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FACTORS INFLUENCING THE GRAIN SIZE DISTRIBUTION OF AUTHIGENIC MINERALS

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ABSTRACT. Authigenic minerals in sediments often have grain size distributions that fall in a relatively narrow size range. A simple possible interpretation of this observation is that nucleation of authigenic mineral crystals must be a singular short-term event, and their subsequent growth takes place concurrently under fairly uniform conditions leading to a relatively narrow grain size distribution. Although such circumstances can be readily obtained in batch reactors, in most natural systems this set of conditions is probably rare.

In this paper we examine processes occurring for assemblages of crystals whose initial size is greater than few tenths of a micron where contributions of surface free energy to mineral solubility are close to negligible. Model results indicate that for systems in which growth occurs without concurrent nucleation the evolving grain size assemblage differs substantially between transport and surface-controlled growth processes, and that the size ratio of the largest to smallest crystals can decrease by orders of magnitude. In an initially steady-state system, where the solution composition is buffered by a metastable precursor phase and rates of nucleation and surface-controlled growth are constant, the net growth rate increases as the cube of time (reaction progress) leading to "quenching" of the system and a relatively narrow and close to uniform distribution of grain size.

INTRODUCTION

Although it is true that authigenic minerals can be found occurring in sediments and sedimentary rocks over a wide range of grain sizes, it is nonetheless remarkable that in certainly many, if not most, sediments minerals formed as a product of diagenesis occur over a relatively narrow size range. This size range is often dominantly from several tenths to ~ 15 microns in diameter (for example, for authigenic pyrite see Love and Amstutz, 1966, fig. 1). The questions therefore arise as to why this is so and what may be consequently inferred regarding the processes controlling formation of authigenic minerals in sediments.

One is drawn initially to relatively straightforward explanations based on classical models for crystal nucleation and growth from solution (Nielson, 1964; Walton, 1967; Strickland-Constable, 1968; Ohara and Reid, 1973; Tiller 1991). The simplest case (fig. 2) is one in which a critical supersaturation is obtained in a solution at which time there is rapid formation of multiple crystal nuclei that grow at approximately the same rate, without further significant nuclei formation, until equilibrium is reached between crystals of close to the same size and the mother solution.

These conditions and results can often be closely achieved in batch chemical reactors, but it is dubious if they are of general pertinence to

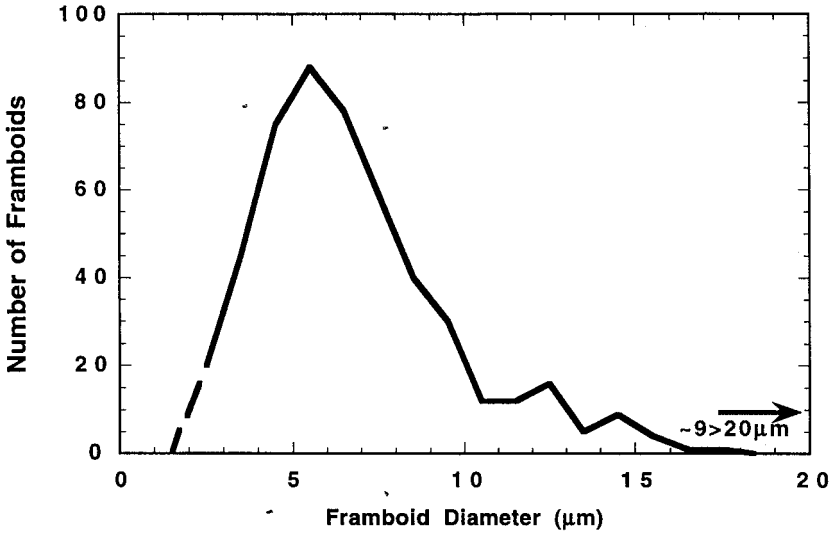

Fig. 1. The size distribution of pyrite framboids (500) in the Chattanooga Shale. Note that the size of the individual grains composing the framboids are usually very uniform in size and that their size is close to proportional to that of the framboid. Based on the data of Love and Amstutz (1966).

