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## 4 **Crystal Growth According to the Law of Proportionate Effect**

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### 8 **ABSTRACT**

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

16 CSDs have three fundamental shapes: lognormal, asymptotic and Ostwald. These shapes  
17 result from different degrees of supersaturation near the time of nucleation. The first two  
18 distribution shapes form according to the Law of Proportionate Effect (LPE) at moderate  
19 supersaturation, and the latter rare distribution forms by Ostwald ripening at large  
20 supersaturation. Initially, the first two distributions have mean diameters of up to tens of  
21 nanometers and grow by surface-limited growth kinetics. The slow step in this reaction is  
22 the incorporation of nanoparticles (bits of crystal or adparticles) onto the crystal surface. As

23 the crystals become larger their demand for nutrients, as calculated by the LPE, increases  
24 exponentially. Then the slow step in the reaction changes to the rate of transfer of nutrients  
25 to the crystal (supply- or transport-limited growth). Crystal diameters often grow the most  
26 during this latter stage, and the initial CSD shapes that originally formed during surface-  
27 limited growth are retained and scaled up proportionately.

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

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

45 **Key words:** Crystal growth, proportionate growth, constant growth, Ostwald ripening,  
46 crystal size distributions, Law of Proportionate Effect, crystallization, nucleation, stochastic  
47 crystal growth

## 48 **GROWTH OF LOGNORMAL CRYSTAL SIZE DISTRIBUTIONS**

49 Minerals most commonly have lognormal crystal size distributions (CSDs; Figs. 1, 15 and 17  
50 in Eberl et al. 1998; Fig. 2 in Kile and Eberl 1999; Figs. 3 and 9 in Kile et al. 2000; Fig. 5b in  
51 Bove et al. 2002; Figs. 1 and 3 in Eberl et al. 2002a; Fig 3 in Kile and Eberl 2003; Figs. 5 and 7  
52 in Badino et al. 2009; Fig. 3 in Eberl 2022). A lognormal distribution (Fig. 1) is described by the  
53 equation:

$$54 \quad g(X) = \left[ \frac{1}{X\beta\sqrt{2\pi}} \right] \exp \left\{ - \left( \frac{1}{2\beta^2} \right) [\ln(X) - \alpha]^2 \right\}, \quad (1)$$

55 where  $g(X)$  is the continuous theoretical frequency distribution of variable  $X$ , where, in this case,  
56 the  $X$ s are crystal diameters that are parallel to a given crystallographic direction. Equation 1 can  
57 be solved if two parameters are known:  $\alpha$  and  $\beta^2$  are the mean and variance of the distribution of  
58 the natural logs of  $X$ . The original scale units for  $\alpha$  need to be specified because it is a log.  $\beta^2$   
59 indicates the breadth of a distribution for a given  $\alpha$ .

60 Iteration of the Law of Proportionate Effect (LPE) is the simple mathematical procedure that  
61 generates the lognormal distribution (Koch 1966) and thereby simulates crystal growth (Eberl et  
62 al. 2000):

$$63 \quad X_{j+1} = X_j + \varepsilon_j X_j, \quad (2)$$

64 where  $X_j$  is the diameter of an individual crystal,  $\varepsilon_j$  is a random number that varies independently  
65 for each crystal between 0 and 1, and  $j$  denotes the calculation cycle for the LPE iteration.  
66 Starting, for example, with 1000 crystals having a diameter of 1 nm, Equation 2 is solved  $j$  times

67 for each crystal by substituting  $X_{j+1}$  back into the equation for  $X_j$ . The distribution evolves from  
68 an even distribution into a lognormal one when the crystal sizes resulting from the LPE  
69 calculation are grouped into equally spaced bin sizes, using the bin centers as  $X$ . For example,  
70 sizes calculated by the LPE that range between 2.5 and 3.5 nm are grouped as 3 nm, and the  
71 number of crystals in the bin is noted. Continued iteration of the LPE leads to an increase in the  
72 mean size and variance of the distribution (Fig. 2 in Eberl et al. 1998).

