

## On geological interpretations of crystal size distributions: Constant vs. proportionate growth

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### ABSTRACT

Geological interpretations of crystal size distributions (CSDs) depend on understanding the crystal growth laws that generated the distributions. Most descriptions of crystal growth, including a population-balance modeling equation that is widely used in petrology, assume that crystal growth rates at any particular time are identical for all crystals, and, therefore, independent of crystal size. This type of growth under constant conditions can be modeled by *adding* a constant length to the diameter of each crystal for each time step. This growth equation is unlikely to be correct for most mineral systems because it neither generates nor maintains the shapes of lognormal CSDs, which are among the most common types of CSDs observed in rocks. In an alternative approach, size-dependent (proportionate) growth is modeled approximately by *multiplying* the size of each crystal by a factor, an operation that maintains CSD shape and variance, and which is in accord with calcite growth experiments. The latter growth law can be obtained during supply controlled growth using a modified version of the Law of Proportionate Effect (LPE), an equation that simulates the reaction path followed by a CSD shape as mean size increases.

### INTRODUCTION

There may be a serious flaw in application of the popular crystal size distribution (CSD) analysis method that uses population-balance modeling. This technique for analyzing CSDs was developed in the chemical engineering industry (Randolph and Larson 1971) and first applied to rocks by Marsh (1988). The problem discussed here differs from the one recently proposed by Pan (2001) concerning inherited correlation, the validity of which has been debated (Schaeben et al. 2002; Marsh and Higgins 2002; Pan 2002a, 2002b). The present problem is related to the assumption, made in most geological papers on the subject, that, once nucleated, all crystals will grow at the same linear rate, a rate that is independent from crystal size.

The solution to the population-balance equation used with these (and other) assumptions is:

$$\ln(n) = \ln(n^0) - L/G\tau \quad (1)$$

where  $n$  is the crystal population density (number of crystals per given size class per unit volume);  $L$  is the characteristic crystal size, measured for a consistent linear direction in the crystals;  $n^0$  is the population density of nucleus-size crystals (it is  $n$  when  $L$  approaches zero);  $G$  is the mean linear growth rate, which is independent of  $L$ ; and  $\tau$  is the average crystal residence time in the system (Randolph and Larson 1988; Marsh 1988; Cashman and Marsh 1988; Mersmann 2001).

Equation 1, which is used both by chemical engineers and by geologists, is a greatly simplified version of the more general population-balance equation. According to Mersmann (2001), the derivation and application of Equation 1 assumes

ideal mixing in a continuously operated industrial crystallizer that is running in a steady-state condition in which there are no fluctuations in operating conditions with respect to time. The feed solution is generally free of crystals, and the slurry is removed continuously at a single flow rate. There is assumed to be no crystal breakage, attrition or agglomeration, and solution and crystals have the same mean residence time ( $\tau$ ) in the crystallizer. In addition, the linear crystal growth rate is assumed to be independent of crystal size, which is the assumption that is the focus of the present paper. Also according to Mersmann (2001, p. 156), Equation 1 applies only to MSMMPR (mixed suspension, mixed product removal) crystallizers.

It will be shown that a linear growth rate is not independent of size, but, rather, that growth rates which generally increase with crystal diameter provide a more robust description of observed CSDs for most crystallizing systems. Other investigations using alternative calculation methods, which have assumed a growth rate that is independent of crystal size (e.g., Kretz 1966; Carlson et al. 1995), and constant growth equations that are discussed in Nielson (1964), Kirkpatrick (1981), Randolph and Larson (1988), and Lasaga (1998) also may be unrealistic. Therefore, geologic conclusions drawn from Equation 1 and from the alternative methods are questionable. These conclusions involve both qualitative models of geologic processes, such as the movement, mixing, and crystallization of magmas, and quantitative calculations such as nucleation rates, residence times, or growth rates for crystals in magmatic and metamorphic rocks.

