

Classroom Index-Card Simulations of Crystal Growth

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ABSTRACT

Using colored index cards as the “building blocks” of two-dimensional “crystals,” students assemble crystals under several sets of instructor-designated conditions of time and geometry. After each simulation, the size and the number of crystals of different sizes are tallied. When all simulations are complete, data from the multiple simulations are compared. At the simplest level, results can be interpreted in terms of cooling- or quenching-time/crystal-size relations commonly introduced in introductory geology. At a higher level, the different conditions of the simulations are examined as analogs for transport and reaction processes operating during crystal growth. Once the basic processes have been illustrated (by analogy) and classified, a framework has been established within which instructors can examine individual transport and reaction processes in more detail.

Keywords: Education – geoscience; education – undergraduate; geochemistry; mineralogy and crystallography.

OBJECTIVES

The purpose of this exercise is to get students to think about the basic physical and chemical processes operating during crystal growth. The exercise can be condensed to emphasize cooling-time/crystal-size relations at the introductory level, or it can be used in a slightly more extensive form to introduce more advanced concepts of transport and reaction processes in crystal growth and geochemical kinetics, in the context of mineralogy, geochemistry, or petrology classes.

Most discussions of morphological crystallography begin with the historical observation that a given crystalline substance can exhibit a range of crystal shapes, all of which can be created by different arrangements of identical three-dimensional “building blocks.” These “building blocks” embody the essential geometric, dimensional (that is, axial ratios), and symmetry characteristics of the crystals. The “building blocks” are in some ways the forerunners of the concept of the unit cell. Many introductions to crystal growth take advantage of this simple geometric understanding of crystal form.

Crystal growth is exceptionally complex; specific atoms, ions, ion groups (“radicals”), or molecules must arrive at the crystal surface and be attached in their proper positions. Fully describing such dynamic chemical processes at the atomic/ionic scale for compounds as structurally and stoichiometrically complex as most minerals is still at the limits of the computational

capacity of large supercomputers. Even then, only extremely small, simplified pieces of the overall crystal structure can be modeled. However, geometric descriptions of crystal-growth processes commonly begin using simple geometric “building blocks” identical with those used in elementary morphological crystallography, and these simplifications, while not describing the growth phenomena in chemical terms, are surprisingly successful at describing the geometry of growing crystals. The exercise described here builds on this geometric approach to crystal growth, using simple two-dimensional “building blocks” (index cards) to demonstrate a few very basic aspects of how reaction and transport processes, and the time-scales over which they operate, affect crystal growth.

CRYSTAL GROWTH “SIMULATIONS”: MATERIALS AND METHODS

Three-by-five-inch index cards in three different colors (for example, red, green, and blue) are distributed to the students, so that each student has one card and about one-third of the class has each color (in smaller classes, each student might receive two cards of different colors). The cards are the “building blocks” of model crystals; collectively, the students represent a cooling magma (or an evaporating aqueous solution). Students might be asked to write mineral names on the cards (for example, red = feldspar, green = pyroxene, blue = oxides, and so forth), to strengthen the connection between the resulting assemblage of different-colored “mineral crystals” and the rocks the exercise is intended to simulate. The object is for the students to assemble the cards on desktops, benchtops, or some other flat surface to make two-dimensional “crystals.” The model crystals are an orderly rectangular lattice, made by matching corresponding edges of index cards of the same color (for example, red with red, and so forth). The greater the number of cards joined together, the larger the crystal. Crystallization starts and stops on the instructor’s command.

The instructor supervises at least the first two (if desired, all three) of the following simulations:

- 1) The instructor signals the start of the simulation. Students move about the room, looking for others with cards of matching color. Orderly “crystals” are assembled wherever students find like-colored cards. The instructor allows sufficient time for a few students to assemble their cards into crystals consisting of a small number of cards, then gives the signal to stop, allowing only a few seconds for crystal growth. The class counts the number and

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size of (number of cards in) the crystals, and the instructor tallies the results on an overhead or blackboard, as shown in Table 1. When the tally is complete, all students retrieve the number of cards they started with and return to their seats. This short simulation should result in many small crystals.