73 The results of the LPE calculation are verified as being lognormal by calculating the  
74 parameters  $\alpha$  and  $\beta^2$  from the numbers of crystals in the binned LPE sizes, where  $\alpha =$   
75  $\sum \ln(X)f(X)$ , and  $\beta^2 = \sum [\ln(X) - \alpha]^2 f(X)$ , where  $f(X)$  is the frequencies of binned crystal  
76 sizes  $X$ . The two parameters are entered into Equation 1, and the theoretical lognormal number  
77 of crystals for each binned size is calculated from Equation 1 by multiplying a normalized  $g(X)$   
78 times the total number of crystals counted, in this case 1000. This distribution is compared  
79 statistically (using the Chi-square test, or the Kolmogorov-Smirnov test for sparse data) to the  
80 distribution of crystals calculated from the LPE to verify the lognormal shape. The same general  
81 procedure is used to test measured distributions for log-normality.

82 The LPE is assumed to be the central equation that describes relative crystal growth rates in  
83 natural and synthetic systems because it duplicates the experimentally measured lognormal  
84 shapes of natural and synthetic CSDs (Eberl et al. 1998; Eberl et al. 2002a). The LPE models  
85 crystal growth as a stochastic process, as opposed to being deterministic. This means that  
86 although crystal growth has a random component ( $\epsilon$ ), this randomness follows a rule (the LPE).  
87 Therefore, although the relative growth rates of individual crystals can not be calculated  
88 precisely, the distribution shape calculated by iterating Equation 2 is predictably lognormal.

89 If the LPE is taken literally, it offers other insights into the growth process. The growth  
90 particles (termed nanoparticles, adparticles or colloids) that attach themselves to a crystal's  
91 surface are a random fraction of a crystal's initial size ( $\epsilon_j X_j$ ) rather than being individual atoms,  
92 ions or monomers. Such crystallization by oriented particle attachment is supported by electron  
93 micrographs that show diverse types of nanoparticles in various stages of attachment (e.g., Fig.  
94 12 in Ivanov et. al. 2014; Fig. 2 in De Yoreo et. al. 2015). Atom by atom or molecule by  
95 molecule growth would not produce lognormal CSDs. Also, according to the LPE, growth by  
96 the coalescence of nanoparticles occurs in discrete cycles ( $j$ ) rather than continuously.

97 The LPE also indicates that the relative rate of crystal growth is a function of the linear  
98 dimensions of the crystal (i.e., of its diameter  $X$ ), rather than of its surface area or volume. In the  
99 older literature this type of growth was termed size dependent growth; but, more specifically, it  
100 is now termed proportionate growth. Whereas previously such growth was considered to be a  
101 rarity, proportionate growth is in fact the most common growth mechanism (Eberl et al. 1998).  
102 The random variable in the LPE also clarifies crystal growth dispersion, whereby individual  
103 crystals, all initially of the same size, and each subjected to identical growth environments, can  
104 grow at different rates (see Eberl et al. 1998, p. 503, for pertinent references).

105 The LPE (Equation 2) is not the complete story, because the predicted growth rate can not be  
106 sustained. Unconstrained iteration of the LPE leads to exponential growth, and eventually to  
107 very large adparticles and distribution variances (Figs. 2 and 3 in Eberl et al. 1998). However,  
108 Equation 2 applies only to the initial stages of growth, immediately during and after nucleation,  
109 when calculation of the growth rate is limited only by the incorporation of nanoparticles ( $\epsilon_j X_j$ )  
110 onto the crystal surface. It is a rate that prevails at distribution mean sizes that range up to tens  
111 of nanometers (as indicated by Fig. 2 in Eberl et al. 1998). At larger sizes calculation of the

112 growth rate is limited by the rate of supply of material to the crystal, rather than by incorporation  
113 onto the surface. Equation 2 is modified for supply-limited growth to account for a limited  
114 volume of nutrients carried to the surfaces during each calculation cycle ( $j$ ) of the LPE (for  
115 details concerning this volume-limiting calculation see Equation 8 in Eberl et al. 1998, or  
116 Equation 2 in Kile et al. 2000). This modification of the LPE leads to the calculation of  
117 adparticles that are limited in size, that are small compared to the size of the growing crystal, and  
118 that preserve  $\beta^2$  during growth. Thus surface-limited growth initially gives the distribution a  
119 lognormal shape, whereas subsequent supply-limited growth preserves this shape (meaning that  
120  $\beta^2$  remains constant) as the mean size ( $\alpha$ ) increases (see Fig. 6 in Eberl et. al. 1998; Fig. 7 and  
121 Table 2 for continuous growth experiments in Kile et al. 2000; see Fig. 3 for a similar  
122 experiment in Eberl et al. 2002a).