### A COMPARISON BETWEEN GROWTH EQUATIONS

Size-independent (constant) crystal growth, for a given crystal in a population of crystals, is described by:

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$$X_{j+1} = X_j + k_j \quad (2)$$

where  $X_j$  is the crystal diameter after  $j$  iterations of Equation 2 (or after  $j$  time steps),  $X_{j+1}$  is the diameter after one additional iteration, and  $k_j$  is constant for all crystals for a given iteration. Equation 2 is a form of an equation known in the chemical engineering literature as “McCabe’s delta L law” (McCabe 1929), which states that geometrically similar crystals of the same material when suspended in the same solution grow at the same linear rate (Canning and Randolph 1967). Such constant growth was later shown by McCabe himself (McCabe and Stevens 1951) to be relatively unimportant for describing growth in industrial crystallizers in comparison to size-dependent growth because of the effect of size on crystal velocity through solution.

At first, growth by McCabe’s law seems to be a reasonable model for calculating how crystals in populations of crystals may grow, especially for crystals that are large enough to be minimally affected by the Gibbs-Thomson effect (i.e., Ostwald ripening; Lasaga 1998). There are no obvious thermodynamic or kinetic reasons to suppose that ions should migrate to or be incorporated into a crystal’s surface at a rate that is directly proportional to crystal diameter. However, the phenomenon of size-dependent growth (often accompanied by growth dispersion in which crystals of the same size grow at different rates) has been reported widely in experiments [see references in Randolph and Larson (1988), Marsh (1988), Eberl et al. (1998a), and Mersmann (2001)]. Marsh (1988; Eq. 56) suggested a completely arbitrary but flexible function to describe this type of growth, but subsequent papers in the geological literature (e.g., most recently, Higgins 2002) continue to assume constant growth. Use of McCabe’s law in the past was justifiable because a simple mathematical expression for size-dependent growth was lacking [although an empirical expression was presented by Canning and Randolph (1967), among others]. However, it will be shown that McCabe’s law is inadequate to describe crystal growth in many systems, and that there may be a better approach.

The consequences of having Equation 2 as the growth law are explored by considering some typical lognormal CSDs (Fig. 1). Lognormal CSD shapes are common for diverse mineral species from many types of igneous, metamorphic, and sedimentary rocks (Eberl et al. 1998a; and references therein). The CSDs in Figure 1 have mean sizes that range over seven orders of magnitude, and they are lognormal by a chi-square test (see significance levels in Fig. 1; significance levels  $>1\%$  indicate that the measured distributions are lognormal). The other commonly observed CSD shape in geologic systems is asymptotic (Eberl et al. 1998a), which also will be discussed below.

