of ice as shown by the horizontal black narrow band in Fig. 2 b. If such a water film exists, its side surface will reflect and refract the light rays in many directions in such a way as to make itself appear as a distinct dark line in the field of view of the microscope. As another possibility, the free surface of ice could rise up at the rim of the contact surface as shown in Fig. 2 c. This situation could also bring the margin line into appearance. In this case the margin line would stand still, keeping its form and position, when a clearance is made between the ice and the glass plate. But, as will be mentioned in the following paragraph, the margin line quickly contracts if the glass plate is moved away from the top surface of the hemispherical ice. Therefore, the last case is impossible and the author believes that there is a water film as shown in Fig. 2 b.

The film at the contact surface must be subjected to the pressure P which is to be calculated in the manner described in the previous section. Therefore, if the film were composed of water of ordinary nature, P would have to be large enough to lower the melting point of ice down to the temperature of the experiment, because the film is in contact with the ice. But the value of P was found to be $80 \sim 90$ kg-wt/cm^2, which pressure was, according to the Clausius-Clapeyron's equation, just enough to lower the melting point not more than $1°C$, whereas the experiment was carried out always below $-3°C$. Therefore, if the film is composed of H_2O molecules, its nature cannot be the same as that of ordinary water. For this reason, the author calls it "water-like" film.

When the plate N of Fig. 1 was pushed down slightly with a finger, the margin

line quickly contracted and shrank to a small circle or separated into two or three circles. When the finger pressure was removed, the circle or circles expanded quickly to recover the initial form of the margin line. Such expansion and contraction of the margin line could be repeated with the same result any number of times and could still be observed after the ice and the glass plate had been left in contact for two months. Even at a temperature as low as −12°C, the above phenomena could be seen. It will be difficult to explain them in any other way than assuming the existence of a stable water-like film between the ice and the glass plate.

As mentioned before, the glass plate G in Fig. 1 against which the hemispherical ice was pressed could be moved horizontally. Figure 5 c shows the changes which occurred in the contact surface between the ice and the glass plate during a very slow movement of the latter. The experiment was made at −3°C and the pressure P was found to be 80 kg-wt/cm^2. The glass plate was moved very slowly for one minute downward as indicated by the arrow in Fig. 5 c. ("Downward" means the direction of movement on the photographs. In the actual experiments the glass plate was moved horizontally.) Figure 5 c shows the contact surface 50 sec after the start of the movement. The top side of the contact surface became dirty due to accumulation of dust particles which had adhered to the surface of the glass plate. During the movement the top side of the margin line shifted gradually downward, but, after the movement was stopped, it returned to its initial position leaving the dust particles where they were at the moment of stopping the glass plate as shown in Fig. 5 d. It is well known that a piece of ice put on a glass plate becomes firmly adhered to the latter. In such a case the contact pressure between the ice and the glass is very small. But in the present experiments the pressure was large. If the ice had adhered to the glass in the present experiments, the contact surface would not be kept flat during the movement of the glass plate as seen in Fig. 5 c. The fact that the contact surface became rough near its top side would probably be due to the formation of a clearance there by the downward shift of the entire water film. Some water left behind on the ice surface froze to produce a rough wavy structure by being released from the pressure P.

IV. Experiments on Single Crystals of Ice

After the preliminary experiments described in the preceding two sections, the author carried out the following experiments in a cold room of −15°C, using columns of single crystals of ice in place of the hemispherical polycrystalline ice.

The apparatus used for the experiments is shown in Fig. 3. In this figure, B is a plate of brass 20 cm long, 3 cm wide and 8 mm thick with a round hole at its center in which a glass plate is firmly fitted. On the bottom surface of the glass plate a column C of single crystal of ice, about 15 mm high and 10 mm in diameter, is fixed by adding water around the top edge of the column by a syringe and letting the water freeze. The bottom surface of the ice column lies on the glass plate G placed on the movable stage T of an inverted microscope. The plate of brass B is stopped by a knife edge K at the left end and is pulled down by weight W at the right end. Thus the ice column is compressed vertically against the glass plate G in the direction of its axis.

