

Ice Under Stress and Pressure, Ice In Order and Disorder

by *Barclay Kamb*

The interest in ice at Caltech goes back at least as far as Linus Pauling's discovery, in 1935, of the important phenomenon of proton disorder in ice and his celebrated explanation of the zero-point entropy of ice. The interest might well go back further still, for what Caltech professor or student, sweltering in Pasadena during the summer months, might not be able to imagine the beauty of field work on ice in Alaska or the Pacific Northwest? But it remained for Bob Sharp to bring any such dreams to realization, with his expeditions to the Seward-Malaspina glacier system in Alaska, beginning in 1948. And it is to Bob that we owe not only the beginning of the work on ice in Caltech's geology division, but also the fostering of a broader view of the geological significance of ice—the significance of its study in the wider context of the rocks and minerals of the earth.

The great pressures at depth in the earth are thought to squeeze the minerals of our everyday experience into novel, super-dense forms. Stresses generated by the forces responsible for earthquakes are thought to deform severely the rocks of the earth's crust and mantle, in the processes by which mountain ranges and other great earth structures are built. In the world of ice, there is a rich variety of similar phenomena. Several dense ice phases are produced by transformations under pressure, and glacier ice is involved in extreme effects of solid deformation. In ice we have a solid-state system exhibiting in classic form the phenomena in which solids respond to pressure and stress.

In the study of ice and its response to pressure

and stress, our approach at Caltech was first and foremost a field effort—an observational approach. But the subject has also developed very rapidly along theoretical and experimental lines in recent years, and we are contributing to this aspect too. Several years ago we began experimental work on ice polymorphism under pressure. Now we have completed construction of a cold laboratory for research on the response of ice to stress. This work had its origins in 1960 when I carried out, in Switzerland, the experiments that are the basis for some of the information presented here and that provide the starting point for the experimental program of the new cold lab. Some other aspects reported in this article are the result of experiments done in collaboration with William F. Brace at MIT, while I was visiting professor there last fall. And in the field program we have had valuable collaborations with Ronald L. Shreve ('52, PhD '57) of UCLA and Edward R. LaChapelle of the University of Washington. Much of the work described here has been supported by the National Science Foundation, the Guggenheim Foundation, and the Sloan Foundation.

ICE UNDER PRESSURE

The effects of pressure on ice are in a sense the most basic. Pressure is, of course, the simplest type of stress—the isotropic one. Whereas the response to non-hydrostatic stress often involves complex irreversible phenomena, the response to hydrostatic pressure is governed by equilibrium thermodynamics and brings into evidence the basic equilib-

rium thermodynamic properties of the H_2O system. These properties are in turn a macroscopic reflection of the underlying structural architecture on the molecular scale—the mechanism of bonding, the nature of the intermolecular forces, and their resistance to bond deformations of various kinds. Application of pressure causes structural collapse, either by simple self-compression, which involves a more-or-less uniform bond shortening, or else by thorough structural reorganizations representing transformations to denser phases. Ordinary ice I transforms at about 2,000 atmospheres to the denser phases ice II or ice III, and these transform at higher pressures to still denser phases. In all, twelve distinct phases of ice are now recognizable, of which nine are produced at high pressure.

