

CRYSTAL GROWTH – FAST AND SLOW

Peter J. Heaney

Department of Geosciences
Princeton University
Princeton, NJ 08544
peter@geo.princeton.edu

Background

Mineral shapes and sizes are spectacularly diverse, and the means by which depositional environments control crystal morphologies remains an exciting area of research. Some minerals never achieve crystal sizes beyond a micron (e.g., kaolinite, many Mn oxides), whereas others can grow as single crystals that weigh several tons and extend many meters from tip to toe (e.g., quartz, feldspar). Likewise, some minerals nearly always exhibit the same habit (e.g., the micas), while 300 different forms have been described for calcite alone.

Most minerals show some variability in the habits they adopt, though sometimes the forms that have developed are hard to discern in natural rocks. In many slow-cooling igneous melts, for example, emergent nuclei crowd each other to the point that no single crystal can evolve a euhedral morphology; in the resulting cumulate textures, minerals are space-filling and can exhibit curvaceous boundaries. Even when parent rocks contain minerals with fully formed faces, erosive processes can erase the original morphology as minerals are recast in sedimentary deposits.

Fortunately for the highly tuned esthetic sense of every mineralogist, many minerals do manage to attain ideal forms. Euhedral crystals are particularly common within rock cavities that have been flushed with supersaturated solutions or vapors. Geodes containing large, prismatic quartz crystals are a well-known example. Similarly, well-developed faces characterize phenocrysts that grow slowly within volcanic magma chambers. The high-temperature annealing that accompanies regional metamorphism can lead to the formation of distinct faces on pre-existing minerals, and the cementation that follows the percolation of fluids through sedimentary rocks can sharpen the boundaries of quartz and calcite grains.

An enormous number of variables will constrain the shape of a growing crystal. Important factors include:

- 1) the temperature and pressure profile of the system;
- 2) the chemistry and structure of the mother phase (vapor, solution, or melt);
- 3) chemical and heat transport properties of the crystal and the mother phase;
- 4) the lattice symmetry of the crystal;
- 5) the surface structure of a given $\{hkl\}$ face; and
- 6) the presence of defects on the growing face.

Transport characteristics of the crystal and the solution are in turn influenced by the density, viscosity, and flow velocity of the parent solution, the growth rate of the crystal face, the area of the solid-solution interface, and the thickness of the boundary layer.

For this laboratory, we will observe directly the role that the rate of crystallization plays in directing crystal shape. If we could perform this laboratory over geological time scales, we might attempt to duplicate the precipitation of common silicates from low-temperature fluids, as occurs in sedimentary environments. But we have only three hours, so we will work with materials that emulate natural crystal growth processes. In the first set of experiments, we will mix solutions from which euhedral crystals grow over one to two weeks. For the second set of experiments, we will observe disequilibrium crystallization over time scales of seconds.

Warnings

- 1) Some of the chemicals used in the slow and fast growth experiments are toxic. Despite their pretty colors, none should be eaten, and hands should be washed following the lab. Likewise, tetrahydrofuran (THF) is an ether and should only be used in well-ventilated areas away from flames or high heat.
- 2) Liquid nitrogen can cause frostbite. Care should be taken to prevent splashing when pouring.

Slow Growth Experiments

Materials for each team of 2 to 3 people:

400-ml beaker
Water (distilled if you have it)
Stirring rod
Weighing paper
Balance
Hot Plate
Thread
Kimwipe & Rubberband

Compounds (Do not eat):

- | | |
|--|--|
| 1) NaCl
Sodium chloride
Halite | 5) $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$
Potassium sodium tartrate hydrate
Rochelle salt |
| 2) $\text{K}_3\text{Fe}(\text{CN})_6$
Potassium ferricyanide
Red prussiate of potash | 6) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Sucrose
Table sugar |
| 3) NaNO_3
Sodium nitrate
Nitratite | 7) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
Alum |
| 4) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
Cupric acetate monohydrate | |

General Procedure

You will create supersaturated solutions by adding the powdered compounds to water in ratios specified below. The solutions will be heated and stirred until the solids have dissolved, and then the liquids will be allowed to cool to room temperature. If seed crystals are available, they can be secured by a thread in a slip knot and suspended in the solution from a stirring rod or pencil lying across the mouth of the beaker. A kimwipe should be placed over the top of the beaker and fastened with a rubber band to keep out dust. Solutions will be monitored over the next two weeks for crystal growth during solvent evaporation.

