Revealing the Surface Structure of Hexagonal Ice through Polymer Etching

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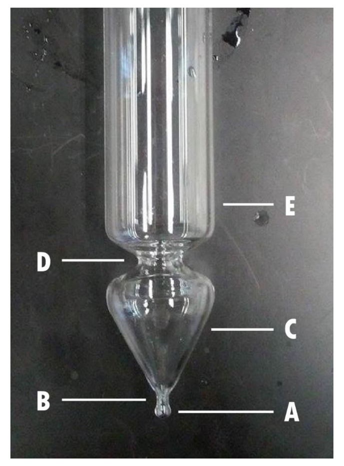
Single-Crystal Ice

The ability to grow large single-crystal hexagonal ice is crucial to the study of hydrogen-bonding at the ice surface and at interfaces.

Growth

The growth process employs a modified Bridgeman-Stockbarger apparatus; a crucible is lowered into a bath whose temperature ranges from roughly 3 °C at the surface to -3 °C at the deepest point.

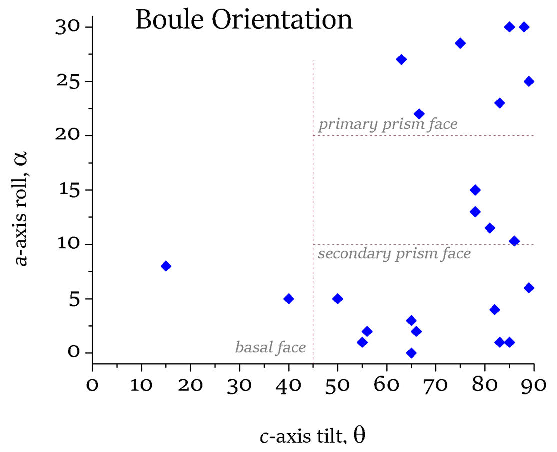


Ice is grown from the melt by seeding growth with a polycrystalline seed in (A). The shape of the crucible bulb (B, C) invokes competitive growth, whereby the most stable face seeds a larger and larger portion of the advancing front. Less stable faces are eliminated, leaving only one, single-crystal domain (D, E).

Face Stability

Since single-crystal growth is a competitive process through which the most stable face emerges victorious, we can determine the most stable face by quantifying which face appears the most frequently.

In general, the basal face is very rarely seen. The secondary prism face is the most frequent, followed by the primary prism face.



Basal face: $\theta \leq 45°$
Primary prism face: $20° \leq \alpha \leq 30°$
Secondary prism face: $0° \leq \alpha \leq 10°$

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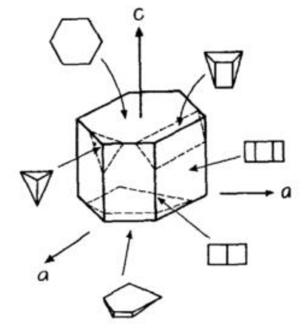
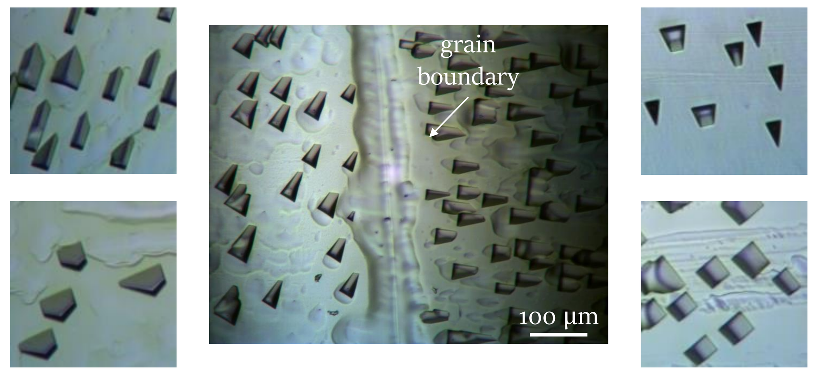
Etching

Formvar® etching provides a way to reveal the crystal structure hidden within the boule. Each etch pit corresponds to a unique orientation of the crystal lattice; this qualitative relationship has been known and used to study ice for over 50 years.