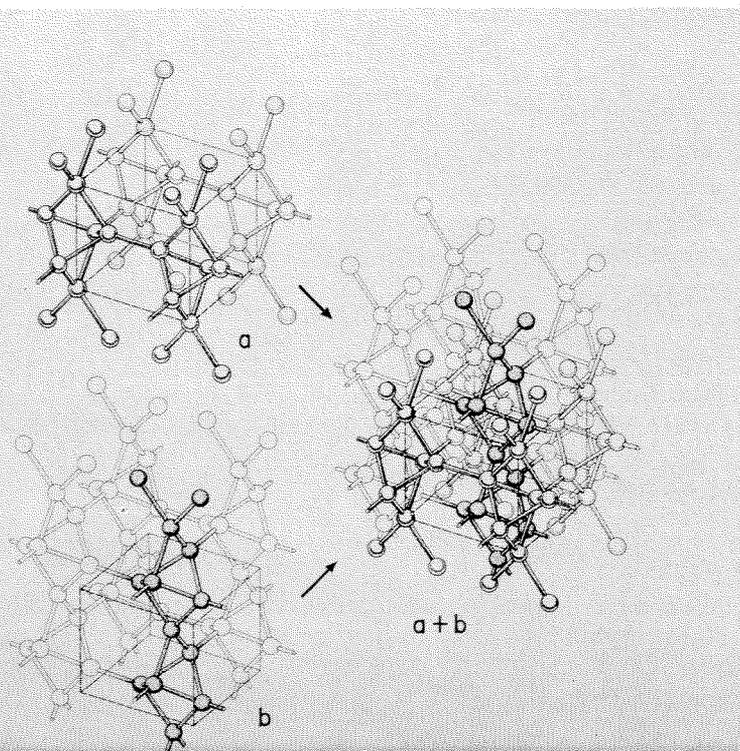
The water molecules in ice I behave tetrahedrally, each molecule forming four hydrogen bonds to neighbors in tetrahedral directions. Because of this tetrahedral geometry, there is an analogy between possible ice structures and structures of silica minerals; and, indeed, ice I is the structural analog of one of the SiO_2 polymorphs, tridymite. Whether the tetrahedral character of the water molecule is retained under the collapse brought about by pressure, and whether the structural analogy with silica polymorphs continues to hold in the dense forms of ice, had to be discovered by determining the structures of the high-pressure phases. Before we began our crystallographic study of the high-pressure forms of ice, it had been proposed that in the dense ice phases hydrogen and oxygen become dissociated as separate H^+ and O^- ions. The implied change from an intermolecular type of crystal bonding (hydrogen bonding) in ice I, to an ionic type of

bonding for the dense ice phases is a very drastic change in the nature of the bonding forces—one that would have to involve a complete reorganization of the electronic structure.

Our crystallographic studies of the high-pressure ices make use of the trick of quenching. The ice is made in a bomb at the appropriate pressure and temperature, and the bomb is then cooled to $-196^\circ C$ by immersion in liquid nitrogen. At this temperature the dense ice does not invert to ice I upon release of pressure but remains metastably in the dense form. The samples can be extracted from the bomb, and individual crystals can be studied by x-ray diffraction as long as they are kept at low temperature.

The type of result obtained is shown for ice VI, below. We find that the integrity of the individual water molecules is retained in the dense phases; there is no dissociation into H^+ and O^- ions. Except at the highest pressures, four-fold coordination of the water molecules remains the basic structural feature, and in this sense the water molecule retains its tetrahedral bonding character. But angular distortions from the ideal tetrahedral bond arrangement of ice I become very large. While the structural analogy with polymorphs of silica remains possible, only one of the dense ice structures is a straightforward analog of a form of silica. But ice VI can be considered the analog of the silicate framework of a zeolite if only half of the structure (part a or b of the drawing below) is considered. Here we see a novel structural feature of some of the dense ice phases: the structure is built up of two separate, independently bonded frameworks, each occupying void space in the other. Surprisingly, no structural analog of quartz—the common form of SiO_2 —occurs among the dense forms of ice. The phase diagrams and thermodynamics of the SiO_2 and H_2O systems, in relation to structure, are in fact very different. This probably reflects a marked difference in the energetics of bond-bending in the two groups of structures, as might be expected from the different nature of the bonding forces.

In the drawing of ice VI (left), the hydrogen

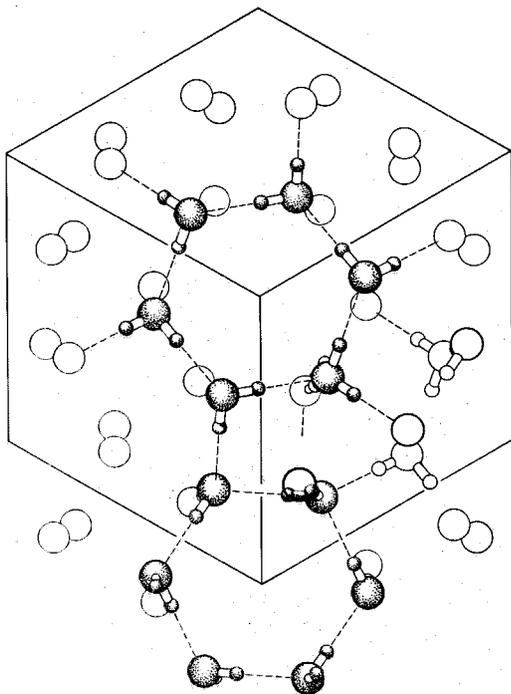


How to construct a dense form of ice (ice VI). Water molecules (balls) are hydrogen-bonded together (sticks) to make the two complete frameworks, a and b at the left. These are then combined within the same space to form the complete structure a + b. Hydrogen atoms are in a disordered arrangement and are not shown here. They are present statistically near one or the other end of each bond.