<u>Compound</u>	<u>Add to 200 cc H₂O</u>
1) NaCl	100 gm
Halite	
2) K ₃ Fe(CN) ₆	93 gm
Potassium ferricyanide	
3) NaNO ₃	110 gm
Sodium nitrate	
4) Cu(CH ₃ COO) ₂ · H ₂ O.....	20 gm
Cupric acetate	
5) KNaC ₄ H ₄ O ₆ · 4H ₂ O.....	260 gm
Rochelle salt	
6) C ₁₂ H ₂₂ O ₁₁	460 gm
Sucrose	
7) KAl(SO ₄) ₂ · 12H ₂ O.....	40 gm
Alum	

Questions -- Slow Growth Experiments

- 1) Many cubic materials (such as halite and galena) precipitate as cubic crystals, with {100} as the dominant family of faces. The vectors from the center of the cube to the 8 apices of the cube are normal to the {111} faces. What does this observation suggest about the growth rates of the {100} faces in comparison with the growth rates of the {111} faces? In general, do the best developed faces of a crystal grow more rapidly or less rapidly than the other faces? (Hint: The correct answer is counter-intuitive for most people.)
- 2) What are hopper crystals? Based on your answers to Question 1, how might you explain the development of these peculiar crystal morphologies?
- 3) Despite the complexity of the crystal growth process, a simple rule formulated by Auguste Bravais in 1860 successfully predicts crystal shapes based only on the translational lattice symmetry of the structure. A modern statement of that law (Zoltai and Stout, 1984) is as follows: *The rate at which a crystal face {hkl} grows is inversely proportional to the interplanar spacing d_{hkl} corresponding to that face.*

Does the prominence of the {100} family of faces for many cubic materials obey this law? Why or why not?

4) Based on Bravais's law, what is the most prominent face expected for:

- a) Galena (cubic: $a = 5.94 \text{ \AA}$)
- b) Almandine (cubic: $a = 11.53 \text{ \AA}$)
- c) Muscovite (monoclinic: $a = 5.19 \text{ \AA}$, $b = 9.04 \text{ \AA}$, $c = 20.08$, $\beta = 95.5^\circ$)?
- d) Zircon (tetragonal: $a = 6.60 \text{ \AA}$, $c = 5.98 \text{ \AA}$)?
- e) Quartz (hexagonal: $a = 4.91 \text{ \AA}$, $c = 5.41 \text{ \AA}$)?

According to Klein and Hurlbut, which faces are commonly observed in natural crystals of these minerals? Does Bravais's law successfully predict the shapes for all crystals?

5) Bravais's law may be rationalized in the following manner: The growth of a given crystal face is accomplished by the addition of individual unit cells to that face. The larger the area of attachment of a single unit cell, the stronger that attachment will be. The stronger the attachment, the faster the growth of that face.

All primitive unit cells for a given lattice must have the same volume. If A_{hkl} represents the area of an hkl face for a primitive cell, and d_{hkl} represents the interplanar hkl spacing, what is the volume for that unit cell?

Does d_{hkl} vary directly or inversely with A_{hkl} ?

By this logic, can you explain the basis for Bravais's law?

6) The equilibrium crystal shape for a mineral obeys the point group symmetry that characterizes the mineral. The space group symmetries for the crystals grown in these experiments are as follows:

<u>Compound</u>	<u>Space Group</u>
Halite	$Fm\bar{3}m$
Potassium Ferricyanide	$P2_1/c$
Sodium Nitrate	$R\bar{3}c$
Cupric Acetate	$A2/a$
Rochelle Salt	$P2_12_12$
Sucrose	$P2_1$

What are the crystal classes associated with these space groups (see Table 3.5 in Klein and Hurlbut)? Using this information, list the sets of ideal forms that might be expected for each compound.

7) One theory that attempts to incorporate the effects of atomic structure in crystal growth processes is called the periodic bond chain (PBC) theory. Many materials contain chains of atoms that are linked by strong chemical bonds. Silicates typically contain these chains as networks of silica tetrahedra. When atoms attach to a growing crystal so as to extend the chain, the attachment is strong and the growth in that direction is fast.

What is the expected morphology for a crystal built of linear tetrahedral chains aligned parallel to c ? What are the typical habits of pyroxene and amphibole? Based on PBC theory, what is the expected shape of quartz crystals? How can PBC theory be used to explain the platy habit of mica?