- 2) Repeat the procedure described for the first simulation, but allow more time. After tallying, students retrieve cards and return to their seats. In comparison to the first simulation, this longer simulation should result in a few large crystals (Table 1).
- 3) Have students tear each card into two to three irregular pieces and throw them into the air. Then students pick up the same number of pieces they created but not necessarily their own. Repeat the assembly, but require simple geometric crystals (perfect fits between torn edges, so that perfect index-card outlines result). Tally the results. Depending on how thoroughly the students subdivide the cards, the time required to assemble orderly "crystals" may be prohibitive, and this simulation can be terminated before any "crystals" are successfully assembled (Table 1).

INTERPRETING THE RESULTS OF THE SIMULATIONS

Once order is restored, the instructor can begin asking the students leading questions about relative rates at which the index-card "crystals" grew, to set up interpretation of the results.

General questions:

Which of the first two simulations "models" the process of rapid cooling (quenching) of the "magma" (or rapid evaporation of the solution)?

What steps or processes must the cards proceed through from the beginning of the simulation to the completion of each "crystallization" simulation?

For each of the three simulations: Which step or process is rate-determining, that is, determines the overall rate at which "crystals" grow? (The answer is not the same for all simulations. Which one is different?)

What is the relation of that step or process to other steps or processes in the simulation?

More specific questions:

Do the transport and reaction steps have to follow one another, or can they happen simultaneously?

In the first two simulations (intact index cards), was arranging them fast or slow compared with transporting them together?

In the last (ripped-up-cards) simulation, was arranging them fast or slow compared with transporting them together?

I have used this exercise as a vehicle to discuss several principles of crystal growth and geochemical kinetics, including the effect of cooling time on the size and number of crystals, the operation of transport

Size (# cards)	1	2	3	4	5	6	7
Simulation #1 – Short simulation time (fast crystal growth)							
Red		1	1	2	1		
Green	1	1	2				
Blue		3	2		2		
Simulation #2 – Long simulation time (slow crystal growth)							
Red					2		1
Green				1		1	
Blue					1	1	1
Simulation #3 – Torn-up cards							
Any color		No completed crystals					

Table 1. Sample data from index-card simulation of crystal growth: ~36 cards.

and reaction processes during crystallization, series and parallel reactions and processes, rate-determining steps and processes in series and parallel, and classification of reactions in terms of the rate-determining step. Several important aspects of crystal-growth kinetics illuminated by these discussions are summarized in the following sections.

Transport and Reaction

The first two simulations can be interpreted in terms of how fast the simulated magmatic system cools (time from onset of crystallization to quenching; "cooling rate" sensu lato), transport processes, and crystal growth. The first question pertains to the first two simulations only: Which of the first two simulations "models" the process of rapid cooling of the "magma"? Students can be queried about what the duration of each simulation signifies in terms of the time available for crystallization in the simulated "magma." Usually, someone quickly recognizes that the duration of the time interval between the start and end of crystallization is inversely proportional to the "cooling rate" in the broad sense. Simulation #1, which allows a short time for crystallization, corresponds to a system quickly cooled to the temperature at which crystallization ceases, and simulation #2 (long time) corresponds to slow cooling. At the introductory level, this illustrates how the time available for cooling can affect the size and number of crystals: Rapid cooling gives rise to a large number of smaller crystals, whereas slow cooling gives rise to a smaller number of larger crystals (Table 1). This level of the exercise may be sufficient for introductory-level classes and classes for non-science majors.

Students might then be asked to list the steps involved in producing a model "crystal" from our model "fluid." At a more advanced level, the first two simulations illustrate the importance of transport processes in crystal growth. The reactants must be transported to a reaction site and must be assembled into an orderly pattern there. In the first two simulations,

getting the reactants into proximity to one another is the hard part. Transport is rate determining, and the rate of transport relative to the amount of time available determines the number and size of crystals.