(Illustration reproduced from *Science*, vol. 150, p. 208, copyright 1965, American Association for the Advancement of Science.)

atoms are omitted because they do not occupy fixed positions but instead are involved in proton disorder—the phenomenon discovered originally in ice I by Pauling. Each water molecule assumes at random any one of six orientations consistent with the network of hydrogen bonding, and in each bond a proton appears at random near one end of the bond or the other. In ice I the disordered arrangement does not “order up” on cooling, but we have evidence suggesting that in ice VI, such an ordering-up does occur. In ice II the tendency toward proton-ordering is so strong that only an ordered structure occurs (below), and there is no disordering at higher temperatures. Because of the proton order, the entropy of ice II is 0.8 entropy units less than that of ice I, in striking confirmation of Pauling’s original calculation of 0.81 entropy units as the entropy of proton disorder in ice I.

The state of order or disorder of the protons has decisive consequences for the physical properties of the ice phases, especially for the electrical properties. The high dielectric constant and the dielectric relaxation of ice I have long been known and admired; they are made possible by the ability of the water molecules in the proton-disordered crystal to change from one orientation to another under the influence of an external electric field. Ice VI has a high dielectric constant and shows dielectric relaxation, whereas ice II has a low dielectric constant without any relaxation.



A proton-ordered form of ice (ice II). The protons of the individual water molecules are in definite positions; the hydrogen bonds are indicated by dashed lines.

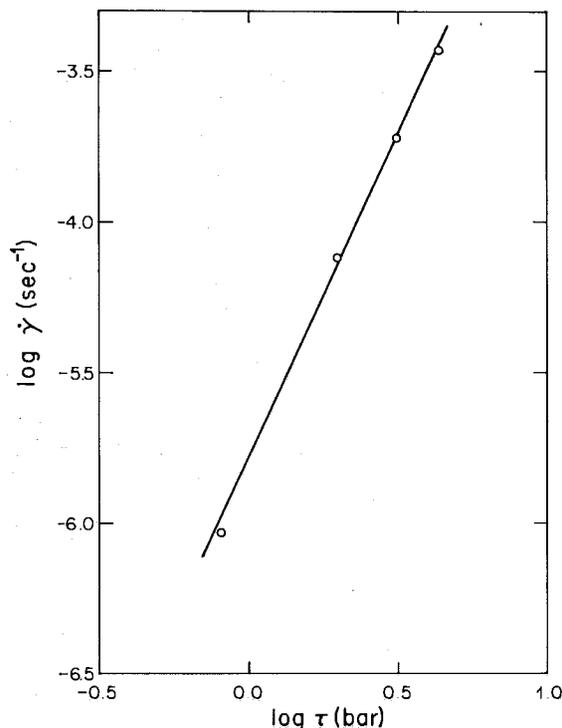
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Highly sheared crystal of ice I. The sloping reference lines (arrows) were originally vertical, but were tilted through an angle of 72 degrees by plastic flow in the crystal, as shown. The total shear strain is 310 percent. The crystal is 8 cm in diameter.

ICE UNDER STRESS

The response of ice to stress, as distinct from simple hydrostatic pressure, brings forth new and interesting phenomena. The celebrated plasticity or flow-response of crystals of ordinary ice I (above) takes place through the motion of defects (dislocations) in the crystalline structure and has some puzzling features—notably the extreme anisotropy (the strength varying by more than three orders of magnitude in different directions) and the prominent nonlinearity of the response (below), which shows up strongly in flow measurements on glaciers. If the motion of dislocations is controlled primarily by the



Relation between applied shear stress τ and strain rate $\dot{\gamma}$ for the ice crystal shown at top of page. If the response were linear, the line would slope at 45 degrees.

ability of the water molecules to rotate from one orientation to another, one might expect a close tie between stress response and electrical response. The dielectric relaxation time in ice III is about 1/100th that in ice I at the same temperature, apparently because the energy barriers to rotation are reduced in the distorted tetrahedral configuration of the denser ice structure. In a recent experiment at MIT, W. F. Brace and I found that ice III is at least two orders of magnitude more plastic than ice I. This discovery suggests a close relation between the electrical and flow phenomena. We plan soon to extend the comparison to ice II, which, according to these ideas, should show little or no plastic response to stress.