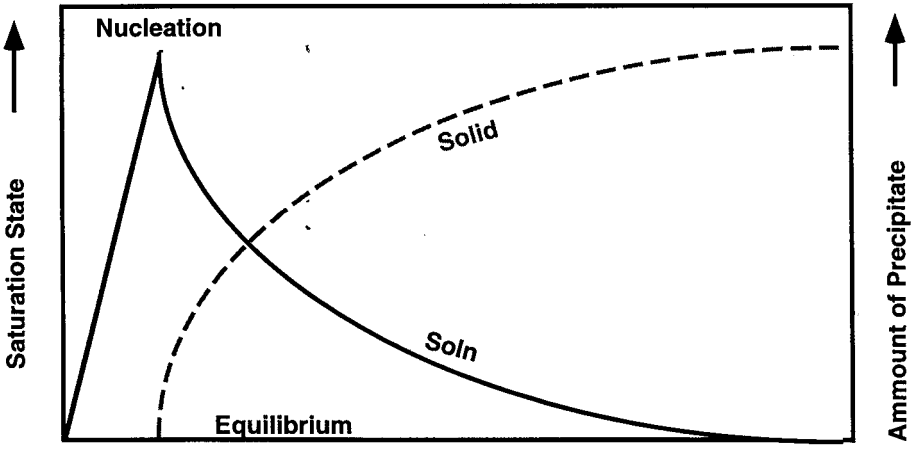

Fig. 2. Schematic model for nucleation and crystal growth.

authigenic mineral formation during diagenesis. This is because often close to steady-state supersaturations are maintained in sediments over extended periods of time via buffering of solution composition by a more soluble metastable phase (for example, aragonite → calcite;

mackinawite → pyrite; opal → quartz). Under such quasi-steady-state conditions nucleation and growth rates should be close to constant. It is also likely that for some phases strongly non-steady-state pore water saturation states may occur that vary widely on a time dependent (for example, seasonal) basis leading to repeated episodic nucleation events and highly variable growth rates. The existence of heterogeneities in natural sediments can lead to "micro-environments" in which differences in saturation states and hence mineral growth rates result (for example, see recent discussion of Nordeng and Sibley, 1996, of the importance of microenvironments for controlling the size distribution of ancient dolomites). Such conditions may contribute to a widening of the spread of authigenic mineral grain sizes but may be at least partially ameliorated during early diagenesis by processes such as bioturbation that lead to physical mixing of sediments.

In this paper we have undertaken a theoretical examination of possible explanations as to why the complex processes associated with authigenic mineral formation in sediments may lead to the commonly observed relatively narrow ranges in grain size.

INFLUENCE OF SURFACE FREE ENERGY ON THE LOWER SIZE LIMIT OF AUTHIGENIC MINERALS

The solubility product of a solid can be calculated from the Gibbs free energy of the dissolution reaction, which is classically considered to be the difference between the Gibbs free energies of formation of the dissolution products and the solid. For example, for a solid A_xB_y, $A_xB_y \rightarrow xA^{y+} + yB^{x-}$ under standard state conditions (25°C, 1 bar) $\Delta G_r^0 = (x\Delta G_{fa}^0 + y\Delta G_{fb}^0) - \Delta G_{fAxBy}^0$. Then $\ln K_{sp(AxBy)} = -\Delta G_r^0/RT$, where R is the ideal gas constant and T is thermodynamic temperature (at 25°C = 298.15 K). Because the thermodynamic activity of a solid is unity, $K_{sp(AxBy)} = a_A^x a_B^y$.

However, surfaces of solids are areas of structural discontinuity that therefore have higher Gibbs free energies than those of bulk solids. For solids with large surface areas, the surface free energy (σ_s) can make a significant contribution to the total molar free energy of the solid and cause an increase in solubility. This relationship can be represented by the following equations (see Definition of Symbols, next page).

$$\ln K_{sp,AxBy} = \frac{-(\Delta G_{r,AxBy}^0 - \sigma_s \bar{A})}{RT} = \ln K_{sp,bulk} + \left(\frac{\sigma_s}{RT}\right)\bar{A} \qquad (1)$$