These simulations illustrate mass transport of the building blocks themselves; in magmatic systems, advective- and diffusive-transport processes operate, and crystallization may be driven by heat transfer. (One aspect of crystal growth this simple analogy ignores is the role of undercooling in magmas or supersaturation in aqueous solutions, in determining the nucleation rate and, consequently, the number of nuclei. This may offend purists, especially petrologists, who may regard it as an inexcusable omission that results in unacceptable misconceptions in the students' minds. On the other hand, class discussion of how comprehensive these "simulations" are – "What does our exercise NOT take into account?" – may itself serve as the introduction to the topic of undercooling/supersaturation and nucleation. Details of crystal nucleation are usually discussed only in more advanced courses, and this omission may be a small price to pay for the simplicity of the exercise.) If the layout of the classroom required students to reach across desks or lab benches to attach their "building blocks" to "crystals," some cards may have been joined only along one edge, forming elongate, needle-shaped crystals, or projections from the outline of the "crystal"; such "dendritic" projections are another possible geometric outcome of the simulation, an outcome also consistent with real crystal growth under transport-limited conditions.

The third simulation introduces an additional phenomenon unrelated to transport. In simulation #3, getting the reactants together is the easy part; getting them into the proper, orderly configuration once they're close together is the hard part. Transport is not rate-determining in this case; rather, the rate of "crystal growth" is limited by the difficulty in overcoming configurational restrictions at the site of the "crystallization" reaction – that is, at the interface of the growing "crystal." This simulation allows the instructor to distinguish transport-limited from reaction-(interface-) limited kinetics.

At this point, the class has identified two basic kinds of processes that influence reaction rates: transport processes that bring reactants together and reaction processes that actually produce products from the assembled reactants.

Series (Chain) Reactions

Another important aspect of geochemical kinetics can be developed by asking how transport and reaction processes interact to determine the reaction rate. Do the transport and reaction steps have to follow one another, or can they happen simultaneously? In the first two simulations (with intact index cards), was arranging them fast or slow compared with transporting them together? In the last (ripped-up cards) simulation, was arranging them fast or slow compared with transporting them together?

Evidently, (A) the two steps must happen in sequence (transporting reactants together must happen before the reaction can take place), and (B) the slower of the two steps determines the overall rate. The overall rate at which the index-card "crystals" grew was governed by the slow step in a series of steps. This illustrates a general principle of chemical kinetics: For series reactions, the slowest step is rate-determining (for example, see Lasaga, 1981, p. 11-13; Lasaga, 1998, p. 28-29). In chain reactions, the overall rate is determined by the rate of the slowest reaction or step in the chain of reactions or steps.

Additional (anthropomorphic) examples of "series" cases can be discussed. Some include evacuating the classroom, or an airplane, in the event of an emergency. In order to evacuate a space, evacuees must be transported to the door, get through the door, and move away from the door. Furthermore, each individual evacuee must perform these steps in sequence (must get to the door before going through it), and each group of evacuees at a given door must pass through the door in sequence (one after another, if the door is small). In a series of evacuation steps, the slowest step determines the egress rate.

Transport, Reaction, and the Rate-Determining Step

The interplay of transport and reaction processes developed thus far by this analogy parallels exactly the conceptual framework presented by Berner (1978, 1980, 1981) and Lasaga (1998, p. 583) for mineral-solution reactions (for example, crystal growth from aqueous solutions, or crystal dissolution during rock and mineral weathering). Any heterogeneous (multi-phase) reaction (for example, a mineral-water reaction, such as dissolution of calcium carbonate in acidic solution, dissolution of halite, or hydrolysis of silicate minerals during rock weathering) requires a sequence of steps in order for the reaction to proceed. Assuming all reactants are available in excess, the following steps must occur (in series) during crystal growth from, or dissolution into, aqueous solution (Berner, 1980, 1981);