IMPLICATIONS

What is the relevance of these ideas of structural reorganization, of response to pressure and stress, of proton order and disorder, for the world of ice as we know it on the earth? The whole subject of how glaciers flow and of how they respond to climatic changes is, of course, intimately concerned with the stress-response of ice. And if transitions to ice II or ice III were to occur, the behavior of the glaciers would be enormously affected. But the thickest ice on earth, 3.5 km in Antarctica, falls far short of the 22 km required to produce ice II or ice III. The required thickness was not approached even at the maxima of the ice ages. (It might, however, be present on Jupiter and Saturn.) The relevance, then, is indirect—the insight into ordinary ice I that is obtainable from interrelationships of structure and physical properties among all of the ice phases. This is clearly seen in the relation between the plasticities of ice I and ice III, which has important implications for the mechanism of plastic flow in ice I by itself.

Another example of these interrelations is seen in the phenomenon of elastic relaxation. Below an oscillation frequency of about 1 kc, some of the elastic constants of ice I decrease by about 5 percent from their high-frequency values. This elastic relaxation has been attributed theoretically to a tendency for the protons to assume an ordered configuration in the elastically strained structure. At first sight this interpretation seems dubious, when we consider that in many of the high-pressure ices, with tetrahedral geometry distorted vastly more than ever occurs in elastic strains in ice I, the protons assume a disordered arrangement. But on closer examination one finds that the magnitude of the order-promoting energy (in relation to elastic distortion) required to explain the observed elastic relaxation is comparable to observed proton-order-

ing energies in relation to distortions of tetrahedral coordination in the high-pressure ices. Thus the observed effects of order and disorder in the high-pressure phases support an order-disorder phenomenon as the cause of elastic relaxation in ice I.

While these examples give some idea of the implications of high-pressure structural information for the world of ice that interests us geologically, it must be admitted that the bridge of interpretation between these two areas of knowledge about ice is far from completely built. It will probably take years to write a coherent story relating ice in its various physical forms and ice in its many natural manifestations. Here I want to jump boldly across this gap and round out the picture of our work on ice at Caltech by telling of some current efforts to understand those impressive natural manifestations of ice, the glaciers.

GLACIERS ON THE MOVE

Our interest at Caltech has tended to concentrate on flow and deformation phenomena in glaciers—on effects of stress and pressure. Lately we have been trying to find out what goes on in that part of the ice nearest the glacier bottom, where the stresses and pressures are the greatest. It is here that the main contributions to glacier motion arise, through rapid plastic deformation of the highly stressed ice near the bottom and through a sliding of the ice mass as a whole over the bedrock underneath. To get information on these effects we have drilled deep boreholes through the ice, have measured the internal deformations taking place, and have brought up core samples to study the structure of the highly stressed ice (*Engineering and Science*, February 1965). We have also excavated tunnels to the glacier bottom, in places where that is feasible, to observe at first hand the sliding of the ice over the rock below.

In the summer of 1967 we carried out a combined attack to study the dynamics of motion in an icefall, a place where ice flow velocities are unusually high (about 0.5 m per day). The study area was a portion of Blue Glacier, our "outdoor laboratory" in Olympic National Park, Washington. The work was a collaborative effort of a Caltech team, led by me, and a University of Washington team led by Edward R. LaChapelle, and was carried out with the cooperation of the U. S. National Park Service.