Since the plate of brass was heavy, the pressure P on the contact surface could not

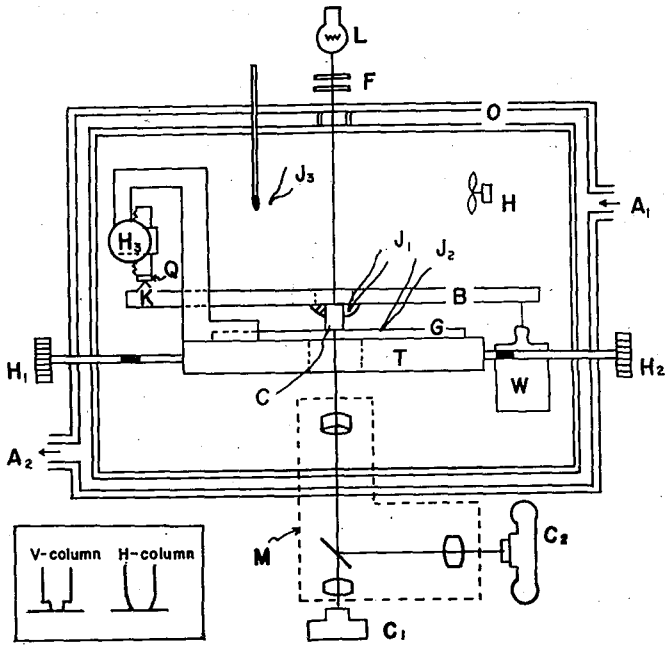

Fig. 3. Schematic diagram of the experimental apparatus for single crystal of ice
C, ice column of single crystal; G, glass plate; T, stage of microscope; B, plate of brass or methacrylate resin; W, weight; K, knife edge; Q, quartz; H_1, H_2, handles to move the stage of microscope; H_3, handle for adjusting plate B; H, fan; L, light source; F, heat ray absorbing filters; M, microscope; C_1, C_2, cameras; J_1, J_2, J_3, thermocouples; A_1, A_2, inflow and outflow of air

be reduced below a certain limit. When small P is required, a plate of methacrylate resin was used in place of the brass plate.

The ice column is illuminated by light from an electric lamp L at the top of Fig. 3 and the bottom surface of the column is observed from below through the inverted microscope M. Two cameras C_1 and C_2 are used for photographing. The camera C_2 works automatically by the aid of a relay and a timer.

The whole apparatus is placed in a double walled case O made of transparent plates of plastic. Air of constant temperature flows between the double walls to keep the inside of the case at a desired temperature lying in a range 0 to −30°C. The circulating air is kept at the desired temperature by a heater and a cooler which work automatically through a sensitive thermostat. Fan H is for stirring the air in the case. The maximum fluctuation of the temperature was ±0.2°C.

Copper-constantan thermocouples (0.3 mm in diameter) J_1, J_2 and J_3 are for measuring temperatures of the ice column, the lower glass plate and the air in the case. The three temperatures were continuously recorded by an automatic balancing recorder and no difference was discerned among them during the experiments.

Handles H_1 and H_2 are for moving the stage T of the microscope from the outside of the case. Any portion of the bottom surface of the ice column can be brought into the field of view of the microscope by turning the handles. Handle H_3 is in the case.

It is used to adjust the position of knife edge K through rack and pinion so as to keep the plate B horizontal.

The ice columns were cut from lumps of single crystal of ice brought from the Mendenhall Glacier, Alaska, in such a way that the crystallographic *c*-axis of the crystals lay either parallel or perpendicular to the axis of the columns. To make such cuts, it was necessary to know beforehand how the *c*-axis was orientated in the lumps. This was achieved by the use of etch figures made on their surfaces by the Higuchi method (Higuchi, 1958). Let the column with the *c*-axis parallel to its axis be called V-column, for the *c*-axis is vertical when the column is stood upright. The other column with the *c*-axis perpendicular to its axis will be called H-column; "H" stands for "horizontal". The columns were narrowed at their bottom ends as shown in the lower left corner of Fig. 3.