- 4) aqueous reactants (for example, hydrogen ions or hydronium), or solvent of appropriate composition (supersaturated for growth, undersaturated for dissolution), must arrive at the mineral-solution interface;
- 5) the reaction must occur at the interface (a variety of specific kinds of reactions and processes can take place at the surface; see Berner, 1980, 1981, and Lasaga, 1998, for details); and
- 6) dissolved products (for example, alkali or alkaline-earth cations, aqueous silica) must leave the site of the interfacial reaction (lest they accumulate to the extent that equilibrium is attained or the reaction is otherwise kinetically suppressed).

Similar processes operate in other situations of geologic interest.

If the first or third step (transport) is slow (rate-determining), the reaction is said to be transport limited. If the second process (reaction) is rate-determining,

the reaction is said to be reaction limited, or kinetically controlled, or, in the case of heterogenous (multi-phase) reactions, interface limited (because the rate-limiting reaction takes place at the interface, also widely termed surface-reaction controlled).

If proper care is taken, classification of reactions into transport-limited and reaction-limited categories is suitable to a variety of geological situations, most of which typically involve heterogenous reactions. Berner (1978, 1980, 1981) applies these concepts to crystal growth and crystal dissolution in aqueous solutions during weathering and diagenesis; Lasaga (1998) examines these and other geological and geochemical examples. Hodder (1990, 1997) employed this same conceptual framework in introducing and interpreting rate laws of mineral-weathering reactions. In magmatic and metamorphic systems, in which crystallization, recrystallization, and melting are involved, the slow (rate-determining) step may be heat transfer rather than diffusive mass transfer. The same basic breakdown applies to homogenous reactions (that is, reactions taking place in a single phase) as well; the reactants must be brought together (transport), the reaction must occur (reaction), and products must be transported away. Thus, homogenous reactions are also either transport limited or reaction (but not interface) limited.

The slowest form of transport is diffusion, but transport-limited reactions should not be termed diffusion controlled because any transport process (for example, advection) could be rate determining in such cases. All diffusion-controlled reactions are transport limited, but not all transport-limited reactions are diffusion controlled. Furthermore, the rate of diffusion, often regarded as the lower limiting rate for transport processes, is actually not a fixed value but depends on the specific context (for example, temperature, geometry) of the individual reaction environment.

Some Important Considerations of Context

Whether any specific reaction is chemical-reaction controlled or transport controlled can be context dependent; many mineral growth or dissolution reactions can be transport controlled under some conditions and kinetically controlled under others, depending on the transport rate in the specific geologic setting being considered. Berner (1978, p. 1236) presents several simple equations to demonstrate this for the case of crystal dissolution. A given dissolution reaction may be transport controlled (by advective transport) at low flushing rates (that is, flow is sluggish), but at high flushing rates, a limiting (surface-controlled) reaction rate is attained, which is independent of further increases in the flushing rate (Berner, 1978). At high flushing rates, the mineral is liberating dissolved products from its surface as fast as it can (the reaction is limited by detachment from the surface), and further enhancement of transport has no further influence on the dissolution rate; the same dissolution reaction that was transport controlled at low flushing rates has become interface controlled at high flushing rates.

At least some minerals can exhibit this full range of behaviors over a geologically reasonable range of flushing rates. For example, if an isolated mineral grain (a ten-micrometer test (skeleton) of biogenic CaCO_3) dissolves in a stagnant solution at a rate slower than the rate of molecular/ionic diffusion (the slowest transport process available), some process slower than diffusion (which is the slowest form of transport) must be rate-determining under these conditions, and crystal growth is kinetically (surface-reaction) controlled. However, a thick bed of these particles at the bottom of a chamber with a flow of undersaturated water over them will produce a flux of dissolved CaCO_3 from the interparticle pore fluid into the overlying flowing fluid. In these conditions, the overall rate of dissolution from the bed responds to the flow velocity, a response that characterizes transport-controlled dissolution processes, not surface-reaction (kinetic) control.