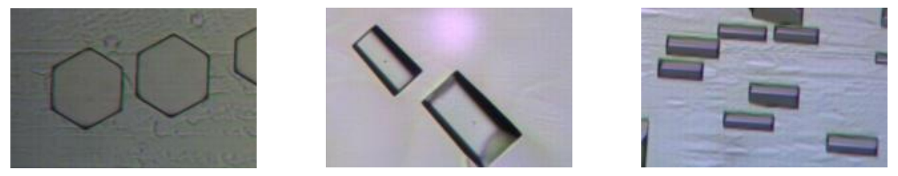


Right: Higuchi, K. *Acta Metallurgica*, **1958**, *6*, 636.

A variety of different etch pits can be seen, as well as grain boundaries that separate single-crystal domains.



Most importantly, the basal, primary prism, and secondary prism faces can be visualized using this etching technique.



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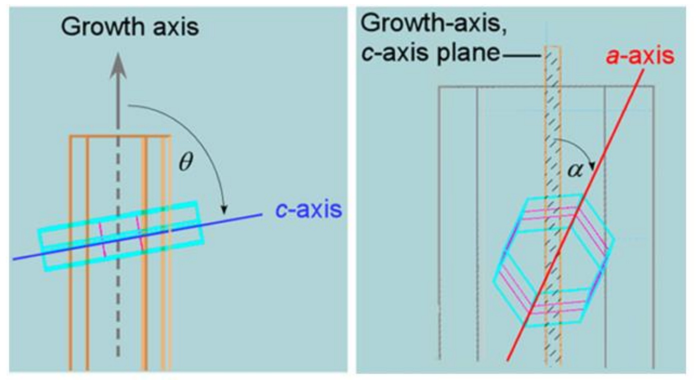
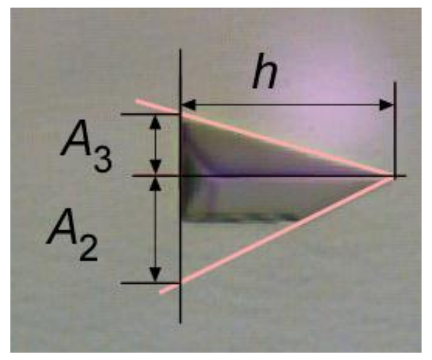
Precise Orientation

The orientation of the crystal lattice within an ice sample can be specified using just two angles: the *c*-axis tilt, θ, and the *a*-axis roll, α.



The *c*-axis tilt is the angle between the *c*-axis and the surface normal, ranging from 0° to 90°; the *a*-axis roll is the angle between the *a*-axis and the line formed at the intersection of the surface-normal plane with the basal face and ranges from $-30°$ to $+30°$.



These two angles can be calculated from cross-section etch pit analysis. By tracing the triangle formed by extension of the primary prism face edges of a pit, two parameters A_2 and A_3 can be specified. h is simply the height of the triangle.

This gives rise to the following formulas for θ and α, where $b = \tan 60°$ and $R = A_2/A_3$:

$$\alpha = \tan^{-1}\left[\frac{(b^2+1)(R+1) \pm \sqrt{(b^2+1)^2(R+1)^2 - 4(R-1)^2 b^2}}{2b(R-1)}\right]$$

$$\theta = \cos^{-1}\left[\frac{(A_2+A_3)/h}{\tan(60°+\alpha)+\tan(60°-\alpha)}\right]$$

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Cutting a Selected Face

The angles θ and α specify the position of the crystal lattice with respect to the ice boule. Therefore, they can be used to locate any desired face. In particular, the three major faces can be cut with ease.

The laboratory axes X, Y, and Z are specified: X–Z is the cutting plane, where Z is the cutting axis. The boule axes x and y are coincident with the laboratory axes X and Y, while the boule axis z corresponds exactly to the axis of the cylindrical boule.

Prism Faces

The prism faces require a rotation of η about the X-axis and of ξ about the Z-axis, where

$$\eta = 180° + \tan^{-1}\left[-\frac{\tan(\alpha+\gamma)}{\cos\theta}\right]$$

$$\xi = \tan^{-1}[\cos\eta\tan\theta]$$

γ is defined as 0 for a secondary prism face and as $\pm 30°$ for a primary prism face, with $\alpha < 0$ or $\alpha > 0$, respectively.