The glass plates against which the ice columns were compressed were of soda lime glass or quartz. They were cleaned in the following manner. After having been bathed in a chromic acid mixture for a long time, the glass plates were rinsed with running city water and then with distilled water. Then they were washed in a bath of extra-pure ethyle alcohol by renewing the alcohol three times and were dried by blowing air which had been cleaned through filters of active carbon and glass fiber.

V. Results of the Experiments on Single Crystals of Ice

The experiments of compressing the columns of single crystal of ice were begun at a temperature near −30°C. At first the bottom surface of the ice column came into contact with the glass plate at a point. But the contact surface expanded quickly and

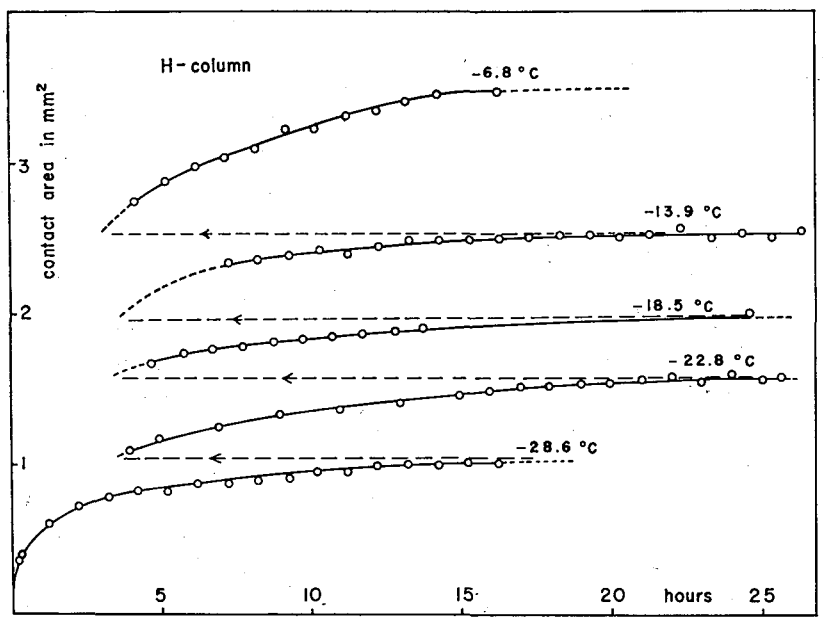

Fig. 4. The change in contact area of a H-column with time and temperatures. V-column gave also similar results

reached an area of about 1 mm^2 in a few hours. After that the contact surface continued widening at a rather constant slow speed as shown by the lowest curves of Fig. 4. Pressure P on the contact surface was given by a compressing force F divided by its area A. Since the weight W in Fig. 3 was not changed, F was kept constant and P decreased as A increased. Twenty-four hours later, after the beginning of the above experiment, the temperature was raised about 5°C without changing the compressing force F.

