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# ACCEPTANCE OF THE MINERALOGICAL SOCIETY OF AMERICA AWARD FOR 1968

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## Mr. President, Dr. Graf, Ladies and Gentlemen:

For me it is a great honor and a great pleasure to be given the MSA award. As I run down the list of past recipients, several of whom are here today, I feel greatly rewarded to think that my own work has been placed in such illustrious company. But, at the same time, I feel rather guilty, because my contributions to mineralogy seem to me meager by comparison with the work of previous recipients and also of many younger men who merit the award. I have spent too much time up in the rain and snow, on a glacier somewhere, to have accomplished as much in mineralogy as I would like.

My first scientific interest was in minerals, and when I entered Caltech, I was one of those rare freshmen, never seen any more, to declare for geology right at the start. But already in those days everyone went into physics, and so, pretty soon, did I. When, several years later I realized that I was really interested in the earth after all, it was with the inspiration that I could help to solve some of the riddles of tectonics and orogenesis which fascinated me. But at that time we knew nothing about sea-floor spreading or transform faults, and no one with any sense believed in continental drift, and I was stumped in trying to find a fruitful lead. Then I happened to meet Linus Pauling and he asked me if I wouldn't like to study the structure of a mineral by X-ray diffraction. It was an exciting opportunity. Doing an accurate structure analysis of even as seemingly simple a mineral as zunyite was, however, a somewhat tedious job in those days, and I'm afraid my contribution was a rather humdrum one—but at least I became launched in mineralogy.

It was Bob Sharp who gave me the idea that problems of tectonics and solid deformation in the earth might be attacked through a study of glacier flow, and this started my interest in ice. Ice is, after all, a mineral, and a beautiful, albeit an evanescent, one. It also has some very remarkable properties, one of which I want to mention: its plastic anisotropy. When you look at the ice structure, it doesn't appear particularly anisotropic, and, as expected, ice has low birefringence and modest anisotropy of elastic constants. When you apply a shear stress across the (0001) plane of the ice crystal, it glides readily, giving strain rates of about



Barclay Kamb

100 year<sup>-1</sup> at stresses of a few bars. But if you compress the crystal uniaxially parallel to the c axis, it shows no plastic yielding *at all*, at stress differences as high as 1100 bars (which Bill Brace and I reached in a recent experiment at M.I.T.). This extreme anisotropy interests me greatly, because I feel that it is a clue to the mechanism of crystal plasticity and because it has strong effects on the flow of glacier ice. Although I can't say that studies of these things have as yet had any revolutionary applications in tectonics, I think that they have revealed interesting and useful information about how ice behaves as a mineral, as a rock (in glaciers), and as a physical substance.

From ordinary ice, I came to an interest in the various other forms of ice, most of which are formed under pressure. Linus Pauling suggested looking into the structures of these phases, and for me this opened up a new world—the world of polymorphism, of which Professor Ito has just spoken. There are about a dozen distinguishable phases in the  $H_2O$ system. Although most of them do not qualify as minerals because they do not occur naturally (except perhaps in the major planets), the relationships between their structures and their stability conditions in the *P*, *T* plane give us basic information about the bonding forces that govern the structure and properties of ordinary ice.

To mineralogists, polymorphism in the H<sub>2</sub>O system probably is of interest less for its own sake than because of its analogy with the SiO<sub>2</sub> system. The structural analogy between tridymite and ice-I extends to several other examples, of which perhaps the most interesting mineralogically is the correspondence between melanophlogite and the ice-like clathrate hydrate 6X · 46H<sub>2</sub>O. But at greater densities, the analogy tends to break down, in unexpected ways. There is no ice analog of quartz, although one was predicted by Bernal and Fowler. Ice-V and coesite have the same space group and same relative density (in relation to the analog phases ice-I and tridymite), and yet their structures are quite different. I think that the structural analogy H<sub>2</sub>O-SiO<sub>2</sub> is made all the more interesting by its imperfections, because these shed light on differences between chemical bonding forces in the two systems. One obvious difference is the tendency for the Si-O-Si linkage to bend so as to achieve a bond angle of about 145° at oxygen, in contrast to the O-H--O hydrogen bond, which appears to be strongest when unbent.

The high-low transitions in the silica and ice phases offer another mineralogically interesting area of comparison. The nature of these transitions in forms of silica has been difficult to clarify in detail, but it seems to involve adjustments in the Si—O—Si bond angles and in motional degrees of freedom made possible by bent Si—O—Si linkages. The corresponding effect does not occur in any form of ice as far as is

known, which reinforces the difference between bent and unbent bonds mentioned earlier. Instead, the high-low transitions in ice can be attributed to an ordering of the water molecule orientations at low temperature. This effect appears to occur in all phases of ice except ice-I, in which the phenomenon of water-molecule orientation disorder was discovered originally by Pauling. The SiO<sub>2</sub>-H<sub>2</sub>O comparison also brings out a difference in the symmetry changes that occur in the high-low transitions. In ice phases, water molecules that are symmetry-equivalent in a disordered structure can (and in some cases must) become symmetrynonequivalent in an ordered structure, whereas no corresponding symmetry change seems to be necessary in the silica structures. Thus in ice-II, 12 molecules that would be symmetry-equivalent in the unit cell of a disorder-averaged structure split into two separate groups of 6 each in the ordered structure, whereas in the transitions  $\beta \rightarrow \alpha$  guartz, " $\beta_3$ "  $\rightarrow$  " $\beta_2$ " tridymite, and  $\beta \rightarrow \alpha$  cristobalite, symmetry degradations occur without any splitting of groups of equivalent Si atoms into smaller subgroups. We have by no means reached the end in interpreting the high-low transitions in these systems, but I think that comparison and contrast between ice and silica will help in thinking about either one.

Another horizon that is emerging, I think, from these studies of the ice phases, and which I wish to mention, is the structural nature of liquid water. Some may question its pertinence to mineralogy, since liquid water is not listed as a mineral in the textbooks, but I follow Ian Campbell's recent G.S.A. Presidential Address in thinking that we should consider water as a mineral resource. In any case, water is of great importance to all of us. Yet great uncertainty remains as to how its remarkable properties (such as the volume decrease on melting) are to be explained in terms of a structural model on the molecular scale. There is reason to think that the type of disturbance in hydrogen bonding that we observe in the dense ice phases also occurs to an important extent in liquid water, and I feel that the study of ice polymorphism will in the future contribute to a better knowledge of the nature of water.

I am gratified that the Mineralogical Society of America has seen in this research, and in other more or less distantly related efforts on my part, enough of mineralogical interest to have justified giving me the M.S.A. award, and I am very pleased and honored.