In a portion of the icefall selected for smoothness of flow, tameness of access, and relatively mild hazard from avalanches and collapsing seracs, we drove a 90-meter tunnel from the surface to the bottom of the ice and drilled 10 boreholes to the bottom in a pattern designed to reveal the broader



A portion of the Blue Glacier in Olympic National Park, Washington, showing icefall descending from Mt. Olympus. The Caltech-Washington tunnel entered the ice at the point marked T and proceeded generally toward the right to the bottom. The boreholes at B were drilled vertically downward to strike bedrock near the tunnel head 70 meters below.

configuration of bedrock in the area of the tunnel head (above). The tunnel was excavated by means of compressed-air-powered chain saws and jackhammers, plus a great amount of plain hard labor. The holes (right) were drilled by means of a thermal borer, and a microswitch sounding device was then used to locate the bottom accurately and to follow changes in its position as the glacier moved along. This was done in order to measure the bed roughness, an important parameter in the relationship sought between basal shear stress and sliding velocity of the glacier.

Another important parameter is the extent of separation between the bedrock and moving ice, due to stresses set up in the flow process (subglacial "cavitation"). To observe this we built a camera that could take pictures of the walls of the two-inch-diameter boreholes. With this instrument we could locate the base of the ice and measure the gap be-



A drill site in the icefall. Barclay Kamb is preparing to lower the borehole camera to determine ice separation at the base of the glacier.



Ice in the tunnel wall near the base of the glacier. The laminated structure is parallel to the flow direction of the ice. Area photographed is 2 ft. long.

tween ice and bedrock. These measurements and observations are "firsts" in the study of glaciers; no one had tried to measure subglacial roughness before, and no one had put an "eye" deep into a glacier before.

AN INSIDE VIEW

The best view was, however, the one from inside the tunnel. In exposures on the tunnel walls one could trace, from the surface inward, a striking

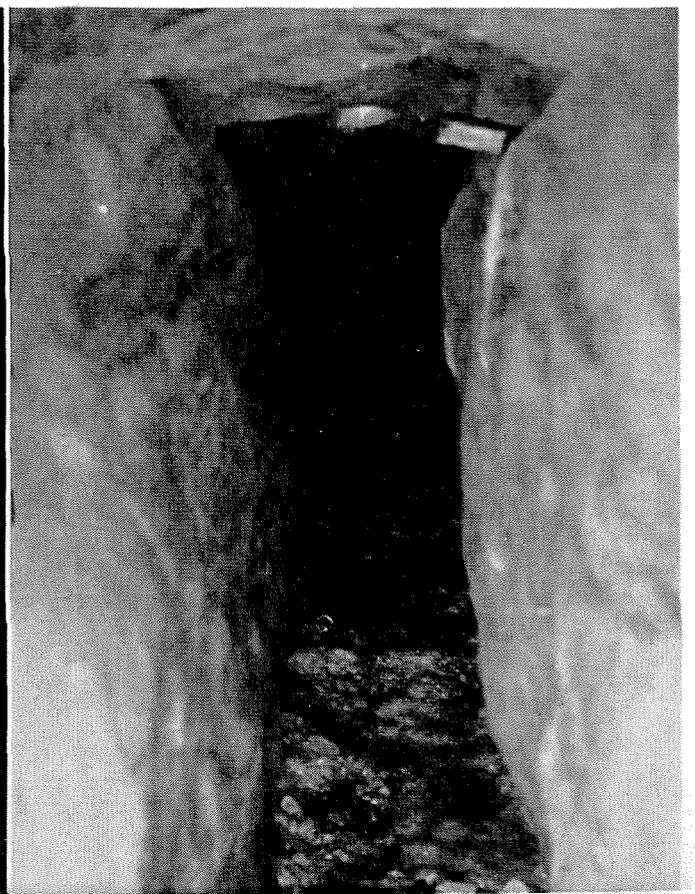
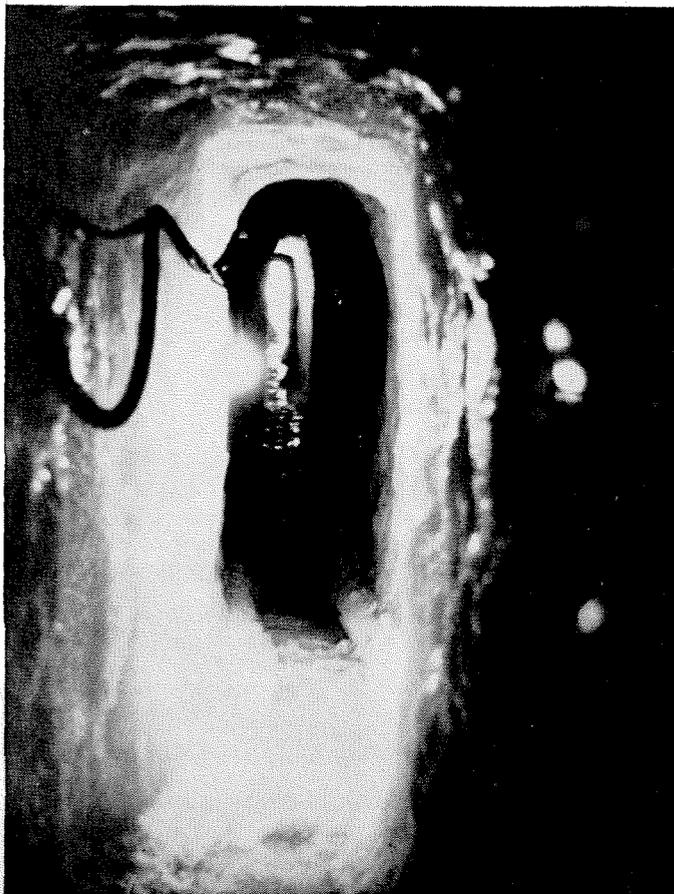
Two views of the glacier tunnel. At the left is the tunnel as it was originally excavated. At the right is a deeper part of the tunnel after some closure has occurred; the originally vertical walls have begun to bulge in and a