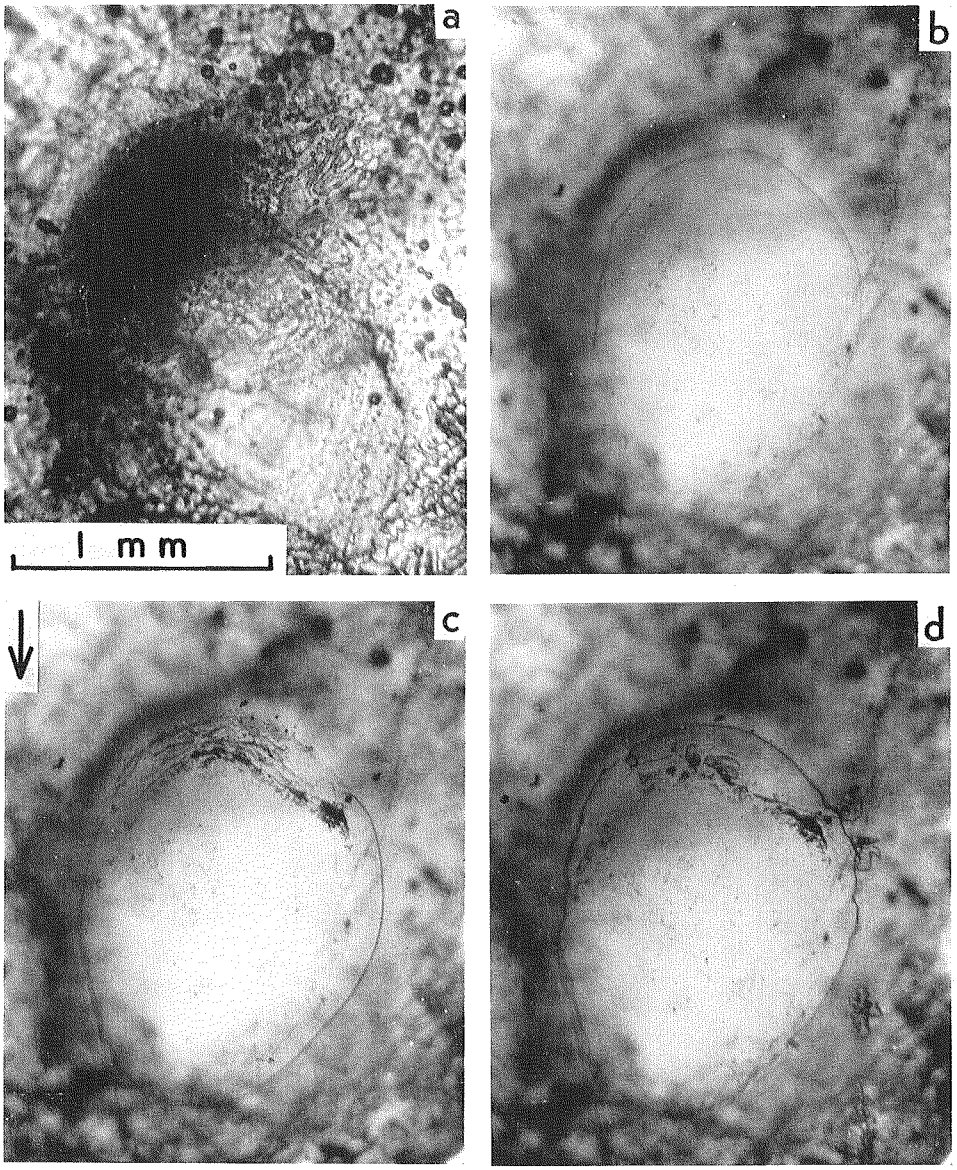

Fig. 5. Contact area between glass plate and the top of a spherical polycrystalline ice. −3°C

a: Top of the hemisphere before contact. b: The thin oval line shows the margin line. 41 min after the top of ice touched the glass plate. P=80 kg-wt/cm^2. c: During slide. d: After the slide

The area of the contact surface expanded following the curves indicated in Fig. 4 beginning with the lowest curve. In this way temperature was gradually raised every twenty-hours and the curves relating the area A of the contact surface with time t were obtained for each temperature as shown in the figure. At the end of this series of experiments the temperature had been raised to about $-5°C$. During the experiments the ice column