The rate-determining process differs between the two situations described because packing so many particles per unit volume allows them to saturate the porewater a short distance from the interface (on the order of the boundary-layer thickness). Thus, part of the overall concentration gradient that governs diffusion occurs in the sediment and part in the boundary layer, and the bed dissolves under mixed kinetic control. Context means geometry and distribution, as well as flow conditions (that is, stagnant versus flowing versus mixing, and so forth). Conditions for the transport control of some mineral-dissolution reactions may be impossible under any Earth conditions; however, lists of absolute kinetic versus transport controlled mineral reactions should be regarded with caution, as the rate-determining process will often be context-dependent.

The motion of students in the simulations might be analogous to diffusion; the rate of this process can be very different depending on the distribution of the desks or tables. For example, the students' movement may be faster and more efficient if the desks or tables are placed against the walls and the area in the center left free, in contrast to having the desks regularly spaced in the room and inhibiting the motions. Organizing the student movement so that they must all move as a flow counterclockwise about the room to reach a table of interest to them might simulate advective transport. Placing a small number of students in the center of the room with poster boards surrounding them, and asking them to build the crystals on the boards, would produce a different response over time than placing a large number of students in the same space; in the latter case, moving students will interfere with each other. Students and instructors might discuss different possible simulation geometries and situations and how suitable each might be as an analog to some specific advective or diffusive transport process in some specific geologic context.

Parallel Reaction Pathways

Other (also anthropomorphic) examples can be contrasted to the examples just discussed, for example, checkout lines at a large grocery store, or toll booths.

Choosing the wrong grocery-store checkout or toll lane, thereby getting behind the slow person and watching people in neighboring lanes leave first, even though they got into their line later than you, is a common experience. In such situations, each individual must enter a lane, be processed, and exit that lane; the steps for an individual must be taken in series. However, the overall rate of traffic flow is determined by the fastest lanes; the slow person in front of you may slow you down but only ties up a few people in that line. Because there are other parallel paths through which other people can pass, and because these paths allow more individuals through them per unit time, the overall rate at which all people passing through can be processed is determined by the fastest lanes, rather than the slowest. This illustrates another general principle of chemical kinetics: For parallel reactions, the fastest step is rate-determining (for example, see Lasaga, 1981, p. 11-13; Lasaga, 1998, p. 28-29). Transport processes in low-temperature aqueous systems (for example, solute transport in ground water) can be used as an example of parallel processes. A dissolved ion can move through the aquifer either by diffusing through aquifer solids (grains) or by diffusive or advective transport around the grains; transport through grains and around grains are alternate, parallel pathways. At low temperatures, diffusion through crystalline solids is very slow compared with transport through pore fluids around the solids, and most transport occurs via the faster of the two parallel pathways.

Different kinds of traffic-flow arrangements, for instance, multiple teller windows at a bank, turnstiles at a stadium, or security checkpoints at an airport, can also be discussed, for combinations of series and parallel "reaction paths." Students might be asked to design a simulation of one or more such examples.

Variations

Other aspects of crystal growth, rock texture, and crystal chemistry can also be addressed using variations of this exercise. For example, a third simulation can be run with intact cards (before tearing them up), in which students holding some specific color are allowed to proceed forming their crystals before other colors begin to crystallize. The other colors may be allowed to crystallize after some delay, and the simulation can be terminated shortly after the onset of "late" crystallization. The resulting distribution of crystals (one mineral occurring as a few large crystals, with the rest occurring as numerous small crystals), mimic the texture and one possible crystallization history of porphyritic igneous rocks. Similarly, introducing a very small number of cards of one color allows one to discuss the behavior of trace constituents and incompatible elements during crystallization. Hiding stacks of colored cards around the room and requiring students to find them as the first step allows discussion of how the origin (sources) and availability of mobile constituents influence the composition and subsequent crystallization of the "magma." Other (reusable) simulation media are also available; multi-colored Lego blocks can be employed in much larger

numbers than is convenient for index cards. With a large population of such blocks, it is easy to show, for example, how relative concentrations of particular reactant species change during the crystallization process and how these may limit porphyroblast growth in the absence of advective fluxes. Instructors and students can construct other constraints and scenarios that can serve as jumping-off points for other lines of discussion.

