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Crystal growth according to the law of proportionate effect

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Abstract

This paper summarizes an approach to crystal growth that was published in parts in various articles over the course of 25 years by the present author and his colleagues. Evidence for this approach, which is confirmed in detail by data in the cited publications and in the figures and equations in the supplementary material that accompanies this paper (see the Online Materials[1]), comes mainly from the shapes of crystal size distributions (CSDs). Such distributions reveal the growth histories of natural minerals and synthetic compounds, histories that can be used to make geological interpretations and to guide industrial syntheses.

CSDs have three fundamental shapes: log-normal, asymptotic, and Ostwald. These shapes result from different degrees of supersaturation near the time of nucleation. The first two distribution shapes form according to the Law of Proportionate Effect (LPE) at moderate supersaturation, and the latter rare distribution forms by Ostwald ripening at large supersaturation. Initially, the first two distributions have mean diameters of up to tens of nanometers and grow by surface-limited growth kinetics. The slow step in this reaction is the incorporation of nanoparticles (bits of crystal or adparticles) onto the crystal surface. As the crystals become larger, their demand for nutrients, as calculated by the LPE, increases exponentially. Then the slow step in the reaction changes to the rate of transfer of nutrients to the crystal (supply- or transport-limited growth). Crystal diameters often grow the most during this latter stage, and the initial CSD shapes that originally formed during surface-limited growth are retained and scaled up proportionately.

Proportionate growth during the supply-limited stage can be simulated approximately by multiplying the diameter of each crystal in a distribution by a constant. Crystals can also grow by a constant rate law in which a constant length is added to each crystal diameter in the distribution. This rare process causes the original CSD to narrow so that its initial shape is not preserved. The growth law that prevails, either proportionate or constant, is determined by the manner in which nutrients are supplied to the crystal. Supply is by advective flow during proportionate growth, with the nutrient solution moving with respect to the crystals. Constant growth relies on the random diffusion of nutrients through a quiescent solution. Proportionate growth is by far the most common growth law, and therefore, nutrient supply by diffusion alone during crystal growth is uncommon.

Distributions formed by Oswald ripening and those formed by other rare processes are also discussed. During Ostwald ripening, nucleation caused by mixing reactants at large supersaturation forms crystals that are extremely fine and numerous. The larger crystals grow at the expense of the finer, less stable crystals, thereby forming, on completion, the universal steady-state CSD shape predicted by the Lifshitz-Slyozov-Wagner (LSW) theory. This unique CSD shape, as well as other rare shapes, then are scaled up to larger sizes by supply limited proportionate growth.

Keywords: Crystal growth, proportionate growth, constant growth, Ostwald ripening, crystal size distributions, Law of Proportionate Effect, crystallization, nucleation, stochastic crystal growth