The surface area per mole of a solid ($\bar{A}$), for solids with common morphologies, can usually be well approximated as $\bar{A} = \beta V r^{-1}$, where β is 3 for a sphere and 6 for a cube. Collecting terms yields

$$\ln K_{sp,AxBy} = \ln K_{sp,bulk} + \lambda r^{-1} \qquad (2)$$

where $\lambda = \beta V(\sigma_s/RT)$. In a system where the solution is in equilibrium with a solid composed of small (submicron) crystals, the solution super-

saturation with respect to large crystals of the solid will be

$$\Omega_{AxBy} = e^{\lambda/r}. \quad (3)$$

Calcite will be used as an example to obtain an idea of the approximate size range over which significant increases in Ω occur. Values used

Definition of Symbols

Symbol	Definition
$\underline{A}$	Surface area of a solid
$\overline{A}$	Surface area per mole of a solid
a_i	Thermodynamic activity of species i
c	Concentration of a dissolved component
c_e	Equilibrium concentration of dissolved component
D	Molecular diffusion coefficient in solution
$\Delta G^0_{f,i}$	Standard state Gibbs free energy of formation of component i
ΔG^0_r	Standard state Gibbs free energy of reaction
J	Precipitation rate
U	Nucleation rate
K_{sp}	Thermodynamic solubility product
k	Rate constant
k	Boltzmann constant
N	Number of grains in a system
n	Order of surface controlled reaction
$P(r_0)$	Initial grain size distribution function
Q(r)	Grain size distribution function
R	Ideal gas constant
r	Radius of sphere or edge length of cube
$\bar{r}$	Average radius
T	Thermodynamic temperature
t	Total elapsed time
v	Radial growth rate
V	Molar volume
α	Pre-exponential constant for nucleation rate
β	Geometric shape factor for crystals
$\Delta(t)$	$= 2DV \int_0^t (c - c_e)dt$ $(2DVc_e \int_0^t (\Omega - 1)dt$
$\nabla(t)$	$= k \int_0^t (\Omega - 1)^n dt$
λ	$= \beta V(\sigma_s/RT)$
ν	Molecular volume (V/Avogadro's Number)
σ_s	Surface free energy of a solid
τ	Time since an event
Ψ	$= -\left(\frac{16\pi}{3}\right)\left[\frac{\sigma^3\nu^2}{(kT)^3}\right]$
$\Omega_{mineral}$	Saturation state of solution with respect to a given mineral

to compute $\Omega_{calcite}$ are V = 36.93 cm^3 mol^{-1}; β = 6 (cube); σ_s = ~80 erg cm^{-2} (Berner and Morse, 1974); T = 298.15 K (25°C). This results in (using μm as the edge length scale) $\lambda = 7.15 \times 10^{-3}$ μm and

$$\Omega_{calcite} = \exp\left(\frac{7.15 \times 10^{-3}}{r}\right). \quad (4)$$

The influence of size on saturation state is less than 1 percent for calcite with an edge length grater than 1 μm but increases substantially below 0.1 μm where the saturation state has risen to about 1.07. This approximate size range for the transition between the surface contribution to solubility being relatively unimportant to becoming of major importance also holds for even much higher surface free energies. For example, if σ_s is tripled to 240 ergs cm^{-2}, the respective saturation states at r = 1 and 0.1 μm are 1.02 and 1.24.

Although it is difficult to obtain accurate values for surface free energies, it has been possible to derive a relation between surface tension of ionic crystals and their solubility (see, for example, Christoffersen and others, 1991) which demonstrates that as solubility decreases, surface free energy increases. For example, potassium chloride, which is very soluble, has a σ_s = 30 erg cm^{-2} (Nielsen and Söhnel, 1971), whereas hematite, which is very insoluble, has a σ_s = 1200 erg cm^{-2} (Langmuir, 1971). Such a relationship may, at least partially, explain the strong tendency of authigenic minerals to follow a paragenetic sequence that is usually in accordance with the Ostwald Step Rule (Morse and Casey, 1988). It is worth noting that the surface areas of minerals with a cubic form and edge length of 0.1 μm are generally in the range of about 10 to 30 m^2 g^{-1} (for example, calcite 22.1 and pyrite 14.4 m^2 g^{-1}).

In summary, for most authigenic minerals of general interest there will be a strong tendency for coarsening to occur as more soluble grains, smaller than a few tenths of microns in size, dissolve, and less soluble larger grains grow by the process known as Ostwald Ripening (see Morse and Casey, 1988, for discussion with respect to sediments). However, the influence of surface free energy on solubility diminishes to what is probably negligible significance as grain size typically approaches about 1 micron. Consequently, it is likely that in most sediments the lower limit of authigenic mineral grain size is set close to a few tenths of microns, where surface energy no longer strongly influences solubility.

