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Giant Facets at Ice Grain Boundary Grooves

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The energy barrier for nucleation on the basal plane of ice has a striking manifestation when the basal orientation is present in a grain boundary groove. As the ice-water interface containing the groove advances, large planar facets grow out of the grain boundary. The facets exhibit dramatic hysteresis, and they can be up to 30 times larger than predicted by equilibrium models. Measurements of the growth direction of the facets yield insight into the nature of the nucleation process. The facets also provide a way to study the relaxation of twist along grain boundaries.

When a polycrystalline solid comes into contact with another phase, small indentations of the solid surface form where grains of different orientations meet. These indentations, termed grain boundary grooves, are observed in a number of contexts, such as at the surface of a polished solid ingot that has been annealed or at the boundary of a solid with its own melt. Grain boundary grooves have a long history in the study of metallurgy (*1*). They are well understood theoretically and experimentally and can provide useful information about material properties, such as interface energies and diffusion constants (*2*).

Grain boundary grooves at a solid-melt interface are analogous to the meniscus of a liquid that wets the wall of a vessel. The liquid rises to a certain height L because it can reduce the surface energy by an amount proportional to σL, where σ is the difference in surface energy between the dry and wet wall. However, the rise in height is limited by the cost in gravitational energy, proportional to $L^3\rho g$, where g is the gravitational constant and ρ is the liquid density. Apart from geometrical factors, the rise L is $(\sigma/\rho g)^{1/2}$. For a grain boundary groove, instead of the cost due to gravity, there is a free energy cost due to the presence of supercooled liquid inside the groove. This cost is given by the product of the volume of supercooled liquid and the difference in free energy between solid and liquid at the average temperature in the groove. Replacing ρg, then, we have $(q_m/T_0)(dT/dx)$, where q_m is the latent heat of melting per unit volume of the solid, T_0 is the melting temperature, and dT/dx is the temperature gradient in the groove. The groove size is given by

$$L \propto \sqrt{\frac{\sigma'}{\frac{q_m}{T_0}\frac{dT}{dx}}} \tag{1}$$

where σ' is the grain boundary interface energy. Anisotropy in the interface energies and the difference in thermal conductivities between the solid and liquid must be considered to calculate the exact groove shape. Indeed, a measurement of the shape can be used to determine the anisotropy in the crystal surface free energy (*3*). Nevertheless, the overall size scale for the groove should be set by the "capillary length" L as given above.

We were therefore surprised to observe plane-faceted grooves in ice whose linear dimensions exceeded the expected value by more than a factor of 30. Adjacent to these faceted grooves were typical rounded grooves whose dimensions were correctly given by the capillary length. Moreover, the facet size was not a single-valued function of the temperature gradient: Considerable hysteresis in facet size was observed as the ice-water interface advanced or retreated. This behavior is explained by a nucleation barrier to growth normal to the plane facets, in contrast to the growth of rounded orientations.

The cell used for the ice growth measurements has been described previously (*4*). Ice is grown in the shape of a thin disk (Fig. 1A). The temperature can be controlled both at the center of the disk as well as around the perimeter of the cell. By adjusting both temperatures, the radius of the ice and the radial temperature gradient can be set independently. The ice was nucleated by briefly touching a cotton tip cooled in liquid nitrogen to the center of the cell. The ice then grew out to some steady-state radius determined by the temperature conditions. Once steady state was reached, the temperature could be ramped so that the ice disk radius slowly increased or decreased. The ice was examined along the axial direction with a microscope, either directly or between crossed polarizers. Images were digitized and stored on computer disk or were recorded on photographic film. A typical ice disk contained from 6 to 10 different domains, divided by grain boundaries. The grain boundaries generally extended radially out to the ice-water interface, where grooves were observed.

There was a large difference in size between faceted grooves and rounded grooves on adjacent grain boundaries (Fig. 1B). To understand the origin of these large facets, we observed their development. As the ice disk radius decreased (Fig. 2A, top row), the facets shrank, but the intersection between the facets did not move until the facets reached a minimum size. After that, the whole groove receded without change of shape or size. As the ice was regrown (Fig. 2A, bottom row), the facets grew, but again the line of intersection was initially fixed. When the facets reached a maximum size, the ice disk edge and facets moved in unison. The facet size was not a single-valued function of the conditions but depended on the manner in which the facet was formed (Fig. 2B). This behavior was reproduced numerous times for the facet shown and for several other facets as well.

