

HIGHLIGHTS AND BREAKTHROUGHS

The search for a universal law of crystal growth: The law of proportionate effect?

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Perhaps no mystery of the mineral kingdom has remained shrouded in the details of its chemistry and physics longer than that of their origin. Scholars have been fascinated by the formation of natural crystals since ancient times. Plato, who was so intrigued by the origin of crystal shapes that the five regular polyhedra now bear his name, speculated in ~360 BCE that “when earth is compressed by air into a mass that will not dissolve in water, it forms stone, of which the transparent sort made of uniform particles is fairer, whereas the opposite kind is coarser” (Caley and Richards 1956). In later ages, luminary figures such as Theophrastus (Caley and Richards 1956), Pliny the Elder (Bostock and Riley 1855), and Georgius Agricola (Hoover and Hoover 1950) all made their own attempts at explaining the formation of mineral particles and crystals.

In the modern scientific era, the advent of atomic theory made it clear that through some combination of processes, atoms could align themselves into regular arrays whose bonding would serve to minimize the energy of the system. The groundwork for studying rates of crystallization was arguably first laid out by Johnson, Mehl, Avrami, and Kolmogorov (Avrami 1939, 1940, 1941) with the derivation of the widely used “JMAK” kinetic equation. We now have many other theoretical tools with which to piece together the formation of minerals. Classical nucleation theory describes the thermodynamics of the incipient stages of crystal formation (Volmer and Weber 1925; Becker and Döring 1935). The electrical double layer model describes the chemical interactions that take place at the surface of a growing particle (Helmholtz 1853), and the order in which minerals will crystallize from a complex, silicate-bearing melt was famously worked out by Bowen (1928). Processes such as homogeneous and heterogeneous nucleation, Ostwald ripening, step and edge formation, oriented attachment, and surface-induced phase stability reversal have been studied in detail, each one contributing a new piece to a complex but ever-growing puzzle.

However, despite the many great advances that have been made in the past century, the complex array of interacting effects and processes has made it seemingly impossible to unite crystallization into a single understandable theory, and many fundamental mysteries remain. In this issue of *American Mineralogist*, Eberl (2024) argues that the so-called “law of proportionate effect” may be a guiding principle that describes a majority of systems in which a large number of crystalline particles form and grow within a homogeneous medium. This law (as used by Eberl) holds that whenever crystals grow via advective transport of nutrients, each crystal grows by an amount that is, on average, proportional to its original size during each time step (muting the absolute growth rate of very small crystals while exaggerating the growth rate of large ones). Eberl (2024) outlines how this law, when applied to an initially uniform distribution of crystal nuclei, quickly transforms the population into a lognormal

distribution of sizes. This distribution then increases its mean and variance as it evolves but retains its fundamental lognormal shape so long as transport-limited growth dominates the system.

This mathematical description of crystallization is obviously not completely universal, and Eberl himself discusses several other processes that can result in alternative distribution styles. He does, however, argue (with abundant examples from lab syntheses and natural systems) that a great majority of homogeneous nucleation and growth processes will result in lognormal size distributions via the law of proportionate effect. In this framework, the mean and variance of a mineral’s lognormal size distribution can help us retrace its crystallization history, whereas non-lognormal distributions can serve as telltale indicators of additional processes that took place at an early stage of crystallization (even when the physical remnants of that process are too heavily overprinted to directly observe).

Regardless of whether the law of proportionate effect is truly universal, this framework offers a chance to systematize crystallization processes and identify them in natural systems using measurable predictions. It also offers hope that even when an array of molecular mechanisms is at work, an element of statistical randomness can (ironically) average them into an understandable and more deterministic net result. Though he would surely have been vexed by descriptions of the underlying electrostatic and quantum interactions, Plato would no doubt have been pleased to have a working classification scheme not only for the beautiful natural crystals that he so admired, but also for the processes that create them.

REFERENCES CITED

- Avrami, M. (1939) Kinetics of phase change I: General theory. *Journal of Chemical Physics*, 7, 1103–1112.
- (1940) Kinetics of phase change II: Transformation-time relations for random distribution of nuclei. *Journal of Chemical Physics*, 8, 212–224.
- (1941) Kinetics of phase change III: Granulation, phase change, and microstructure. *Journal of Chemical Physics*, 9, 177–187.
- Becker, R. and Döring, W. (1935) Kinetische behandlung der keimbildung in übersättigten dämpfen. *Annalen der Physik* 24, 719.
- Bostock, J. and Riley, H.T. (1855) *The Natural History, Pliny the Elder*. Taylor and Francis.
- Bowen, N.L. (1928) *The Evolution of the Igneous Rocks*. Dover Publications, New York.
- Caley, E.R. and Richards, J.F.C. (1956) *Theophrastus on Stones: Introduction, Greek text, English translation, and commentary*. The Ohio State University, Columbus.
- Eberl, D.D. (2024) Crystal growth according to the law of proportionate effect. *American Mineralogist*, 109, 2–7.
- Helmholtz, H. (1853) Ueber einige gesetze der vertheilung elektrischer ströme in körperlichen leitern mit anwendung auf die thierisch-elektrischen versuche. *Annalen der Physik und Chemie*, 165, 211–233.
- Hoover, H.C. and Hoover, L.H. (1950) *De Re Metallica: Translated from the first Latin edition of 1556*. Dover Publications, New York.
- Volmer, M. and Weber, A. (1925) Nucleus formation in supersaturated systems. *Zeitschrift für Physikalische Chemie*, 119, 277–301.

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