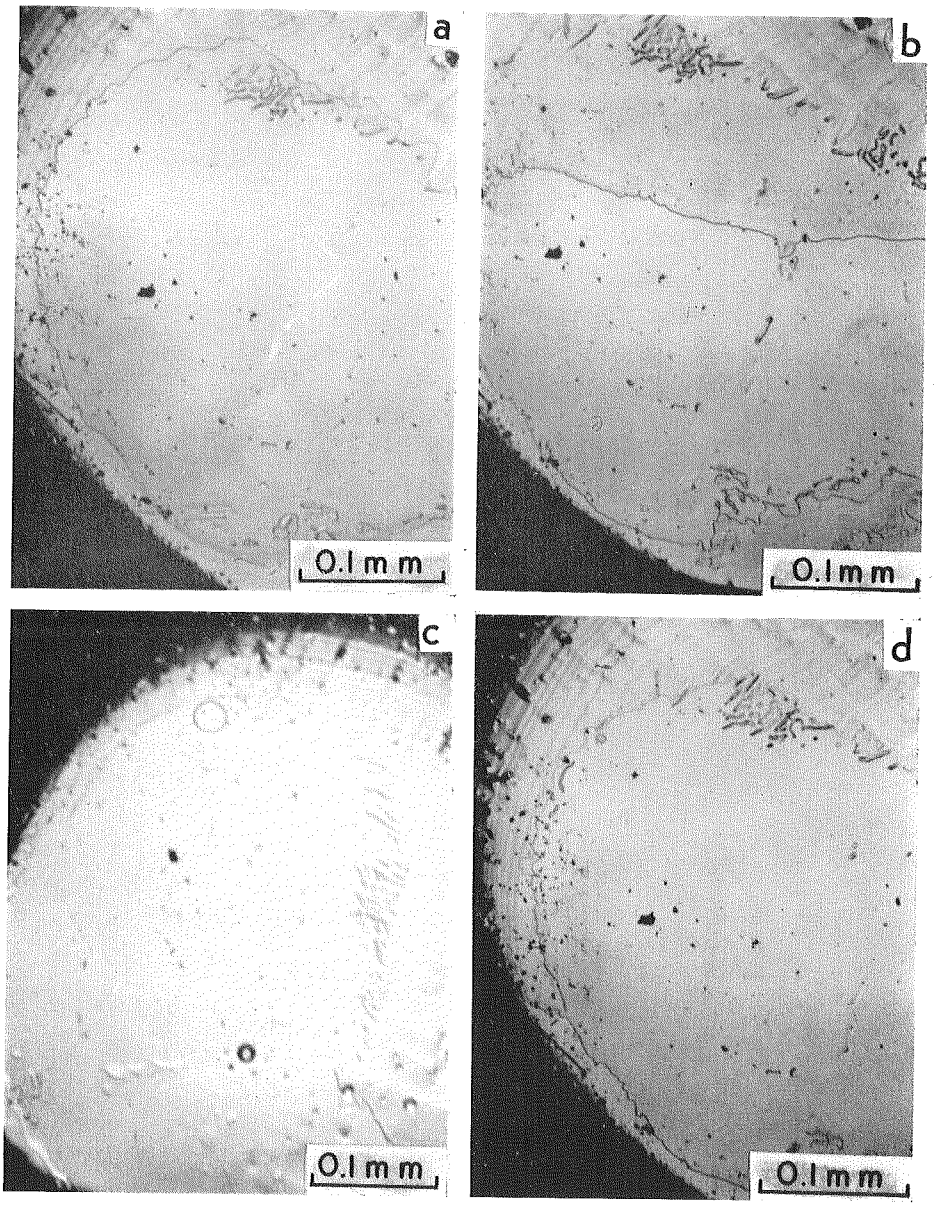

Fig. 6. Contact area between glass plate and V-column of single crystal of ice. $-7.2°C$
a: 27 hours after the contact. $P=69$ kg-wt/cm^2. Flat part is the contact area. b: Contact area contracted due to a small reduction of the compressing force. c: Contact area reduced to a small circle near the top due to further reduction of the force. d: After the force was restored to the initial value

thinned due to the evaporation from its side surface, and in some cases the whole area of the bottom surface of the ice column was finally brought into contact with the glass plate.