REDUCTION OF RELATIVE SPREAD IN GRAIN SIZE THROUGH SIMULTANEOUS MULTI-CRYSTAL GROWTH

Basic concepts.—Before embarking on our presentation of a mathematical model to explain how it may be possible to produce a relatively narrow range of grain sizes for authigenic minerals in sediments, we believe it is useful to first put forth the central concepts of the model in relatively simple approximate form. This will be followed by a model for crystal growth in a system where there is an initial population of differently sized crystals but no new nuclei form[ed], and then a more complex

model will be presented in which continuous nucleation and growth take place.

For our example we specify a solution that contains only 2 crystals: one with an initial radius $r_{1(0)} = 0.1$ μm, and the other with an initial radius of $r_{2(0)} = 10$ μm. The initial crystal size ratio [$r_{2(0)}$:$r_{1(0)}$] is therefore 100. The solution is supersaturated with respect to the crystals at a constant value so that there is a constant radial growth rate v (μm h^{-1}). In this example, we neglect the probably small influence of grain size on solubility. It should be noted that in industrial fluidized-bed reactors, for some, but not all salts studied, it was observed that large particles can grow faster than small particles. This is primarily due to hydrodynamic influences associated with the faster sinking velocity of the larger particles and is known as the solution velocity effect. It has been demonstrated that this occurs for particles greater than 500 μm in diameter (Mullin, 1974). Consequently, although our assumption of a constant radial growth rate for small particles of differing size in a uniform environment is probably a reasonable approximation for fine grains in a sediment, it should not be taken as true without exception.

The radius of a crystal as a function of time of precipitation (t) will be

$$r_{i(t)} = r_{i(0)} = vt. \tag{5}$$

If the velocity of growth is equal to $0.1r_{1(0)}$ per unit time, then the ratio of r_2:r_1 with time will be

$$\frac{r_2}{r_1} = \frac{100 + 0.1t}{1 + 0.1t}. \tag{6}$$

Results are shown in figure 3 for a 50 percent increase in r_2 to 15 μm. Note that the relative difference in size between r_2 and r_1 changes from a factor of 100 to only about 3. Although considerably simplified from natural systems, this example demonstrates how differences in *relative* crystal sizes can be reduced substantially during crystal growth.

Multiple sized crystal growth without nucleation.—We next will consider a system in which the degree of supersaturation is high enough to cause growth of existing crystals but below that required for formation of new nuclei. Consequently, the number of grains will remain constant, but their size will change with time. Again for the sake of simplicity the saturation state of the solution will be held constant (growth rate changes for diffusion-controlled growth). Both diffusion-controlled and surface-controlled growth mechanisms will be considered and examples given using an initial broad Gaussian distribution of grain size. It should be noted, however, that particle size frequency distributions produced for systems where Ostwald ripening is controlling are often close to log normal when particle size is divided by the mean particle size (see examples and discussion of Eberl and others, 1990).

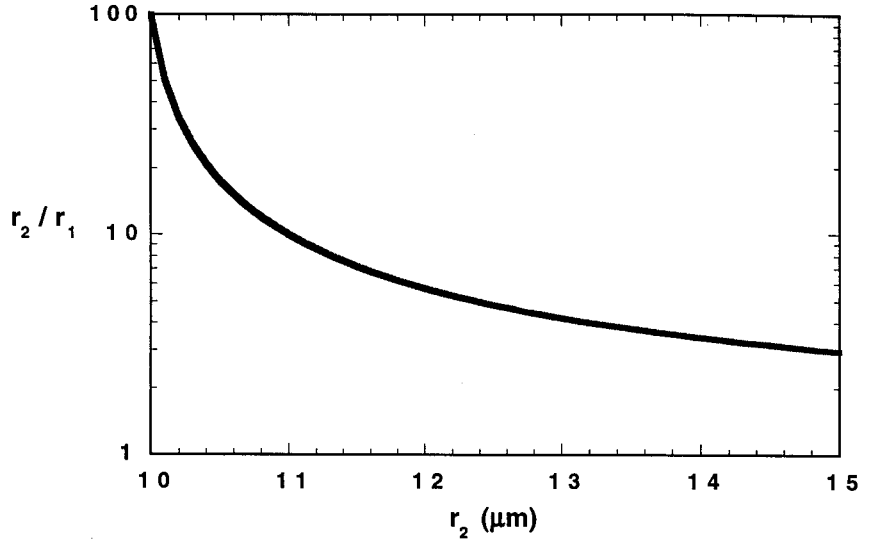

Fig. 3. Change in the size ratio of two crystals as a function of the radius of the larger crystal. See text for discussion.