Fast-Growth Experiments

Materials: Binocular microscope
(For each person) Petri dish (5 cm diameter)
2 glass microscope slides (3" x 1")
2 cover slips (24 x 40 mm)
2 medium (No. 50 or No. 20) binder clips
Pipette
2 2" x 2" sheets polarizing film (size is not critical)
Styrofoam cup

Chemicals: Tetrahydrofuran (THF)
Liquid Nitrogen
Copper Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (optional)
Methanol (optional)

General Procedure

A stock solution for these experiments is prepared by mixing pure THF with water in a ratio of 1.5 : 1 by volume. Once this THF solution is mixed, 2 or 3 drops should be placed in the center of a microscope slide. A glass cover slip is then placed at each end of the slide. The cover slips should not touch or interfere with the THF solution; they serve merely as spacers. The second glass slide is placed over this assemblage and is clamped into place with a binder clip at each end of the sandwich. Ideally, the THF solution forms a thin film in the center of the assemblage.

A petri dish is placed under the binocular scope, and liquid nitrogen is poured from a styrofoam cup into the petri dish. The THF assemblage then is placed above the boiling nitrogen on the petri dish. The student should focus the binocular scope on the solution and observe the crystallization of the THF.

(Optional for those with no hope of obtaining liquid nitrogen) A cupric chloride solution can be made by scooping a few grams of CuCl_2 into 100 ml of methanol (exact amounts are not important). A few drops of this solution may be placed on a glass slide, and rapid crystal growth may be observed by binocular or petrographic microscopes as the alcohol solution evaporates.

Questions -- Fast Growth Experiments

- 1) Once crystallization begins, do the crystals grow rapidly or slowly? Do the crystals advance haltingly, or at a constant velocity, or does velocity increase as the crystals grow larger?
- 2) At equilibrium conditions, this THF solution crystallizes at 2°C . The temperature of boiling liquid nitrogen is 77 K. Do you think that crystals start to form exactly when your solution reaches 2°C or when the temperature is considerably lower? Why might a solution require a large degree of undercooling to initiate crystal growth? Do you suppose that the reverse process of melting requires a similar degree of overheating before liquid appears? Why not?

- 3) Draw the textures produced by your crystallized solution of THF. These crystal shapes are called dendrites, based on their branching morphology (the Greek root means tree-like). In what natural settings have you observed dendritic crystals?
- 4) Dendritic crystallization can occur when a very steep temperature gradient exists across the crystal-solution interface. In other words, the temperature of the solution decreases rapidly away from the crystal face. A steep gradient is typical of strongly undercooled disequilibrium conditions. If a crystalline protrusion appears on an otherwise smooth crystal face, why might a steeply dipping temperature gradient promote the growth of that bump?
- 5) Will the tendency for a material to crystallize with dendritic morphologies increase or decrease with:
 - a) Steeper temperature gradients between the solid and the liquid?
 - b) Higher latent heats of crystallization (the heat energy produced by the process of solidification)?
 - c) Higher thermal diffusivities for the solid and the liquid (i.e., the ability of the solid and liquid to transport latent heat away)?
 - d) Higher heat capacities for the solid and liquid?
 - e) Increasing impurity concentration at the solid-liquid interface?
- 6) Place the frozen THF assemblage between cross-polarized films. Does any light pass through the crystals? What does this tell you about the symmetry of the crystals? These structures are called clathrates, which are structurally similar to zeolite. At the bottom of the ocean, clathrate structures that consist of an H₂O framework encaging methane molecules are quite common.
- 7) Allow the THF crystals to melt. Disassemble the slides. Wipe off the THF solution, and place 2 to 3 drops of pure water on the slide. Reassemble as before and place over liquid nitrogen. How does the crystallization of ice-I differ from that of the THF clathrate?
- 8) Place the frozen water between crossed polarizing film. Does light shine through? What does this result tell you about the symmetry of ice-I? Is the structure of ice-I the same as the structure of THF clathrate?

(Optional for those working with cupric chloride)

- 9) What is the shape of the crystals that form upon evaporation of the solvent? Are individual crystals isolated, or do they occur as clusters? What is the geometric shape of the clusters?
- 10) Acicular (needle-like) crystal growth is strongly analogous to dendritic growth. Filamentous THF crystals grow from solutions undercooled using liquid nitrogen, and the THF solutions are characterized by strong temperature gradients due to the proximity of liquid nitrogen. Acicular CuCl₂ crystals grow from evaporating solutions at constant temperature, but disequilibrium of another sort promotes fibrous crystal growth. What kind of gradient develops around an emerging crystal in an evaporating solution? Does the gradient become steeper or more shallow with increased evaporation of the solvent? Why might the growth of a protuberance on a smooth crystal face be accelerated under these conditions? Using these ideas, can you provide a general explanation for acicular growth from an evaporating solution?