Basal Face

The basal face requires a rotation about the X-axis by $90° - \theta$.

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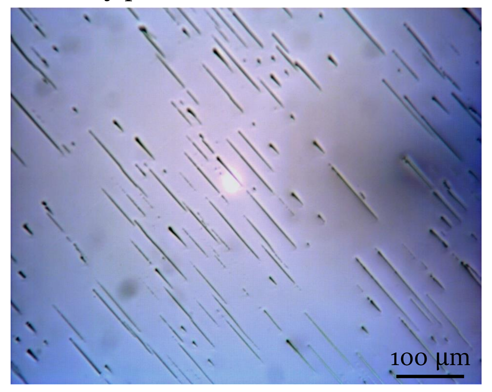
Surface Features

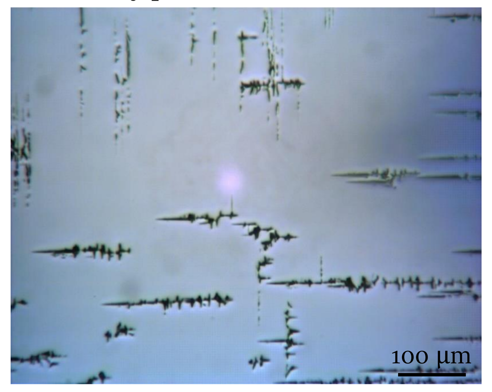
Recently, samples were left to self-anneal over the course of multiple days at -18 °C prior to etching. Contrary to the flat surfaces that were expected as a result of self-annealing, irregularities appeared on the surface of the ice.

Prism Faces

Primary prism face:



Secondary prism face:



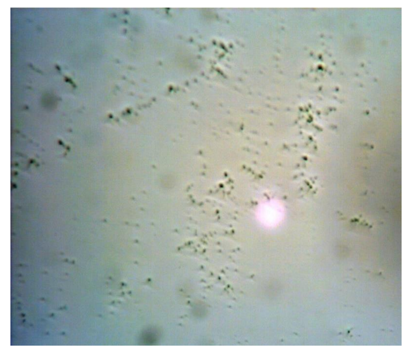
The lines that are visible are believed to correspond to a decrease in elevation on the surface. Each terrace is terminated by a specific face, which is thus exposed along the drop-off to the terrace beneath it.

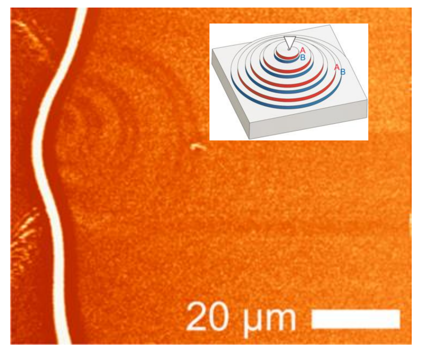
For the primary prism face, this likely corresponds to the lines being viewed along a vertical exposed basal face. The secondary prism face displays two sets of perpendicular cuts; one set corresponds to a termination by the basal face, and the other to a termination by the primary prism face.

Work to confirm this will be done this year for my Senior Honors Thesis, using differential interference contrast microscopy (DIM).

Basal Face

The basal face had circular indentations around which etch pits were observed to form. It is possible that the defects seen were an example of previously reported work: Sazaki *et al.* have studied spiral growth on the basal face that originates at an induced screw dislocation.

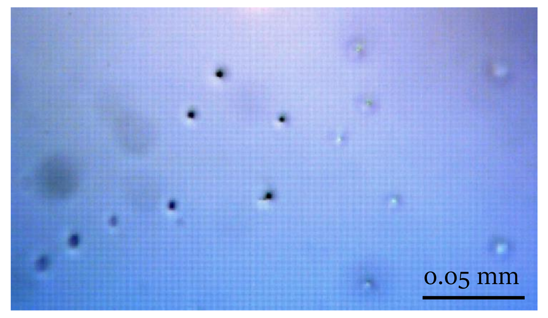


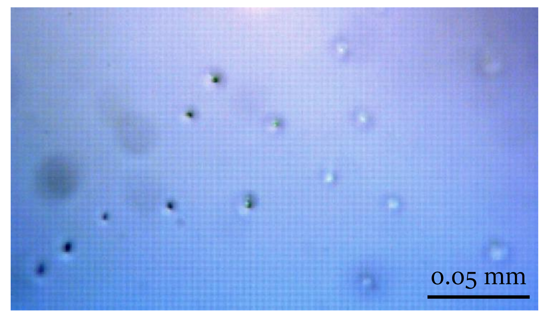


Right: Sazaki, G., et al. *Cryst. Growth Des.* **2014**, *14*, 2133.