The explanation is as follows: The surface of a crystal may have orientations that are either "flat" or "rough" (*5*, *6*). A flat orientation is smooth on a molecular scale and consists of a single crystal plane. Growth on a flat plane requires the undercooling to be larger than a threshold value to nucleate a two-dimensional (2D) island. The value of the threshold undercooling ΔT corresponds to an energy barrier for the formation of a nucleus of a critical radius; nuclei smaller than this will shrink, whereas larger ones will grow (*7*). Conversely, there is no barrier to growth on a rough orienta-

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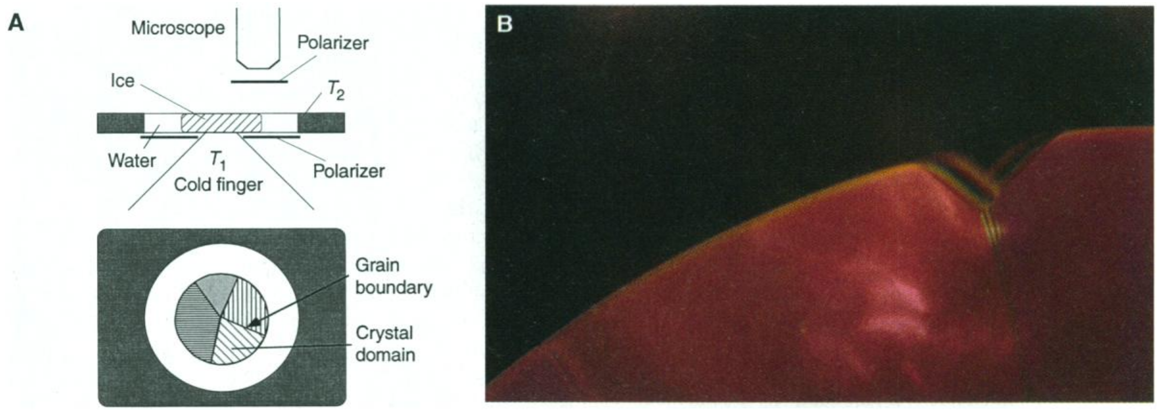


Fig. 1. (**A**) Experimental setup. Ice is grown from a cylindrical disk-like region of water 0.8 mm in height and 1.9 cm in diameter that is faced by a thin plate of glass on the bottom and a polymer membrane on top. Capillary lines that enter through the sides allow the cell to be filled with water and also allow excess water to escape as the water freezes. (**B**) A faceted grain boundary groove and a typical rounded groove (bottom left corner) at adjacent grain boundaries. The photographed region is 0.6 cm by 0.25 cm. The temperature gradient in the ice at the disk edge is ≈0.7°C cm^{-1}. The two facets form a "V"-shaped notch at the edge of the ice disk. The facet planes are not perfectly vertical, but rather are tilted back slightly. Thus, the facets intersect the cell windows in a larger "V" at the top and a smaller "V" at the bottom. The interference fringes along the grain boundary result from the birefringence of the ice. The spacing of the fringes depends on the grain boundary orientation.

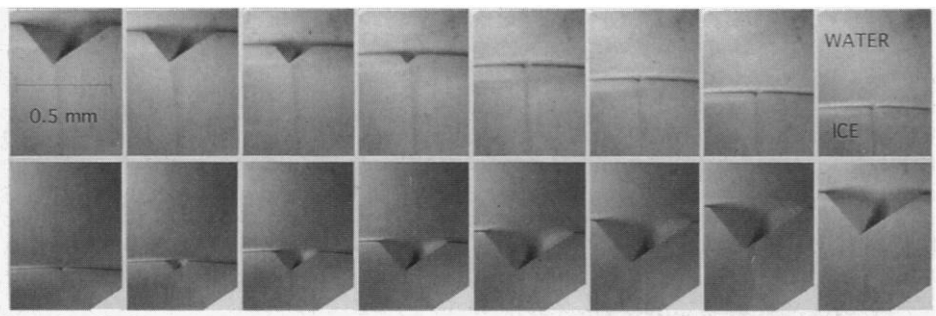
tion because it is always covered by many steps and crevices. Growth on a rough surface proceeds at any undercooling (5).

For ice crystals close to 0°C, the plane normal to the *c* axis (the "basal" plane) is flat and other orientations are rough. Measurements of the ice crystal growth velocity perpendicular to a dislocation-free basal plane were first performed by Hillig (8), who found a form for the growth velocity that was consistent with an activated nucleation process (5, 6). Below a supercooling approximately equal to 0.03°C, he found no measurable growth.