References

- Arend, H. and Hulliger, J., Eds. (1989) *Crystal Growth in Science and Technology*. Plenum Press, New York. (A collection of articles drawn from a NATO symposium. The treatment is highly quantitative, and the readability is variable.)
- Bentley, W.A. and Humphreys, W.J. (1931) *Snow Crystals*. Dover, New York. (Dover has reproduced the original manuscript with 2,453 photographs of snow crystals for only \$15.)
- Holden, A. and Morrison, P. (1989) *Crystals and Crystal Growing*. MIT Press, Cambridge, MA. (Simple discussions of crystallography aimed at the informed lay reader with lots of recipes for crystal growth.)
- Klein, C. and Hurlbut, C.S. Jr (1993) *Manual of Mineralogy*, 21st edition. John Wiley and Sons, New York. (Chapter 2 contains an in-depth and well-illustrated discussion of crystal forms and their relation to the crystal classes.)
- Langer, J.S. (1989) Dendrites, viscous fingers, and the theory of pattern formation. *Science*, 1150-1156. (An advanced review of mathematical models of dendrite formation.)
- Smelik, E.A. and King, H.E., Jr. (1997) Crystal-growth studies of natural gas clathrate hydrates using a pressurized optical cell. *American Mineralogist*, 82, 88-98. (A recent article that describes the equilibrium growth forms for clathrate hydrates and the design for a cooling stage on a petrographic microscope.)
- Zoltai, T. and Stout, J.H. (1984) *Mineralogy: Principles and Concepts*. Burgess Publishing Co., Minneapolis. (Chapter 7 contains the nicest discussion of crystal growth processes among the general mineralogy texts.)

where T_M is the melting temperature, T_∞ is the temperature of the fluid at an infinite distance from the crystal surface, L is the latent heat, and c is the specific heat of the fluid. Higher latent heats will raise the temperature of the fluid at the interface and thus decrease the amount of undercooling. However, latent heat must be normalized by c , the degree to which the temperature of the fluid will increase in response to the heat absorbed. The higher the heat capacity, the smaller the change in temperature for a given latent heat, and the more likely that a steep temperature gradient will be maintained. Similarly, steep temperature gradients are difficult to maintain when thermal diffusivities are high. The presence of impurities often serves to lower thermal diffusivities by acting as an energy sink or barrier, and thus impurities can help maintain a disequilibrium thermal profile near the surface.

In summary, the tendency for dendritic crystallization:

- a) Increases with steeper temperature gradients;
 - b) Decreases with higher latent heats;
 - c) Decreases with higher thermal diffusivities;
 - d) Increases with higher heat capacities;
 - e) Increases with higher impurity contents.
-
- 6) The THF clathrate hydrates are cubic and isotropic, and no light passes through cross polars.
 - 7) Although H_2O obviously can form beautiful dendrites in snowflakes and rime frost, in my experience the crystallization of ice in this experiment produces a cumulate texture.
 - 8) As ice-I is isostructural with tridymite, its symmetry is hexagonal and its optical character anisotropic. Birefringent colors should be apparent in cross-polarized light.
 - 9) Cupric chloride crystals typically grow as acicular crystals within spherulitic clusters. In contrast to the dendrites observed with THF clathrate hydrates, these cupric chloride crystals rarely exhibit secondary and higher level branching.
 - 10) Whereas undercooling can lead to steep thermal gradients near the crystal-liquid interface, evaporation can lead to solutions that are extremely supersaturated, and steep compositional gradients develop near the interface. Adsorption on the crystal surface leads to a local depletion of solute, but concentrations rise sharply with greater distance from the surface. A small protuberance will come in contact with solute-rich regions and continue its growth, setting up a positive feedback dynamic that is analogous to dendritic growth in undercooled conditions.

Acknowledgments

I am indebted to Eugene Smelik, who suggested the use of THF solution for the fast growth exercises, and to Douglas Yates, who helped design the fast growth experiments. Thanks also go to Dexter Perkins, Michael Velbel, and Ken Windom for their thoughtful suggestions for improving this lab.