As well known, H- or V-columns of single crystal of ice undergo very little plastic

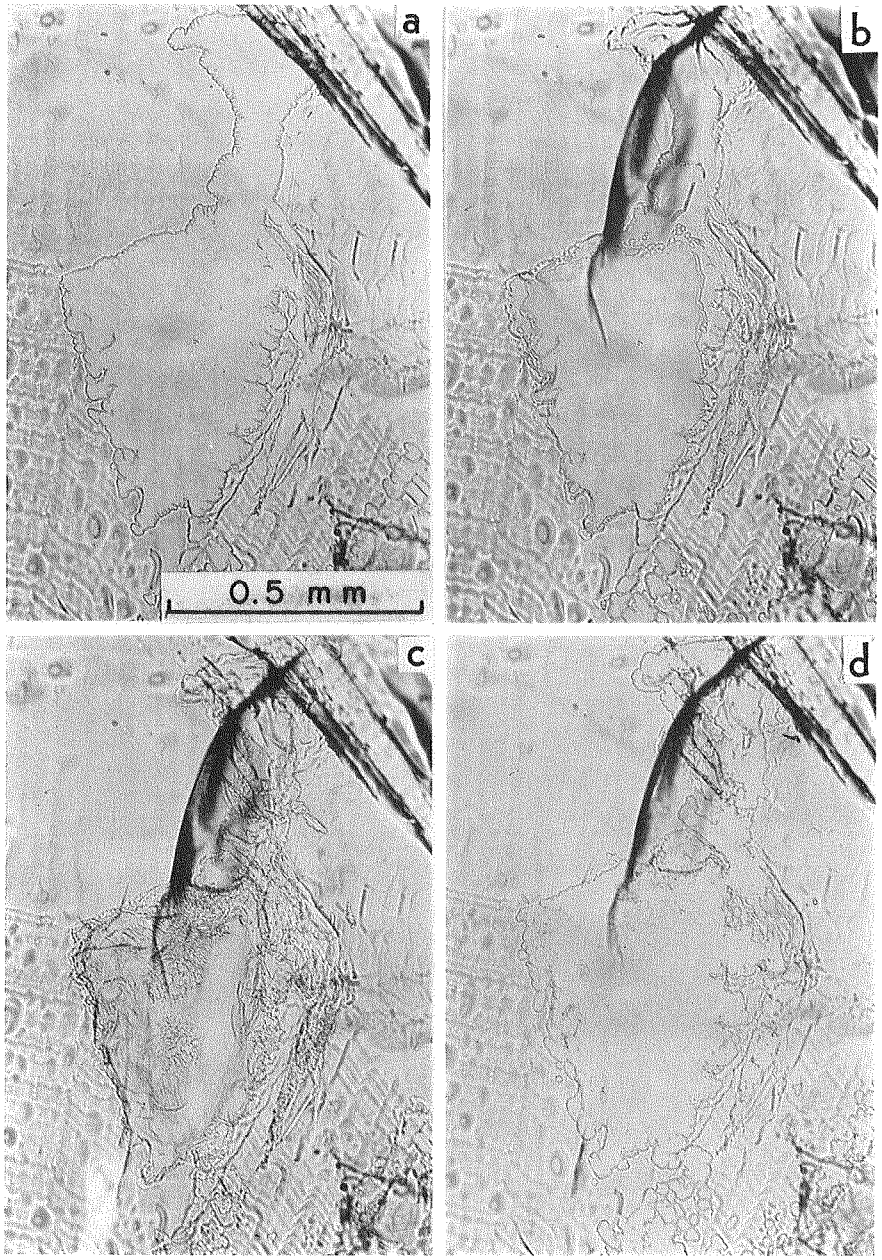

Fig. 7. Contact area between glass plate and V-column of single crystal of ice. −28.8°C
a : 30 min after the contact. $P=400$ kg-wt/cm^2. b : Contraction of the contact area due to the reduction of the compressing force $P=220$ kg-wt/cm^2. A crack appeared in the column by a shock at the reduction of the force. c : A slide of the column made some portions of the contact area rough. d : After the force was restored to the initial value

deformation when compressed along their axis. The hemisphere of polycrystalline ice used in the preliminary experiments must have been subjected to a large plastic deformation at its top. Despite the smallest degree of deformation, the water-like film was still seen on the end surface of H- or V-columns even at temperatures as low as −30°C.