123 The growth of a distribution during supply-limited growth can be duplicated approximately by  
124 multiplying the crystal sizes in the distribution by a constant ( $k$ , which is a constant of  
125 proportionality or scale factor). Equation 2 then reduces to  $X_{(j+1)} = kX_j$ , where the constant  $k$   
126 substitutes for the random variable  $(1 + \varepsilon_j)$ . This procedure increases the distribution's mean size  
127 while keeping its variance constant. However, this calculation, although convenient, is not  
128 completely satisfactory because multiplication by  $k$  does not express the random tendency for  
129 growth found at small diameters. Multiplication by  $k$  causes the growth rate of individual  
130 crystals to be predictable. A more realistic calculation applies the volume adjusted growth limit  
131 for each iteration of the LPE, as was discussed above. The shape of the resulting distribution is  
132 the same for either calculation, but the sizes of individual crystals differ because the latter  
133 calculation contains a random number rather than a constant (Fig. 2B in Eberl et al. 2002a).

134 CSDs that have very different mean sizes, ranging from nanometers (e.g., illite crystal  
135 thicknesses; see Fig. 5b in Bove et al. 2002) to meters (giant gypsum crystals in Naica's Cueva  
136 de los Cristales that range to >11 m long; see Figs. 5 and 7 in Badino 2009), have lognormal  
137 shapes with similar variances (e.g., Fig. 16 in Eberl et al. 1998 and Fig. 7 in Kile et al. 2000).  
138 Such shapes most likely result from the proportionate growth of lognormal distributions that  
139 were formed according to LPE growth early in crystallization. Other growth mechanisms, such  
140 as ripening, constant growth or entirely random growth, would quickly destroy the lognormal  
141 shape and alter the variances (Fig. 8 in Eberl et al. 1998; Figs. 2 and 3 in Eberl et al. 2002a).  
142 Therefore, control of the initial CSD shape during and immediately after nucleation is key to  
143 controlling the shape of the final CSD because the earlier shape is scaled up during supply-  
144 limited growth.

## 145 **FORMATION OF CSD SHAPES OTHER THAN LOGNORMAL**

146 Diverse conditions near the time of nucleation can lead to a variety of CSD shapes. These  
147 shapes include the commonly found asymptotic CSD, and the rare Ostwald, transitional, non-  
148 Ostwald and multimodal CSDs.

149 Nucleation occurs in supersaturated solutions when crystals appear that have radii ( $r$ ) greater  
150 than that of the critical radius ( $r^*$ ). If  $r > r^*$  crystals can nucleate and grow. If  $r < r^*$  they dissolve.  
151 A crystal having a size equal to  $r^*$  is in equilibrium with the solution, and neither grows nor  
152 dissolves. A solution needs to be supersaturated, rather than simply saturated, to form growing  
153 nuclei because the saturation state for a mineral (i.e., its solubility product) is determined for the  
154 infinitely large crystal, and, therefore, does not address an increase in solubility related to an  
155 increase in specific surface energy for finer crystals. Furthermore, concentrations measured for a  
156 bulk solution do not address inhomogeneities present in a solution at the nanometer scale

157 (particularly upon mixing), further complicating the calculation of  $r^*$ . In addition, the value for  
158  $r^*$  may increase during nucleation and growth if the saturation level falls as crystallization  
159 proceeds.

160 Experiments with calcite nucleation and growth and with computer simulation (Eberl et al.  
161 1998; Kile et al. 2000; Eberl et al. 2000) indicate that variations in nucleation history can lead to  
162 CSD shapes that are not lognormal. For example, if nucleation occurs over an extended time at a  
163 constant or accelerating nucleation rate while previously formed nuclei grow according to the  
164 LPE, an asymptotic distribution (Fig. 1) results in which the smallest size category has the  
165 largest frequency (see also: Table 2 and Figs. 4 and 13 in Eberl et al. 1998; Fig. 2 in Kile et al.  
166 2000). After an initial period of nucleation and growth, this shape can be preserved ( $\beta^2$  is held  
167 constant) and scaled up by subsequent supply-limited proportionate growth, as was discussed.  
168 This commonly occurring asymptotic shape can be described approximately using the lognormal  
169 equation (Equation 1), but it doesn't often pass the statistical test. It can readily evolve into a  
170 lognormal shape if nucleation ceases while surface-limited growth continues (Figs. 6 and 7 in  
171 Bove et al. 2002).