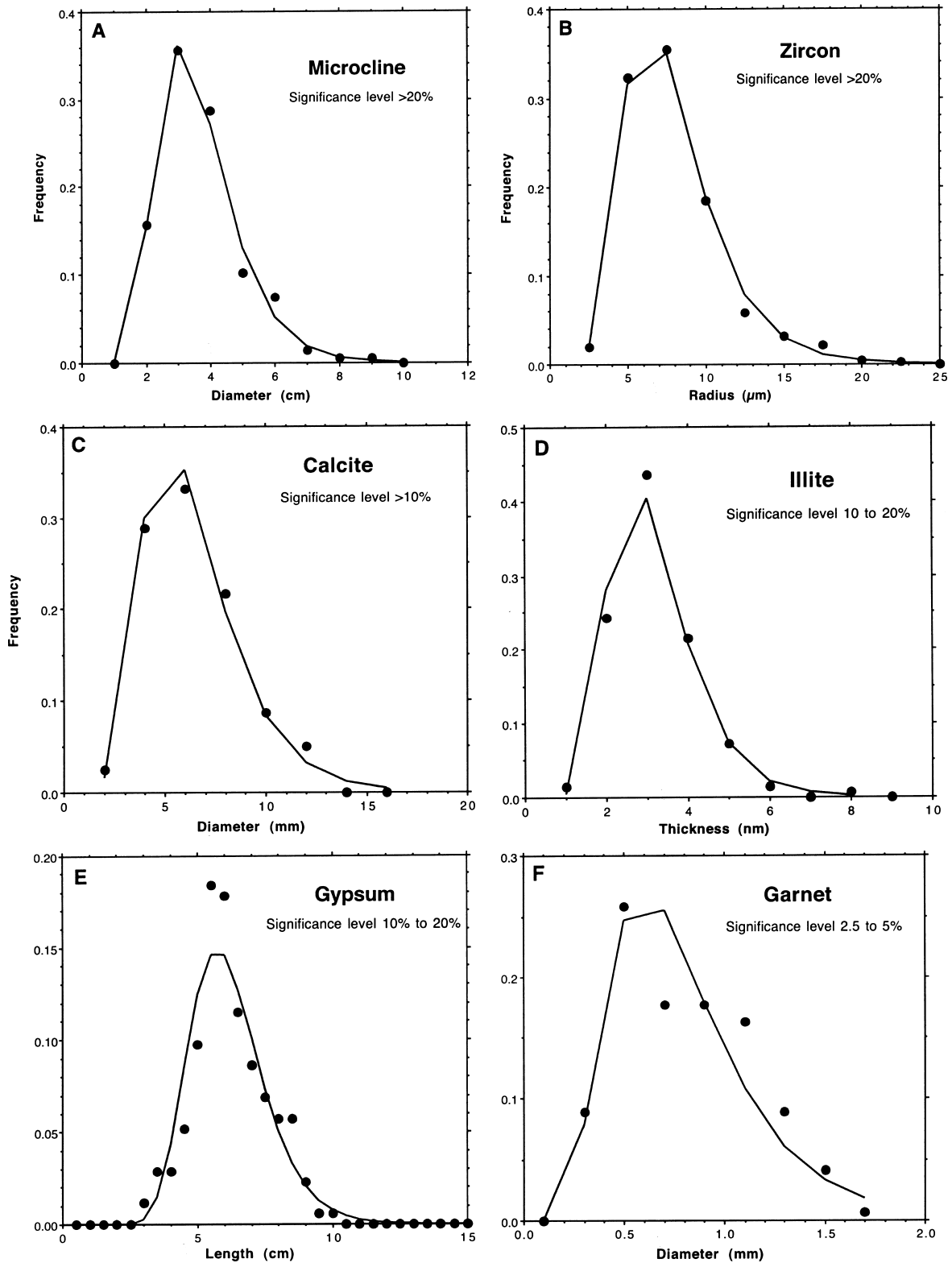
A lognormal CSD (e.g., Fig. 1A) cannot be generated readily by a constant-growth mechanism. For example, if all of the crystals nucleated simultaneously and grew according to Equation 2, the entire CSD would be represented by a single point in Figure 1A with a frequency of 1.0 and with a size that depends on the constant linear growth rate and time. If nucleation occurred through time at a constant rate, the CSD would be a line parallel to the  $x$  (size) axis. The only way to generate a lognormal-appearing CSD using a size-independent growth

rate in a batch system (i.e., in a system in which crystals cannot leave or enter) is to assume that the nucleation rate varied through time. For example, the CSD in Figure 1A could be generated if nucleation were to start slowly to yield the right side of the CSD, to build to a maximum rate to generate the mode, and then to die out quickly to give the short left tail of the CSD. Alternatively, the nucleation rate could have increased exponentially with time, but at the end of the process the fine crystals were resorbed, or annexed, or starved for reactants to give the down-turn on the left side of the CSD (e.g., Marsh 1998). In an open system where crystals can enter and leave (e.g., through magma mixing or crystal settling), various complex scenarios can be imagined that could approximate this CSD shape. However, the probability of fortuitously generating a lognormal CSD by one of these constant-growth mechanisms is highly unlikely to account for its common occurrence in diverse geological environments. Thus, to generate a lognormal shape frequently by differential nucleation, one would have to assume some unknown mechanism that would consistently nucleate a lognormal CSD. However, even if such a mechanism prevailed in the great diversity of systems that contain lognormal CSDs, subsequent crystal growth according to Equation 2 would destroy the CSD’s lognormality, because *a lognormal shape can be retained by multiplying its crystal sizes by a constant (Crow and Shimizu 1988), but not by adding a constant.*

Another argument against a constant growth rate according to Equation 2 is the general observation that nucleation occurs over a relatively short period of time at initially high levels of supersaturation (e.g., Lasaga 1998). The level of supersaturation drops quickly as nuclei appear and grow, rendering extended nucleation less likely. If the lognormal CSD was developed quickly by differential nucleation while the crystals were in the sub-micrometer size range, the absolute size difference between crystals would be maintained as crystals grew according to Equation 2 into the millimeter size range. In other words, if nucleation ceased while all of the crystals were still less than one micrometer in diameter, at the end of growth into the millimeter size range all of the crystals would be almost exactly the same size, differing by less than a micrometer. Alternatively, one could argue that nucleation occurred over a long interval. For example, the 2 cm crystals in the CSD in Figure 1A could have nucleated when the currently 4 cm-size crystals previously had grown to 2 cm; then both sizes grew to their current sizes at the same rate. This scenario requires a convoluted growth process whereby: (1) a large level of supersaturation was maintained over a long interval; and (2) crystals of all size classes would have had to nucleate and grow in the manner described to give a lognormal shape to the distribution at the growth limit.