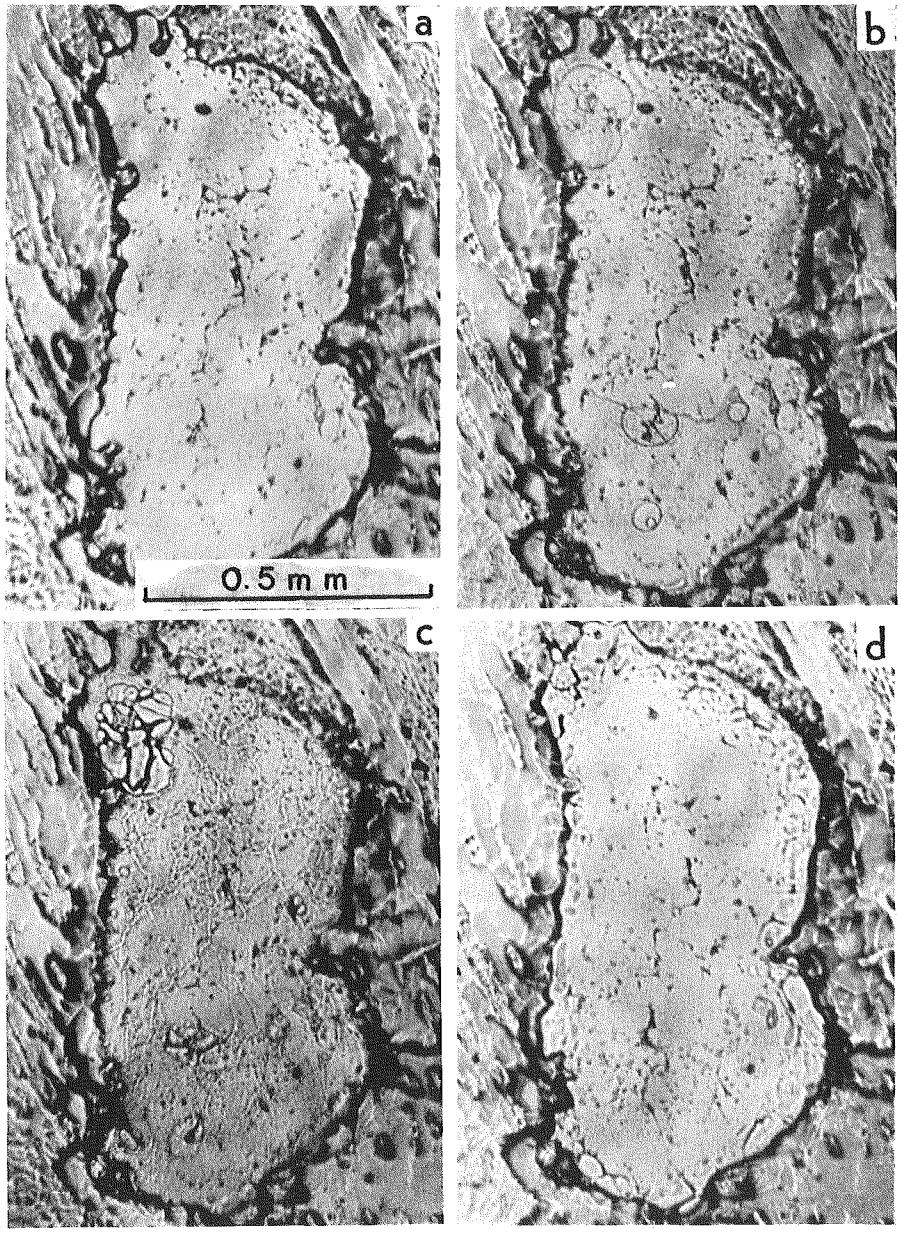

Fig. 8. Contact area between quartz plate and V-column of single crystal of ice. −27.2°C
a: Contact area is bordered by a thick line. $P=55$ kg-wt/cm^2. b: Contact area is reduced. The contact is made on the areas surrounded by circular thin lines. c: The water-like films on the contact areas in b had frozen when observed 2 hours later. d: The original contact area was recovered by the application of the initial compressing force