transition from the jumbled, chaotic ice near the surface to ice at depth having a very orderly structure with beautiful laminations aligned along the flow direction (left). This orderly structure is produced by deformation under the high stresses in the deep ice. Another effect of stress is an aligning of the individual ice crystals into certain definite orientations with respect to the flow direction. These changes from disorder to an orderly structure in glacier ice under stress are reminiscent, on the macroscopic scale, of the proton order induced under pressure and stress within individual crystals, on the microscopic scale.

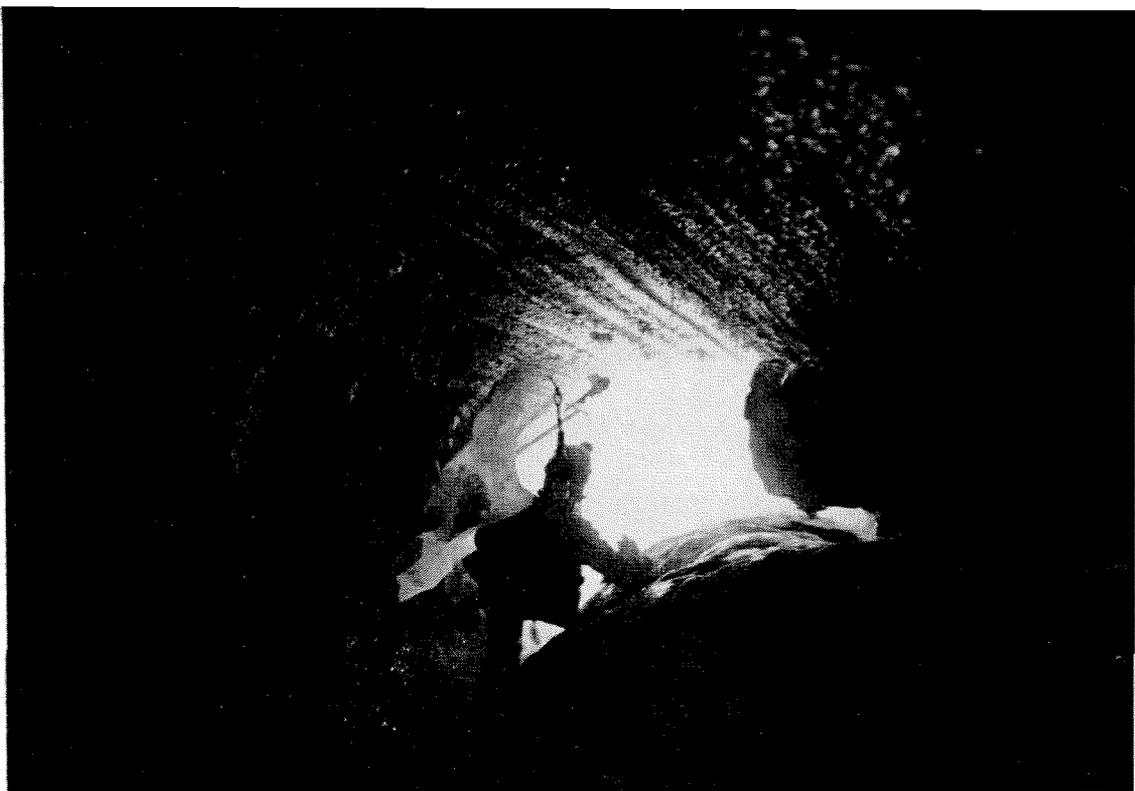
As we approached the bottom of the glacier the tunnel (below) began to squeeze shut rapidly under the pressure of the overlying ice; the walls were closing in as much as two or three centimeters overnight. This made completion of the tunnel to bedrock difficult because a large proportion of the digging effort had to be expended just to keep the passageway open. On a hint from the borehole measurements, we excavated the tunnel in the shape of a Y, so as to reach bedrock at two places. We found that flow conditions at the two places, only about 15 m apart, were vastly different.