IMPLEMENTATION

I have used the index-card simulations and the follow-up class discussion for several years in my undergraduate "Mineralogy and Geochemistry" class. Getting up and moving around in performing the exercise is a great way to introduce some variety into a lecture, and using "student-generated" data stimulates interest in the discussions (basically, they want to see where we're going with this activity). The exercise is easily managed, takes only a few minutes, and routinely yields clear results (see Table 1) in groups of two to three dozen people; it has also been used successfully in groups as small as four to six people. The principles raised by the third (torn-card) simulation are beyond the scope of introductory geology classes, and the activity itself is probably unmanageable in large lecture sections; however, the activity may work in smaller lab or discussion sections of larger classes.

Many (although by no means all) mineralogy, geochemistry, and petrology textbooks cover basic crystal growth. Such text material serves as a focal point around which class discussion and in-class interpretation of the "simulation" results can be directed. This exercise has been used in conjunction with Blackburn and Dennen (1994), who devote an entire chapter to crystal growth, and Gill (1996), who devotes an entire chapter to introductory geochemical kinetics and part of another to crystal growth. The exercise has also dovetailed well with the excellent crystal-growth lab exercise of Heaney (1997) and the halite dissolution-kinetics exercise of Velbel (1997).

SUMMARY

"Index-card" simulations can be used to illustrate several principles of crystal growth and geochemical kinetics:

- 1) Rapid cooling (or evaporation) produces a large number of smaller crystals; slow cooling gives a smaller number of larger crystals. This can be applied even to introductory courses.
- 2) Both transport and reaction steps are involved in producing a model "crystal" from our model system.
- 3) For series reactions, the slowest step is rate-determining; for parallel reactions, the fastest step is rate-determining.
- 4) Reactions can be classified based on the nature of the rate-determining step. Transport-limited reactions are those in which transport of reactants to or products away from the reacting interface is the

slow step or process; reaction- (interface-) limited reactions are those in which the chemical reaction at the interface itself is rate-determining. This framework allows for relatively easy transition to more rigorous discussions of various thermally activated transport (for example, diffusion, advection) and reaction processes, as suits the requirement of more advanced classes.

I have found this exercise a useful device for introducing undergraduate students to elementary geochemical kinetics.

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Food for Thought

Anyone committed to the view that science should be a basic part of our intellectual tradition will soon find grounds for concern. Even among educators, scholars, and commentators of our culture, one now hears all too often scientific research described as being an unpleasant, soulless activity, merely "logical," "linear," "hierarchical," and devoid of all human passion. Any practicing scientist knows this to be an absurd characterization, one that at best might be excused as an opinion formed while taking a bad science course – if any – in school.

Gerald Holton, 1996, *Einstein, history, and other passions – The rebellion against science at the end of the twentieth century*: Reading MA, Addison-Wesley Publishing Company, 240 p. (from p. 40-41).

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Brady, D.W. Mogk, and D. Perkins III, editors, Teaching mineralogy: Mineralogical Society of America, Washington, D.C., p. 119-130.

Table 1

Size (# cards) 1234567 Simulation #1 - Short simulation time (fast crystal-growth)

Red 1121 Green 112 Blue 322 Simulation #2 - Long simulation time (slow crystal-growth)

Red 21 Green 11 Blue 111 Simulation #3 - Torn-up cards

Any color No completed crystals Table 1 - Sample data from index-card simulation of crystal growth: ~36 cards