(1) In each of Figs. 6, 7 and 8, the first photograph a shows the contact area bordered by the "margin line". As the end surfaces of the columns did not form a perfect plane, the contact area did not cover the end surface completely. Temperature and pressure were −7.2°C, 69 kg-wt/cm² in the case of Fig. 6, −28.8°C, 400 kg-wt/cm² in the case of Fig. 7 and −27.2°C, 55 kg-wt/cm² in the case of Fig. 8. It should be noted that even the pressure of 400 kg-wt/cm², the greatest of the above three pressures, reduces the melting point of ice only by 4°C. When the compressing force F acting on the ice column was reduced by diminishing the weight W in Fig. 3, the margin line contracted as shown in Photo. b of each of Figs. 6, 7 and 8. In the case of Fig. 8, the margin line contracted so much that it separated into several small circles. The small circle near the top of Fig. 6 c shows also the margin line of the water-like film when the force F was reduced further.

Photograph d of each of Figs. 6, 7 and 8 shows the state of the contact surface when the force F was restored to its original value. At the restoration of the force the contracted margin line expanded quickly and returned to its original position.

As stated before, the present author takes it as the strongest evidence for the existence of a water-like film that the contact area between the ice and the glass plate is bordered by a distinct movable margin line as shown in Figs. 6, 7 and 8.

(2) When the temperature was above −20°C, no change was observed in the contact area if the ice column was slid on the glass plate by moving the brass plate to which the column was fixed. The sliding was smooth, which could be taken as another evidence for the existence of water-like film at the contact surface.

At temperatures below −20°C, however, the clear and flat contact area became rough in some portions as shown in Fig. 7 c, when the ice column was moved. As long as the contact area was not entirely roughened and a clear and flat part was still seen, the ice column could be slid. But, when the whole contact area became rough, a strong application of force was required to move the column still further. Often an internal fracture appeared in the ice column and pieces of ice were found firmly adhered to the glass plate. There is little doubt that the water-like film changed into ice in the rough portions of the contact area due to the shock caused by the movement of the column.

(3) The water-like film froze also when it was left at a much reduced pressure for a long time. As mentioned before, Fig. 8 b shows the state of the contact area where the water-like film contracted and separated into several circular films due to the reduction of the compressing force F. In this case the force F was made so small that the pressure F/A was also diminished to a small value despite the decrease in the contact area A. Two hours after the reduction of the force, the author found that the circular films in Fig. 8 b had changed into irregularly patterned patches as shown in Fig. 8 c. In all probability, these patches were composed of polycrystalline ice. As the author did not maintain continual observation, he does not know when the circular water-like films froze. But it was not earlier than 20 minutes after the reduction of pressure. When the pressure was increased to the initial value again, the frozen patches melted and expanded to recover the original water-like film as illustrated in Fig. 8 d.

It is noted that the water-like film was kept unfrozen for two or three weeks when it was in a large area under high pressure.

(4) The light for illuminating the contact surface was passed through green filters to eliminate heat rays. Therefore the contact surface was illuminated by a nearly monochromatic light. When the margin line contracted due to the reduction of the compressing force, interference fringes appeared outside the margin line where a clearance came into being between the surfaces of the ice and the glass. This fact shows that the water-like films were more than a few wave lengths of light thick.

Hori (1956) observed that water films sandwiched between two glass plates neither froze nor evaporated if they were made thinner than a certain limit. A water film less than 10 μ thick showed no indication of freezing even at temperatures lower than $-90°C$. Even in vacuum and at high temperatures, water films did not evaporate if they were thinned to 0.1 μ or less. There is an important difference between Hori's film and that of the present author: the boundaries of the water film were both glass in the former and one of them was ice in the latter. But the great stability of the Hori's film might be regarded to render support to that of the present author's.

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