Let the initial grain size distribution be described by a function $P(r_0)$ such that the total number of grains (N) is

$$N = \int_0^\infty P(r_0)dr_0 \tag{7}$$

and the average grain size ($\overline{r_0}$) is

$$\overline{r_0} = \frac{\int_0^\infty r_0 P(r_0)dr_0}{N}. \tag{8}$$

Initially the number of grains lying in the size range between r_0 and $r_0 + dr_0$ is $P(r_0)dr_0$, and as time progresses the size range becomes r to r + dr. The size distribution then becomes Q(r), and because the number of grains remains constant we have

$$P(r_0)dr_0 = Q(r)dr \text{ or } Q(r) = \frac{P(r_0)dr_0}{dr}. \tag{9}$$

Q(r) will change during the growth process in a manner that depends on the growth mechanism. For diffusion-controlled growth, the crystal growth rate is often well approximated as (Nielsen, 1969)

$$\frac{dr}{dt} = \frac{DV(c - c_e)}{r} = \frac{DVc_e(\Omega - 1)}{r} \tag{10}$$

where D is the molecular diffusion coefficient in solution, c is the concentration in the bulk solution, and c_e is the equilibrium concentration. Integration of eq (10) leads to

$$r = [r_0^2 + \Delta(t)]^{1/2} \tag{11}$$

where

$$\Delta(t) = 2DV \int_0^t (c - c_e)dt = 2DVc_e \int_0^t (\Omega - 1)dt.$$

Substituting into eq (9) and rearranging terms we obtain

$$Q(r) = \frac{P(r_0)[r_0^2 + \Delta(t)]^{1/2}}{r_0}. \tag{12}$$

Q(r) increases with the growth process indicating that the range in grain size must decrease. This can be illustrated using the following example in which at t = 0 the grains lie in a size range between 0.1 and 10.1 μm in a broad Gaussian distribution such that

$$P(r_0) = \left(\frac{10^7}{2\sqrt{2\pi}}\right)\exp\left[\frac{(r_0 - 5.1)^2}{8}\right]. \tag{13}$$

Results calculated for grain size distributions at different degrees of reaction progress are shown in figure 4. As in our previous simple 2-grain

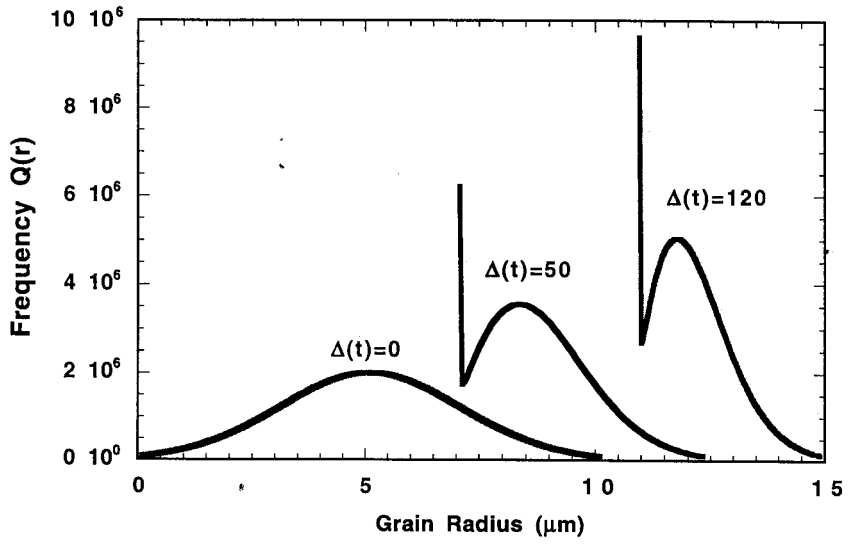

Fig. 4. Grain size frequency distribution versus grain radius for transport controlled growth at *different extents of reaction*, Δ(*t*).