172 A second complication in CSD shape is related to nucleation that occurs when concentrated  
173 solutions are suddenly mixed. Such an event, which is rare in nature, can lead to the universal  
174 steady state shape that is expected for supply-limited Ostwald ripening, a distribution that is  
175 skewed opposite to that of lognormal (Fig. 1). The equation for this shape was derived  
176 independently by Lifshitz and Slyozov (1961) and by Wagner (1961) in what is known as the  
177 LSW theory. As was similarly discussed for the lognormal distribution, the LSW equation that  
178 describes the Ostwald distribution (Equation A20 in Eberl et al. 1998) differs from the simple  
179 equation that is iterated to simulate the distribution (Equation 10 in Eberl et al. 1998, presented



180 by Markworth 1970). Experiments and calculations (Kile et al. 2000) have shown that this  
181 unique universal steady-state shape forms initially at very large levels of supersaturation, where  
182 abundant and extremely fine nuclei precipitate. A large contrast in specific surface areas among  
183 these particles leads to growth of the larger nuclei ( $r > r^*$ ) at the expense of the dissolution or the  
184 incorporation of the smaller, less stable nuclei ( $r < r^*$ ) according to the Ostwald ripening  
185 mechanism, with  $r^*$  approximated by the mean radius.

186 According to LSW theory, the CSD for any mineral that has undergone sufficient ripening will  
187 have the identical negatively skewed distribution shape when the data are plotted on reduced  
188 axes (size/mean size vs. frequency/maximum frequency), a shape that is independent from the  
189 initial, pre-ripened CSD shape, and that has a cutoff at large sizes (Fig. 1; see also Fig. 4 in Kile  
190 et al. 2000). The coincidence of CSDs on a reduced plot means that the variances are equal. The  
191 Ostwald shape, which has a constant and small variance of about 0.06, is scaled up by supply-  
192 limited growth, which leads to an increase in mean size while the variance is preserved. The  
193 resulting crystals all have nearly the same size (Fig. 8 in Kile et al. 2000).

194 The Ostwald CSD forms initially at large supersaturation, whereas the lognormal shape forms  
195 initially at smaller supersaturation. Nuclei precipitated at smaller saturation are larger and fewer,  
196 and therefore are less subject to ripening. Calcite crystallization experiments (Table 1 and Fig. 6  
197 in Kile et al. 2000) showed that lognormal CSDs formed at initial omegas ranging from 22 to 40,  
198 where omega is defined as the ion activity product of the solution divided by the mineral  
199 solubility product. Therefore a solution with an omega of one is at equilibrium with a crystal  
200 that has negligible specific surface energy. However, the Ostwald CSD appeared at initial  
201 omegas  $> 100$ , where nuclei formed having very large specific surface energies. Between these  
202 values (28 to 69) CSDs crystallized that had transitional shapes between lognormal and Ostwald,

203 indicating incomplete ripening prior to the preservation of their shapes by supply-limited  
204 proportionate growth (Fig. 5 in Kile et al. 2000).

205 The Ostwald and transitional CSD shapes were readily crystallized in the laboratory where  
206 they formed for calcite by the rapid mixing of concentrated calcium and carbonate solutions  
207 (Kile et al. 2000). However, such environmental conditions are rare in nature. The Ostwald  
208 shape has been found for garnets in metamorphic rock by Miyazaki (1991). Carlson (1999)  
209 objected to this interpretation because the surface energy driving force for the ripening of such  
210 large porphyroblasts would be negligible. Carlson correctly reasoned that ripening should not be  
211 effective for crystals larger than a fraction of a  $\mu\text{m}$ . However, as was discussed, the Ostwald  
212 distributions likely formed from extremely small crystals during and immediately after  
213 nucleation. These shapes then were preserved for the garnets during supply-limited  
214 proportionate growth.