At the tip of one arm of the Y, the ice was separated from bedrock over wide areas, forming impressive caverns roofed by the grooved and striated

"crease" has developed at the ceiling corners. By the time this picture was taken, the still deeper part of the tunnel—in the darkness up ahead—had closed in completely due to the overburden pressure.



The bottom of the glacier, as encountered at the head of the first branch of the tunnel. The picture is taken from inside a large subglacial cavern, and the roof overhead is the sole of the moving ice mass. The bright area is where the cavern is penetrated by the tunnel. You are looking down along the flow direction of the ice, as shown by the grooving of the sole.



sole of the moving ice mass (above). Here the sliding velocity was 35 cm per day, and most of the motion observed at the glacier surface was the direct result of this sliding. At the tip of the other arm of the Y, in contrast, the ice was in almost complete contact with the bedrock, and the sliding velocity was only 1 cm per day. In this arm of the tunnel the glacier motion was accommodated instead by very large plastic deformation rates within the ice, in a zone about 10 m thick at the bottom. Where this zone was penetrated by our boreholes, the holes tilted by more than 25 degrees in a two-week period, as a consequence of the ice deformation. When we consider that in large glaciers the maximum tilts are commonly only about 25 degrees *in a whole year*, we can appreciate how unusually large the shear strain rates observed here are. They are about 6 percent per day, an order of magnitude larger than ever measured in a glacier before.

We have not yet fully evaluated the implications of these observations, but a general conclusion stands out. Heretofore, we have tended to think of glacier motions as being fairly smooth, simple, one-valued functions of the driving forces or stresses, because we have tended to think of the motion-controlling mechanisms as being well defined by the pertinent stress variables. But in the present instance we see that the whole style and mechanism of flow can vary enormously from place to place near the glacier bed, in response to seemingly minor differences in conditions there. There appears to be a kind of instability in the controlling mechanisms for the over-all motion. On one hand, the

ice may conform well to the bedrock, the shear stresses are large, and large plastic strain rates within the ice are responsible for most of the motion. On the other hand, with a relatively slight change in conditions, the ice may separate extensively from the bedrock, the shear stresses are widely relaxed, and a large sliding rate of the ice mass over bedrock occurs.

The situation may arise, I suspect, where this instability leads to a spreading out of the areas of extensive ice separation over a large part of the glacier bed, resulting in a great acceleration of the ice motion. I surmise that this is what happens in the hitherto unexplained catastrophic advances shown by some glaciers, notably in Alaska (the "galloping glaciers"), where motions of as large as 50 or even 100 meters per day sometimes occur.

These thoughts about complex natural phenomena, involving the combined action of many different physical forces and responses, seem to take us a long way from the basic and straightforward concerns about molecular structure of forms of ice and about forces of interaction between individual water molecules. Yet we hope ultimately to understand the natural phenomena of glacier flow in just such basic structural terms. Only in such terms could our understanding be adequate to extrapolate ideas from the world of ice to other worlds, such as the solid earth of silicate minerals below. And while striving for this understanding, we shall also, I hope, come to understand better the substance H₂O as a whole, in all its aspects—a substance that is, after all, one of the most important on our planet.