Heated Self-Anneal

When a primary prism face sample was allowed to self-anneal for an extended period of time at -5 °C, indentations in the surface were observed. These marks were mobile and were seen to travel along the surface in varied directions.



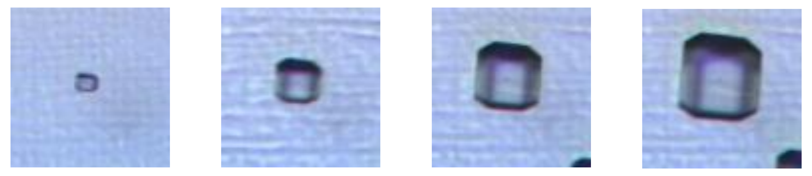


All of the dots in the photos above were seen to travel in photos taken at 2 minute time interval. Here, the second photo shown was taken 8 minutes after the first.

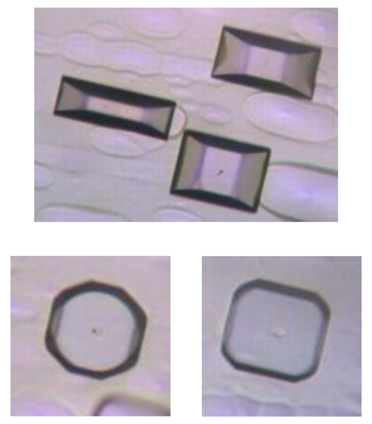
The mobility of these marks are a demonstration of the quasi-liquid layer that is present at -5 °C. Temperatures as cold as -18 °C do not display this feature, and thus the indentations present at -18 °C were stationary features.

High Index Faces

Surprisingly, on a perfect primary prism face cut, the etch pits that form are not just the rectangular pits that are characteristic of the primary prism face. As each pit grows, subtle, rounded edges develop into refined, higher index faces.

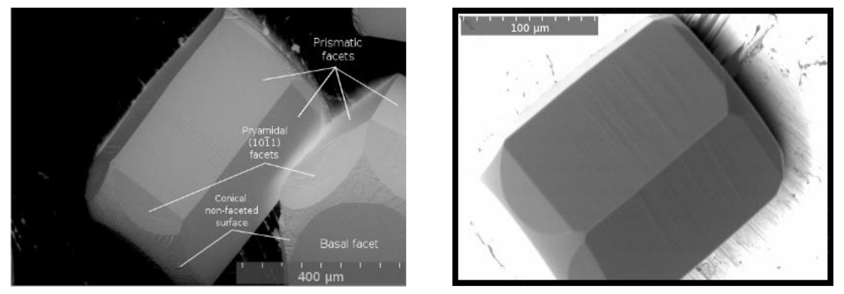


Some pits retain their rectangular shape while displaying a larger number of shaded areas, granting visibility into other faces as the pit grows.



Other pits are octagonal, indicating that higher index faces are appearing, smoothing the transition from the primary prism face to the basal face.

There is precedence for high index faces: in 2010, Pfalzgraff *et al.* published reports of the $\{10\bar{1}1\}$ and $\{20\bar{2}1\}$ faces in growing and ablating crystals, the former of which was confirmed via molecular dynamics simulations.



Pfalzgraff, W. C., Hulscher, R. M., and Neshyba, S. P. *Atom. Chem. Phys.*, **2010**, *10*, 2927.

Acknowledgements

References

1. Shultz, M. J., Bisson, P. J., and Brumberg, A. *J. Phys. Chem. B*, **2014**, *118* (28), 7972.
2. Shultz, M. J., Brumberg, A., Bisson, P. J., and Shultz, R. Accepted to *PNAS*, October 2015.

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