215 An entire sequence of CSD shapes, from Ostwald to transitional to lognormal, has been found  
216 on Mars for hematite concretions (Martian blueberries; Figs. 2 and 3 in Eberl 2022). Concretion  
217 diameters were measured from photographs taken during a traverse by the Opportunity rover.  
218 This set of distribution shapes indicates differences in initial relative levels of groundwater  
219 supersaturation with respect to hematite solubility (see Fig. 6 in Kile et al. 2000 for analogous  
220 calcite experiments). Concretions likely precipitated from hydrothermal solutions that were  
221 generated suddenly by bolide impact on groundwater or permafrost (Eberl 2022). Iron for the  
222 hematite may have come from the bolide.

223 There is another kind of ripening, other than Ostwald, during which crystals dissolve  
224 randomly with respect to size, thereby supplying nutrients for other crystals to grow. During  
225 such supply-limited random ripening (also termed non-Ostwald ripening) something other than

226 specific surface area influences solubility. For example, some crystals could be less stable due to  
227 lattice strain, polytype, or because they are located in hotspots. Assuming that the less stable  
228 crystals disappear completely, the initial CSD shape ( $\beta^2$ ) remains constant as mean size increases  
229 (Fig.11 in Eberl et al. 1998), thereby mimicking supply-limited growth; but this process differs  
230 because it occurs in a closed system (here defined as a system in which nutrients for growth  
231 come from the dissolution of the crystals themselves), and because a large amount of material  
232 passes through solution for a small increase in mean size. It is not known if random ripening is  
233 an important growth mechanism in nature because its CSD does not have a distinctive shape of  
234 its own. Evidence for such ripening has been noted experimentally in isotopic studies of the  
235 growth of Fisher calcite crystals treated hydrothermally in a closed system at 500° C for various  
236 lengths of time (Figs. 18 and 19 in Eberl et al. 1998).

237 Mineral CSDs may have other shapes. For example, samples that have undergone several  
238 nucleation events can be composed of multiple lognormal distributions (Fig. 2C in Kile et al.  
239 2000). These distributions can be decomposed into their component lognormal CSDs by fitting  
240 them with appropriate means and variances using Equation 1. In addition, CSD shapes that have  
241 undergone mixing or winnowing by sediment transportation can be recognized by the relation  
242 between  $\alpha$  and  $\beta^2$ , the values for which may lie outside a field expected for *in situ* crystal  
243 growth, as was demonstrated for the clay mineral illite in Yukon River sediments (Fig. 18B in  
244 Eberl 2004). In a like manner, the reaction path for illite crystals can be ascertained from their  
245 thickness distribution shapes by plotting distribution parameters onto an  $\alpha$  vs.  $\beta^2$  diagram, as was  
246 shown for illite crystals from the San Juan Mountains, Colorado (Figs. 6 and 7 in Bove et al.  
247 2002).

248

## ORIGIN OF PROPORTIONATE GROWTH

249 CSDs may increase in mean size by proportionate growth or by constant growth (Eberl et al.  
250 2002a). The latter growth law, which is expressed  $X_{(j+1)} = X_j + k$ , often is assumed in modeling  
251 (e.g., population balance modeling; McCabe's  $\Delta L$  law; JMAK equation), but rarely is found in  
252 nature. Growth experiments with centimeter size K-alum crystals having a variety of initial sizes  
253 indicate that, for such large crystals, proportionate growth occurs in stirred systems, whereas  
254 constant growth occurs in systems that are not stirred (Figs. 1 and 2 in Kile and Eberl 2003).  
255 Thus, the advective supply of nutrients to crystals favors proportionate growth, whereas diffusion  
256 in still solutions leads to constant growth. The reason for this behavior is attributed to a nutrient  
257 depleted boundary layer in solution next to a crystal. This layer is progressively thinned by the  
258 greater velocity necessary for a solution to contour around larger crystals, thereby tending to  
259 increase growth rate based on crystal diameter, as has been modeled by Stefan-Kharicha et al.  
260 (2020).