The problems of forming and maintaining the shape of a lognormal CSD are solved if the shape is produced during growth rather than during nucleation. As has been discussed previously (Eberl et al. 1998a), a lognormal CSD can be generated mathematically from previously nucleated crystals by size-dependent (proportionate) growth according to the Law of Proportionate Effect (LPE):

$$X_{j+1} = X_j + \epsilon_j X_j \quad (3)$$



**FIGURE 1.** CSDs (solid circles) and lognormal fits (lines) with significance levels for chi-square test between the two. (A) Microcline, 1989 (Kile and Eberl 1999); (B) Zircon B, L total (Nemchin et al. 2001); (C) Calcite, SE Colorado (Kile et al. 2000); (D) Illite, Zempleni (Srodoń et al. 2000); (E) Gypsum from Jet, Oklahoma (this paper); (F) Garnet, Specimen 2 (Kretz 1966). Only the zircon CSD measurement (Fig. 1B) possibly is subject to stereological problems because it was measured from thin section.

where  $X_j$  is the initial diameter of a crystal in a population of crystals;  $\epsilon_j$ , termed system variability, is a small random number that ranges between limits (generally between 0 and 1), and that differs for each crystal and for each growth cycle; and  $X_{j+1}$  is the new crystal diameter after one growth cycle (i.e., one iteration) of Equation 3. Calculations using Equation 3 that are repeated several times for many crystals yield a lognormal size distribution. The number of iterations correspond to time in some, as yet, undetermined manner. The  $\epsilon_j X_j$  term leads both to size-dependent growth and to growth dispersion.

Equation 3 is basically empirical, but is assumed to be a fundamental crystal growth law because we know of no other way to form the lognormal distribution by growth, and because it provides a robust description of the observations. The lognormal shape can form in surface-controlled growth during which the volume of reactants available for growth during each cycle of Equation 3 is essentially unlimited. As crystallization proceeds, the growth type may change spontaneously from surface-controlled, in which the natural log-based variance [ $\beta^2 = \Sigma(\ln X - \alpha)^2 f(X)$ , where  $f(X)$  is the frequency of size  $X$ ] of the CSD increases linearly with the natural log-based mean size [ $\alpha = \Sigma(\ln X) f(X)$ ], to supply controlled, during which  $\beta^2$  may remain almost constant as  $\alpha$  increases. The growth mechanism may change as crystals grow larger because surface-controlled growth requires an exponentially increasing supply of reactants through time, and therefore cannot be sustained.

In the calculation for supply controlled growth, growth is limited proportionately by the volume of reactants available during each growth cycle (see Eq. 8 in Eberl et al. 1998a). Most of the crystal mass may be added during this type of growth, and the relative shape of the earlier-formed CSD (be it lognormal, asymptotic, Ostwald, or some other shape) is maintained. By this mechanism, for example, one can find the universal steady-state CSD shape for Ostwald ripening (which has a negative skew) at crystal sizes that are far too large for ripening to have occurred [because surface energy differences between crystals are too small; e.g., calcite in Kile et al. (2000); garnet in Miyazaki (1991)]. The Ostwald shape is formed by ripening at small sizes, and then the relative shape is preserved during supply controlled proportionate growth.

The above approach is favored by nearly exact (according to chi-square test) simulation fits [using the GALOPER computer program (The GALOPER program for simulating CSD growth is available from: [ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/mac\\_version](ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/mac_version) (or...[pc\\_version](ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/pc_version))/GALOPER); Eberl et al. (2001)] to the observed shapes of CSDs from diverse mineral systems [e.g., ice, dolomite, garnet, and galena in Eberl et al. (1998a); microcline and quartz in Kile and Eberl (1999); calcite in Kile et al. (2000); illite in Środoń et al. (2000)]. In addition, the preservation of CSD shapes during supply controlled proportionate growth has been demonstrated experimentally (Kile et al. 2000).

