

## CRYSTAL GROWTH – FAST AND SLOW

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### 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<br>Sodium chloride<br>Halite   | 5) $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$<br>Potassium sodium tartrate hydrate<br>Rochelle salt |
| 2) $\text{K}_3\text{Fe}(\text{CN})_6$<br>Potassium ferricyanide<br>Red prussiate of potash     | 6) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$<br>Sucrose<br>Table sugar   |
| 3) $\text{NaNO}_3$<br>Sodium nitrate<br>Nitratite  | 7) $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$<br>Alum  |
| 4) $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$<br>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 H<sub>2</sub>O</u>
1) NaCl .....	100 gm
Halite	
2) K <sub>3</sub> Fe(CN) <sub>6</sub> .....	93 gm
Potassium ferricyanide	
3) NaNO <sub>3</sub> .....	110 gm
Sodium nitrate	
4) Cu(CH <sub>3</sub> COO) <sub>2</sub> · H <sub>2</sub> O.....	20 gm
Cupric acetate	
5) KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O.....	260 gm
Rochelle salt	
6) C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .....	460 gm
Sucrose	
7) KAl(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> 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<sub>hkl</sub> 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  $\text{CuCl}_2$  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  $2^\circ\text{C}$ . The temperature of boiling liquid nitrogen is 77 K. Do you think that crystals start to form exactly when your solution reaches  $2^\circ\text{C}$  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 H<sub>2</sub>O 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 CuCl<sub>2</sub> 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

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