In the present experiment, the 2D nucleation barrier results in the formation of large facets during growth. Suppose that a basal orientation is present on both sides of a grain boundary groove. The coldest temperature of supercooled water adjacent to the facet planes is proportional to the size of the groove and the temperature gradient in the cell (Fig. 2C). Initially, growth can only occur in a direction parallel to the basal planes because the undercooling is too small for nucleated growth. As the ice disk radius increases, the facets grow and the temperature at the intersection of the two planes drops. When the undercooling exceeds the threshold value, crystal growth perpendicular to each facet plane ensues, and the faceted groove progresses with little change of shape or size. The maximum size of the facets corresponds to the undercooling needed for the faceted groove to advance at the same velocity as the ice disk edge. Repeating the experiment for other temperature gradients, we found that the maximum size of the facet depends inversely on the gradient, as expected. Our measurement of the threshold undercooling temperature is in reasonable agreement with that measured by Hillig (8).

Faceting that results from the anisotropic growth of crystals has been studied both experimentally and theoretically in a number of contexts (9). What is distinctive in the present experiment is that the facets evolve from crystal orientations in a grain boundary groove, and once formed, the facets persist indefinitely, even in the absence of further growth of the ice disk. The latter point is a result of a self-limiting aspect to the facet growth: If the ice disk radius is fixed, growth normal to a facet plane (from the adjacent supercooled water) will result in a decrease in the facet size, which in turn reduces the supercooling; when the supercooling drops below the threshold value, the facets will cease to shrink (Fig. 3).

The 2D nucleation on facets may be heterogeneous or homogeneous. In contrast to homogeneous nucleation, heterogeneous nucleation occurs preferentially along the boundaries of a flat surface. This results in a decreased nucleation barrier and a reduced threshold undercooling. In Hillig's experiment, he concluded that the nucleation was homogeneous because the growth rates were not affected by the foreign substrate



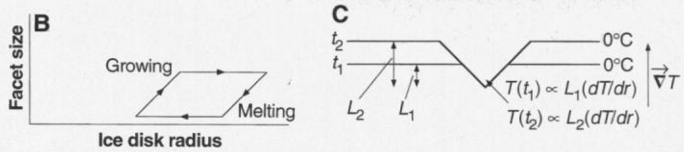


Fig. 2. (**A**) Sequence showing the evolution of the facets as the ice disk melts (top) and grows (bottom). The elapsed time for each series was 1 hour. (**B**) Diagram of the hysteresis in facet size. (**C**) Evolution of facets. A cross section of the disk is shown at times t_1 and t_2. The temperature at the ice disk edge is pinned to 0°C. For a constant radial temperature gradient in the ice near the edge, the temperature at the vertex decreases as the facets grow.

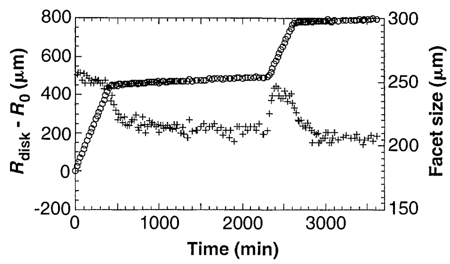


Fig. 3. Facet size (crosses) and ice radius (circles) plotted versus time. Initially, the temperature is ramped so that the facets and ice disk edge advance in unison. During this stage the supercooling (and corresponding facet size) is slightly larger than the threshold value. When the temperature is held fixed, the ice disk edge becomes nearly stationary, and the facets relax to a smaller size, which effectively "shuts off" further relaxation. (This sequence is subsequently repeated.) The ice radius at the start of the run R_0 ≈ 0.6 cm.

(glass) that formed the perimeter of the basal plane. Our geometry differs from Hillig's in that each facet is bounded by both a foreign material (the cell windows) and the other facet. This geometry allows us to measure the relative growth velocity of the two facet planes. The maximum undercooling is the same for both faces. The ratio of the velocities of the two faces determines the direction of advance of their intersection. If the velocity v of each face is given by an independent nucleation process, then this ratio will be given by (*10*)

$$\frac{v_1}{v_2} \propto e^{-(\alpha_1 - \alpha_2)/\Delta T} \qquad (2)$$

where α_1 and α_2 are related to the nucleation barriers on the individual facet planes. For a homogeneous 2D nucleation process, $v_1 = v_2$, predicting a specific direction for the facet growth. For heterogeneous nucleation, $\alpha_1 \neq \alpha_2$, and as the supercooling is decreased, the velocity of one of the planes would predominate, causing the facets to move in a different, well-defined direction.