261 A contrary result was found during the experimental nucleation and growth of fine (28  $\mu\text{m}$   
262 mean) calcite crystals (Fig. 3 in Kile and Eberl 2003). They exhibited proportionate growth by  
263 retaining a lognormal CSD for both stirred and unstirred systems, an effect attributed to their  
264 small size and to solution movement during initial mixing or to visually unobserved convection  
265 and/or Brownian motion (Kile et al. 2000). However, calcite CSDs did show the narrowing  
266 effect expected for constant growth when grown from concentrated solutions in a silica gel-filled  
267 column (Kile and Eberl 2003). Silica gel was used to minimize advection and increase nutrient  
268 supply by diffusion. These calcite crystals grew to a mean diameter of about 310  $\mu\text{m}$ , and had a  
269 very small variance of 0.02. An initial Ostwald distribution shape and variance ( $\beta^2 = 0.07$ ) was  
270 recovered by subtracting a constant 140  $\mu\text{m}$  from each crystal diameter, indicating that constant

271 growth began to alter an Ostwald distribution shape at a mean diameter of about 170  $\mu\text{m}$  (Fig. 4c  
272 in Kile and Eberl 2003).

273 Two examples of constant growth were discovered in natural flow-restricted environments  
274 (Kile et al. 2000). Calcite CSDs within a molar tooth structure (Proterozoic Belt Supergroup,  
275 Western Montana, USA), having a mean size of 13  $\mu\text{m}$  and a variance of 0.02, started constant  
276 growth at 7.5  $\mu\text{m}$  from an initial Ostwald distribution shape (Fig. 5 in Kile and Eberl 2003).  
277 Possible greigite crystals, found in a diatom test in Pyramid Lake, NV, also may have undergone  
278 some constant growth that deformed an initial Ostwald CSD (Fig. 6 in Kile and Eberl 2003).

279 There may be a practical application for these observations. If one wants to create a CSD  
280 containing uniform sizes (for example, a non-scoring abrasive or a congruently dissolving drug),  
281 one could encourage the initial formation of an Ostwald CSD by nucleation at large  
282 supersaturation, followed by constant growth in an immobile solution which would further  
283 decrease variance (Eberl et al. 2002b). It may also be possible to encourage a narrowing of  
284 CSDs through rapid stirring or flushing, whereby the flow of solution around crystals is fast  
285 enough to be minimally affected by crystal diameters.

## 286 **IMPLICATIONS**

287 The LPE, and the related volume constrained LPE, offer a concise and simple explanation for  
288 some of the baffling features concerning crystal growth, including size dependent growth, crystal  
289 growth dispersion, the common lognormal shape, and the narrow range of variance for each of  
290 the three basic types of CSDs (Fig. 7 in Kile et al. 2000). The equation also indicates that growth  
291 depends on the incorporation of nanoparticles rather than single atoms, a prediction that accords  
292 with electron micrograph evidence mentioned previously.

293 A random number lies at the heart of this equation; but what are the consequences of  
294 accepting randomness? As was discussed, randomness means that the growth rate of individual  
295 crystals can not be calculated precisely, but only the distribution shape can be predicted. In an  
296 analogy to crystal growth, randomness also appears in the foundations of quantum mechanics.  
297 The double slit experiment indicates that one can not calculate (based on the Schrödinger  
298 equation) the precise location of an electron fired through double slits onto a fluorescent screen,  
299 but one can only predict the shape of the distribution of a large number of electrons striking the  
300 screen. Likewise, one can not predict the moment for the radioactive decay of an individual  
301 atom, but only the decay rate for a large group of atoms. Stochastic models also are used to  
302 model chemical reactions (Gillespie 2007). In fact, many natural systems likely have such built-  
303 in randomness (Mann 1970), especially if they express a lognormal distribution. The presence of  
304 a random component means that experimental results are not precisely reproducible no matter  
305 how much care is taken. However, on the positive side, the presence of randomness frees us  
306 from a completely deterministic world view.