Jackson (1961, p. 31) may have been the first to suggest that lognormal size distributions found in rocks could be related to size-dependent growth, for olivine, chromite, and bronzite crystals in the Stillwater Complex, Montana. The mechanism that leads to proportionate growth is not well-established in the literature, but it has been suggested that such

growth results in part from a faster relative solution velocity around larger crystals during stirring (e.g., McCabe and Stevens 1951), or from a greater proportion of defects on the surfaces of large crystals (Garside and Jancic 1976), or from the effects of elastic strain (Ristic et al. 1997).

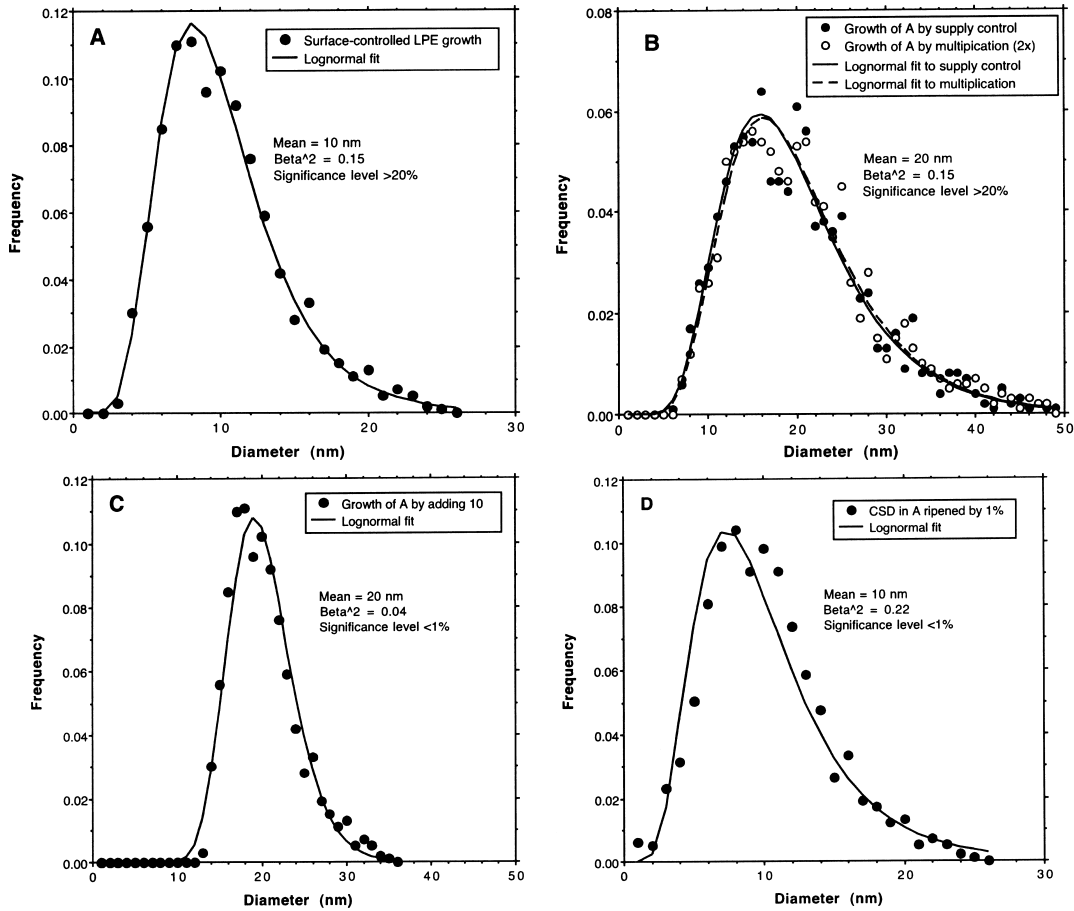
Although a definitive mechanism for the proportionate growth of crystals is lacking, there is ample evidence that the LPE (Eq. 3), and its modification during supply controlled growth, provide a robust empirical description of CSD behavior both in experimental systems (Kile et al. 2000, and references therein) and in natural systems (e.g., Nordeng and Sibley 1996; Kile and Eberl 1999; Makowitz and Sibley 2001).