When the temperature is ramped quickly, causing the ice perimeter to advance at a high velocity, the facets grow out in a purely radial direction (Fig. 4). This is what might be expected when the growth rate of each facet is limited by the dissipation of latent heat. In the limit of slow growth, we expect the facet growth to be governed by interface processes such as 2D nucleation. On reducing the growth rate, the growth direction changes and approaches a new heading that is rate-independent. Interestingly, this direction is not the one obtained by assuming either homogeneous or heterogeneous nucleation. Consequently, we speculate that the growth process for each plane is not independent of the other, but rather is controlled in some nontrivial way by their common boundary.

The presence of the facets also provides an opportunity to study the relaxation of twist along grain boundaries. As the ice interface grows out, the grain boundary orientation at the ice edge is pinned to the line of intersection of the two basal facets. Once formed, however, a grain boundary would like to relax to an orientation that minimizes its free energy. In the absence of any anisotropy in the interfacial energies, the minimum energy orientation would be vertical (perpendicular to the plane of the ice disk) because this minimizes the grain boundary area. When anisotropy is included, the grain boundary may prefer some other orientation. In Fig. 1B, the grain boundary has relaxed from the pinned orientation at the edge to a more energetically favored one at smaller radius.

The faceted grooves observed here were not rare examples: typically, 10 to 20% of all grooves were faceted. This percentage is attributed to the cell geometry and the manner in which the ice is nucleated. Nucleation is accomplished by suddenly imposing a sharply lower temperature at the center of the top face of the cell, forcing a temperature gradient normal to the window plane. Initial growth is in the same direction, during which the fastest growing domains may wedge out other orientations. Because ice grows fastest along the a axis, the result is to produce domains with the c axis mostly in the plane of the ice disk.

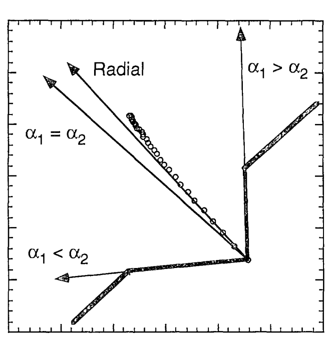


Fig. 4. The position of the vertex (circles) plotted relative to the ice-water interface (bold line) at equally spaced time intervals. The vertex initially grows out quickly in a radial direction but converges to a new direction as the growth slows. Also shown are the theoretical directions for homogeneous nucleation ($\alpha_1 = \alpha_2$) and heterogeneous nucleation ($\alpha_1 \neq \alpha_2$).

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10. We have made an implicit assumption here that the prefactor multiplying the exponential is the same for growth on both faces [(*6*), p. 184]. However, our main point is that we can test the predictions of various models with the experimental technique we describe.
11. We acknowledge many fruitful discussions with J. Wettlaufer and J. Cahn. Supported under National Science Foundation grant DMR-9400637 and Office of Naval Research grant N00014-90-J-1369.

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Partitioning of Tungsten and Molybdenum Between Metallic Liquid and Silicate Melt

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The "excess" of siderophile elements in Earth's mantle is a long-standing problem in understanding the evolution of Earth. Determination of the partitioning behavior of tungsten and molybdenum between liquid metal and silicate melt at high pressure and temperature shows that partition coefficients ($D_{metal/silicate}$) vary by two orders of magnitude depending on whether metal segregated from a basaltic or peridotitic melt. This compositional dependence is likely a response to changes in the degree of polymerization of the silicate melt caused by compositional variations of the network-modifying cations Mg^{2+} and Fe^{2+}. Silicate melt compositional effects on partition coefficients for siderophile elements are potentially more important than the effects of high pressure and temperature.

If core formation in the Earth was a simple equilibrium process whereby metal segregated from silicate, then the abundance of siderophile (metal-seeking) elements retained in the silicate mantle of the Earth should reflect the conditions of equilibrium. On the basis of metal/silicate partitioning data collected at 1 atm and low-temperature conditions (1600 to 1900 K) (*1*, *2*), siderophile elements are overabundant in the Earth's upper mantle by as much as several orders of magnitude (*3*). Recent numerical models of the thermal history of the early Earth that are based on large-impact accretion models (*4*) predict large or wholesale melting of the proto-Earth (*5*, *6*). If