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313 to acknowledge pioneering papers on the use of CSDs in geology by Marsh (1988), Cashman  
314 and Ferry (1988), and Cashman and Marsh (1988), papers that were partly based on  
315 investigations of crystal growth in continuous-flow industrial crystallizers by Randolph and

316 Larson (1971). Such geological studies generally assume a constant-rate growth law in a  
317 population balance equation, whereas the present paper emphasizes a different approach. I am  
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## 320 REFERENCES CITED

- 321 Badino, G.V., Ferreira, A., Forti, P., Giovani, P., Giulivo, I., Infante, G., Lo Mastro, F., Sanna,  
322 L., and Tedeschi, R. (2009) The Naica caves survey. Fifteenth International Congress of  
323 Speleology At: Kerrville, Texas, 1764-17869.
- 324 Bove, D.J., Eberl, D.D., McCarty, D.K., and Meeker, G.P. (2002) Characterization and modeling  
325 of illite crystal particles and growth mechanisms in a zoned hydrothermal deposit, Lake  
326 City, Colorado. American Mineralogist, 87, 1546-1556.
- 327 Carlson, W. (1999) The case against Ostwald ripening of porphyroblasts. Canadian Mineralogist,  
328 37, 403-413.
- 329 Cashman, K.V., and Ferry, J.M. (1988) Crystal size distribution (CSD) in rocks and the kinetics  
330 and dynamics of crystallization iii. Metamorphic crystallization. Contributions to  
331 Mineralogy and Petrology, 99, 401-405.
- 332 Cashman, K.V., and Marsh, B.D. (1988) Crystal size distribution (CSD) in rocks and the kinetics  
333 and dynamics of crystallization ii. Makaopuhi lava lake. Contributions to Mineralogy and  
334 Petrology, 99, 292-305.
- 335 De Yoreo, J.J., Gilbert, P.U.P.A., Sommerdijk, N.A.J.M., Penn, R.L., Whitelam, S., Joester, D.,  
336 Zhang, H., Rimer, J.D., Navrotsky, A., Banfield, J.F., Wallace, A.F., Michel, F.M.,  
337 Meldrum, F.C., Cölfen, H., and Dove, P.M. (2015) Crystallization by particle attachment

- 338 in synthetic, biogenic, and geologic environments. *Science*, 349, print extended abstract  
339 at pg. 498, online at aaa6760 DOI: 10.1126/science.aaa6760.
- 340 Eberl, D.D. (2004) Quantitative mineralogy of the Yukon River system: Changes with reach and  
341 season, and determining sediment provenance. *American Mineralogist*, 89, 1784-1794.
- 342 Eberl, D.D. (2022) On the formation of Martian blueberries. *American Mineralogist*, 107, 153-  
343 155.
- 344 Eberl, D.D., and Srodon, J. (1988) Ostwald ripening and interparticle-diffraction effects for illite  
345 crystals. *American Mineralogist*, 73, 1335-1345.
- 346 Eberl, D.D., Srodon, J., Kralik, M., Taylor, B.E., and Peterman, Z.E. (1990) Ostwald ripening of  
347 clays and metamorphic minerals. *Science*, 248, 474-477.
- 348 Eberl, D.D., Drits, V.A., and Srodon, J. (1998) Deducing crystal growth mechanisms for  
349 minerals from the shapes of crystal size distributions. *American Journal of Science*, 298,  
350 499–533.
- 351 Eberl, D.D., Drits, V.A., and Srodon, J. (2000) User's guide to GALOPER --: a program for  
352 simulating the shapes of crystal size distributions—and associated programs: U.S.  
353 Geological Survey Open-File Report, OF 00-505, 44 pp.
- 354 Eberl, D.D., Kile, D.E., and Drits, V.A. (2002a) On geological interpretations of crystal size  
355 distributions: Constant vs. proportionate growth. *American Mineralogist*, 87, 1235–1241.
- 356 Eberl, D.D., Kile, D.E., and Hoch, A.R. (2002b) Crystallization of powders having uniform  
357 particle sizes by Ostwald ripening at large levels of supersaturation. U.S. Patent  
358 6,379,459, April 30, 2002.