The consequences of growing a lognormal CSD by different mechanisms is explored in Figure 2 using GALOPER calculations. The lognormal CSD in Figure 2A was simulated by surface-controlled LPE growth (Eq. 3; option 5 in GALOPER). It has a mean size of 10 nm and a variance ( $\beta^2$ ) of 0.15. It then was doubled in mean size (Fig. 2B, solid circles) by proportionate growth (supply controlled growth modification of Eq. 3; option 6 in GALOPER), which yielded another lognormal curve (significance level for chi-square test >20%) with the same  $\beta^2$ . In other words, the relative shape of the CSD in Figure 2A was preserved during proportionate growth. When the mean size of the CSD in Figure 2A is doubled by constant growth (Eq. 2), however, it loses its lognormal shape (Fig. 2C; significance level <1%; chi-square value is 49.08 vs. a critical value of 37.57 required for >1% significance, and the fit becomes worse with continued growth), and  $\beta^2$  decreases to 0.04. Continued growth by this mechanism would cause  $\beta^2$  to approach zero (no matter what the original CSD shape). Then all of the crystals would appear to have the same size. In other words, growth by Equation 2, if it occurred to a significant extent, could be recognized in the shapes of CSDs, and lognormal CSDs could not be maintained. In fact, with sufficient growth, CSDs in general could disappear, because at large sizes, all of the variation in size could be collected into a single size class. Hence, constant growth (Eq. 2) is unrealistic, especially for minerals having lognormal CSDs.

Figure 2D further indicates how sensitive the shape of a lognormal CSD is to modification by other growth mechanisms. The lognormal CSD in Figure 2A was subjected to a simulated Ostwald ripening by GALOPER to yield the CSD in Figure 2D. Although ripening was minimal (only 1% of the mass of the crystals passed through solution), this type of reaction destroys the CSDs lognormal shape (significance level is <1% in Fig. 2D), and can be recognized immediately in the CSD shape.

The growth of CSDs simulated by supply control (Fig. 2B) also can be modeled approximately if the crystal sizes in the initial distribution (Fig. 2A) are multiplied by a factor ( $f = \bar{X}/\bar{X}_0$ , where  $\bar{X}_0$  and  $\bar{X}$  refer to the initial and final mean sizes; e.g.,  $f = 20/10 = 2$ ), as is indicated by open circles in Figure 2B. Multiplication by  $f$  retains both the lognormal shape of the original distribution and its  $\beta^2$ . Therefore multiplication approximately models GALOPER-simulated, supply controlled crystal growth, during which  $\beta^2$  remains relatively constant, although the two methods of calculation have not yet been related in a mathematically formal manner.

The change in  $f$  with mean size for supply controlled growth,



**FIGURE 2.** The effect of growth mechanisms on the shape of a lognormal CSD. (A) Initial lognormal CSD (circles), simulated in GALOPER by LPE growth (Eq. 3; GALOPER option 5), with lognormal fit (line). (B) CSD in (A) is doubled in size by supply controlled growth (solid circles; GALOPER option 6) and by multiplication of the crystal sizes by 2 (open circles). (C) CSD in (A) is doubled in size by adding 10 nm to each crystal size. (D) CSD in (A) is Ostwald ripened (GALOPER closed system option 1), allowing 1% of the crystal mass to pass through solution.

in which reactants are available to the surface at a constant rate, can be derived from the empirical Equation 9 in Eberl et al. (1998a), which is based on GALOPER calculations:

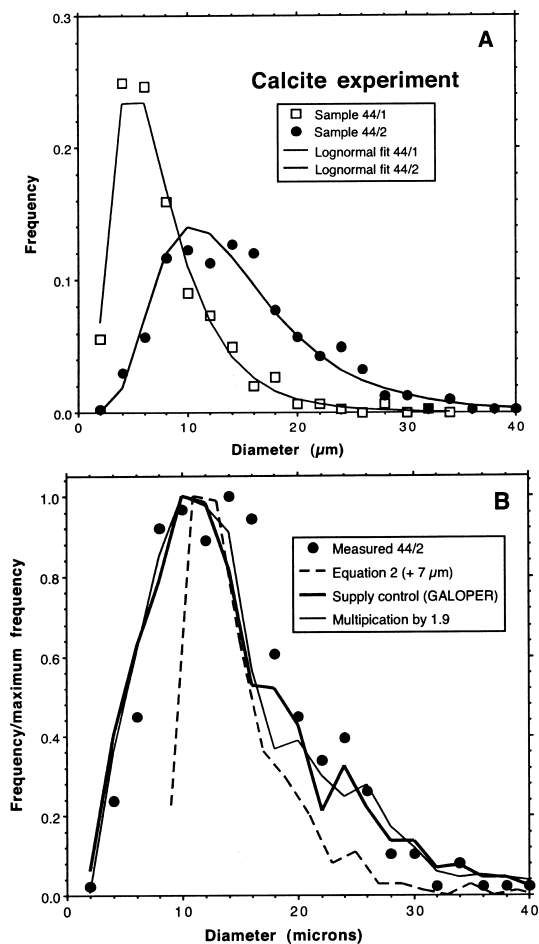
$$f = 1 + \frac{cn^{1/3}}{\bar{X}_0} \quad (4)$$

$\bar{X}_0$  is the initial mean size;  $n$  is the number of growth cycles (which may be a function of time); and  $c$  is a constant that is proportional to the constant total volume added during each growth cycle. Equation 4 can be used to predict the evolution of a CSD only if the initial and final CSDs have approximately the same  $\beta^2$ . Furthermore, Equation 4 cannot be used to predict the growth rate for individual crystals within a CSD, but only growth for the CSD as a whole, because  $f$  approximates a set of random numbers that vary for each crystal between certain limits (e.g., predictions for individual crystals differ for the two calculation methods shown in Fig. 2B, but the predicted CSD shapes are the same).

A critical laboratory experiment (Kile et al. 2000), designed

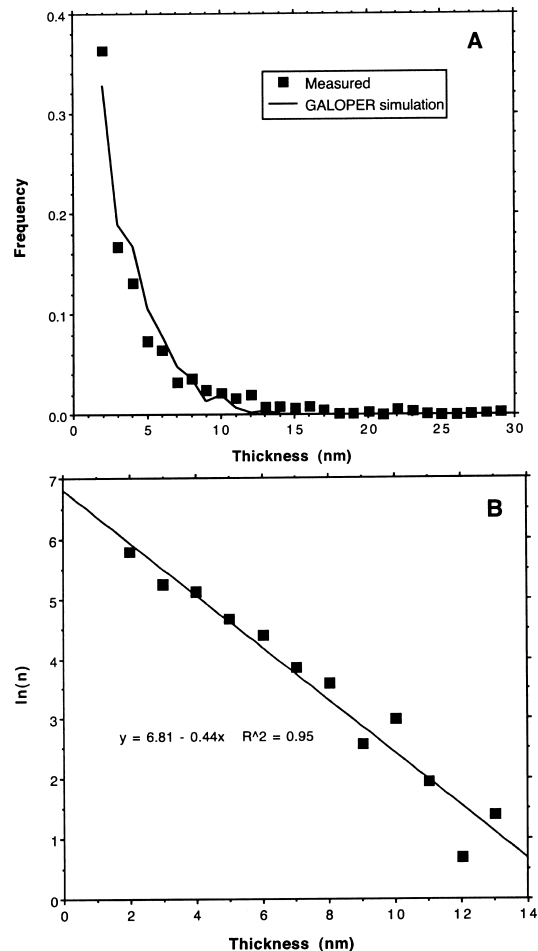
to simulate the previous calculations, was performed to distinguish between the growth behaviors described by Equations 2 and 3. In this experiment, calcite was nucleated and grown from a supersaturated solution, and the evolution of the CSD was measured through time. Both the initial and the final CSDs (Fig. 3A) were shown to be lognormal by chi-square test. Growth of the initial CSD by Equation 2, whereby all of the crystals grow by a constant amount, into the final CSD, while preserving the lognormal shape, is not possible. For example, increasing the mean size of the first distribution (7.8  $\mu\text{m}$ ) to that of the second CSD (14.8  $\mu\text{m}$ ) by adding 7  $\mu\text{m}$  to the size of each crystal (Eq. 2) yields a CSD that is too narrow (dashed line in Fig. 3B), whereas simulating the reaction path from CCNG-44/1 to CCNG-44/2 using Equation 3 with the supply controlled growth modification (option 6) in the GALOPER computer program (heavy line in Fig. 3B) yields a much better fit to the measured distribution. One also can multiply the sizes of the original CSD by the factor  $f = 14.8/7.8 = 1.9$  to realize an equivalent result (thin, solid line in Fig. 3B).