- 359 Gillespie, D.T. (2007) Stochastic simulation of chemical kinetics. *Annual Review of Physical*  
360 *Chemistry*, 58, 35-55.
- 361 Ivanov, V.K., Fedorov, P.P., Baranchikov, A.Y., and Osiko, V.V. (2014) Oriented attachment of  
362 particles: 100 years of investigations of non-classical crystal growth. *Russian Chemical*  
363 *Reviews*, 83, 1204-1222.
- 364 Kile, D.E., and Eberl, D.D. (1999) Crystal growth mechanisms in miarolitic cavities of the Lake  
365 George ring and vicinity, Colorado. *American Mineralogist*, 84, 718-724.
- 366 Kile, D.E., and Eberl, D.D. (2003) On the origin of size-dependent and size-independent crystal  
367 growth: Influence of advection and diffusion. *American Mineralogist*, 88, 1514-1521.
- 368 Kile, D.E., Eberl, D.D., Hoch, A.R., and Reddy, M.M. (2000) An assessment of calcite crystal  
369 growth mechanisms based on crystal size distributions. *Geochimica et Cosmochimica*  
370 *Acta*, 64, 2937-2950.
- 371 Koch, A.L. (1966) The logarithm in biology 1. Mechanisms generating the lognormal  
372 distribution exactly. *Journal of Theoretical Biology*, 12, 251-268.
- 373 Lifshitz, I.M., and Slyozov, V.V. (1961) The kinetics of precipitation from supersaturated solid  
374 solutions. *Journal of Physics and Chemistry of Solids*, 19, 35-50.
- 375 Markworth, A.J. (1970) The kinetic behavior of precipitate particles under Ostwald ripening  
376 conditions. *Metallography*, 3, 197-208.
- 377 Mann, C.J. (1970) Randomness in nature. *Geological Society of America Bulletin*, 81, 95-104.
- 378 Marsh, B.D. (1988) Crystal size distribution (CSD) in rocks and the kinetics and dynamics of  
379 crystallization. 1. Theory. *Contributions to Mineralogy and Petrology*, 99, 277-291.

- 380 Miyazaki, K. (1971) Ostwald ripening of garnet in high P/T metamorphic rocks. Contributions to  
381 Mineralogy and Petrology, 108, 118-128.
- 382 Randolph, A.D., and Larson, M.A. (1971) Theory of Particulate Processes: Analysis and  
383 Techniques of Continuous Crystallization, 1st Edition, 251 p. Academic Press, New  
384 York.
- 385 Stefan-Kharicha, M., Kharicha, A., Zaidat, K., Reiss, G., Essl, W., Goodwin, F., Wu, M.,  
386 Ludwig, A., and Mugraue, C. (2020) Impact of hydrodynamics on growth and  
387 morphology of faceted crystals. Journal of Crystal Growth, 541, 1-11.
- 388 Wagner, C. (1961) Theorie der alterung von niederschlägen durch umlösen (Ostwald reifung).  
389 Zeitschrift Fuer Elektrochimie, 65, 581–591 (in German).

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## Figures

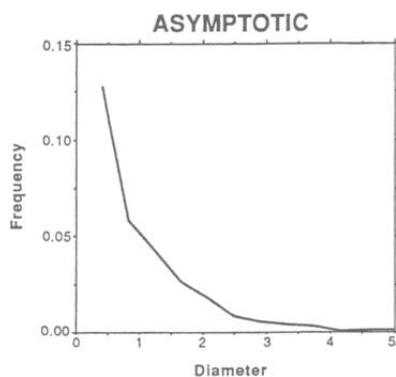
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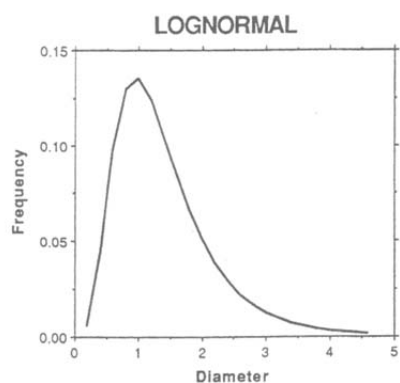
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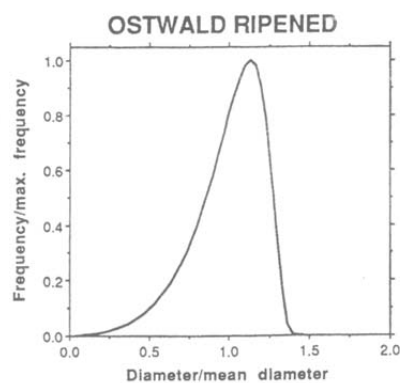
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407 **Figure 1.** The three fundamental shapes for crystal size distributions. All have been produced in

408 synthesis experiments, by calculation, and have been found in nature. This figure is from

409 Kile et al. (2000).