In addition to the lognormal distribution, the asymptotic distribution (Fig. 4A) is another common CSD in rocks. As-



**FIGURE 3.** CSDs measured (Kile et al. 2000) and calculated for calcite growth experiments. (A) Initial, measured CSD (CCNG-44/1; squares) and final, measured CSD (CCNG-44/2; circles) with lognormal fits (solid lines). The two calcites were taken from the same solution after different reaction times. (B) The final, normalized, measured CSD (CCNG-44/2; circles) modeled from the initial CSD (CCNG-44/1) by Equation 2 (broken line), by supply controlled modification of Equation 3 using the GALOPER program (thick solid line), and by multiplying by a constant (thin solid line).

suming constant growth (Eq. 2), this shape has been attributed to nucleation at an exponentially increasing rate (e.g., Higgins 2002). Assuming proportionate growth, however, this type of distribution is simulated in GALOPER by the mechanism of constant-rate (or accelerating-rate) nucleation with simultaneous size-dependent growth. In support of this mechanism, the asymptotic CSD shape has been produced in constant-rate nucleation experiments with calcite (see Fig. 2 in Kile et al. 2000). A semi-log plot (Fig. 4B) conveniently represents this particular CSD as a straight line. However, previous geological conclusions drawn from similar semi-log plots, using Equation 1 and the assumption of a constant linear growth rate, may be misleading. For example, if constant-rate nucleation occurs over an extended period, the semi-log plots yield curved (rather than straight) lines that are concave upward, as also has been



**FIGURE 4.** CSD for the thicknesses of illite crystals (Le Puy illite; Eberl et al. 1998b). (A) Measured distribution compared with GALOPER simulation; (B) Natural logarithm of the number ( $n$ ) of crystals per size class per 1000 nucleated crystals (from GALOPER simulation) vs. crystal thickness. The y-axis differs slightly from that used in population balance modeling, for which the units are the natural logarithm of the number of crystals per size class per unit volume of the system.

noted by Marsh (1988). This shape is related to the faster growth of larger crystals during simultaneous nucleation and growth. Such concave curves are shown, for example, in the plots of Higgins (2002, Fig. 2a) for crystals from andesite lavas, and in Cashman and Marsh (1988, Fig. 4) for Makaopuhi lava lake plagioclase, although the curvature is interpreted differently by these authors.

### GEOLOGICAL HISTORY FROM CSDS

Both experimental and natural mineral CSDs are empirically described by size-dependent growth (Eq. 3, and its modification during supply controlled growth), but are inconsistent with constant growth (Eq. 2). These two growth laws lead to very different interpretations of geologic history that can be deduced from CSDs. For example, assuming constant growth

(Eq. 2), the oldest crystals in the CSDs shown in Figure 1 are the largest (those in the extreme right tails of the distributions) because these crystals must have nucleated first. Proportionate growth (Eq. 3), however, indicates that all of the crystals could have nucleated at the same time, with those in the right tails having grown larger as a result of size-dependent growth and growth dispersion. If Equation 2 is assumed, the CSDs record nucleation history, whereas Equation 3 indicates that these particular CSDs developed in response to a growth mechanism, but tells us little about nucleation history. Assuming constant growth and reasonable growth times, some workers (e.g., Cashman and Marsh 1988) have used Equation 1 to extract nucleation and growth rates from CSDs, using plots similar to that shown in Figure 4B, whereas it may not be possible to determine rates accurately in this manner when assuming size-dependent growth, especially for log-linear plots that are curved.

Although absolute rates for crystallization processes cannot be calculated from CSD shapes alone, the relative reaction history of a mineral can be deduced because CSD shape may be reaction-path dependent (Eberl et al. 2000, 2001). Such histories may be modeled by simulating CSDs with GALOPER, or with similar computer programs. It may be possible to link these relative growth rates to absolute rates by finding the relation between time measured in the field or in laboratory experiments and the number of growth cycles found by simulation.

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