example, the size ratio between the largest and smallest grains decreases from about 100 to 3 as the maximum grain radius grows from about 10 to 15 microns. This results in a "squeezing" of the original Gaussian distribution into an "h" type size frequency distribution. The height of the "tail" increases with increasing reaction progress and is the result of smaller grains increasingly catching up in size with the next larger grains at a constant total number of grains (this is analogous to traffic congestion resulting from faster cars catching up with slower cars). With further reaction progress observed apparent grain size distributions would approximate a large number of grains in a narrow minimum size range with rapidly decreasing numbers of grains of larger size.

Next we will consider the case where the precipitation rate is controlled by the rate of reaction on the crystal surface rather than by transport processes in solution. This type of rate control is probably of greater importance for most authigenic minerals (see, for examples, papers in Stumm, 1990).

For crystal growth where surface reactions are rate controlling and the influence of surface free energy on solubility is negligible, the increment of grain size change with reaction progress will be the same. Another way of stating this is that at a given supersaturation the radial growth velocity will be the same for grains of all sizes so that if the rate follows the general equation

$$v = k(\Omega - 1)^n \tag{14}$$

then

$$r = r_0 + k \int_0^t (\Omega - 1)^n dt = r_0 + \nabla(t). \tag{15}$$

Combining eqs (9) and (15) leads to

$$Q(r) = P(r_0) \tag{16}$$

This relationship demonstrates that under the given conditions, although grain size will increase with reaction progress, the pattern of grain size distribution will remain constant (fig. 5). However, the range of relative grain size will sharply diminish (fig. 6).

It is interesting that the results of our model indicate that different rate-controlling crystal-growth mechanisms lead to different patterns of grain size distribution. Thus it may be possible in some cases to infer whether transport processes or surface reaction mechanisms controlled the formation of an authigenic mineral. Also, of note is that in crystal growth controlled by Ostwald Ripening different growth mechanisms lead to different normalized size distributions (see fig. 10 in Morse and Casey, 1988). Thus, it is possible that different rate-controlling growth mechanisms may "feed" differing initial size distributions from the very fine grained size range into the size range considered here where the

influence of rate-controlling reaction mechanism continues to influence grain size distribution.

Crystal growth at a constant nucleation rate.—As discussed in the introduction, for several important authigenic minerals, most crystal growth

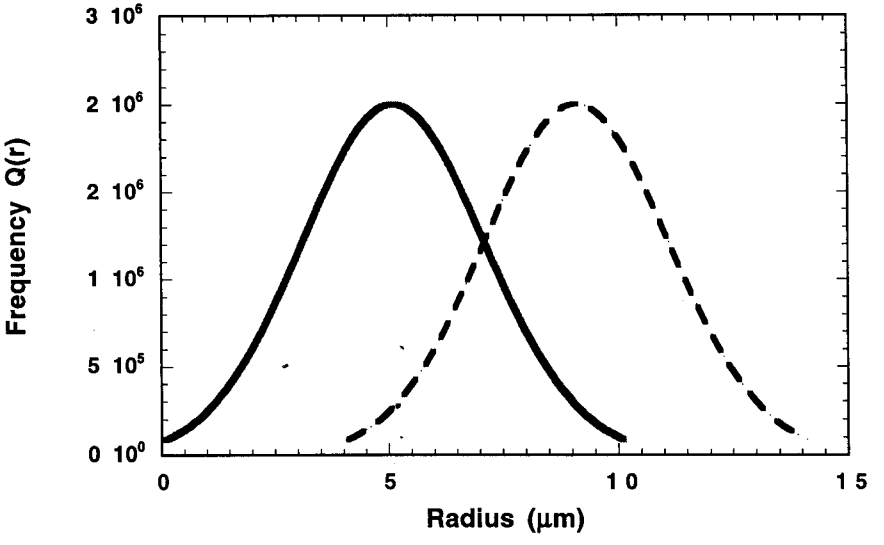

Fig. 5. Change in grain size frequency [Q(r)] from initial distribution (solid curve) to that after an arbitrary extent of reaction progress (dashed curve).

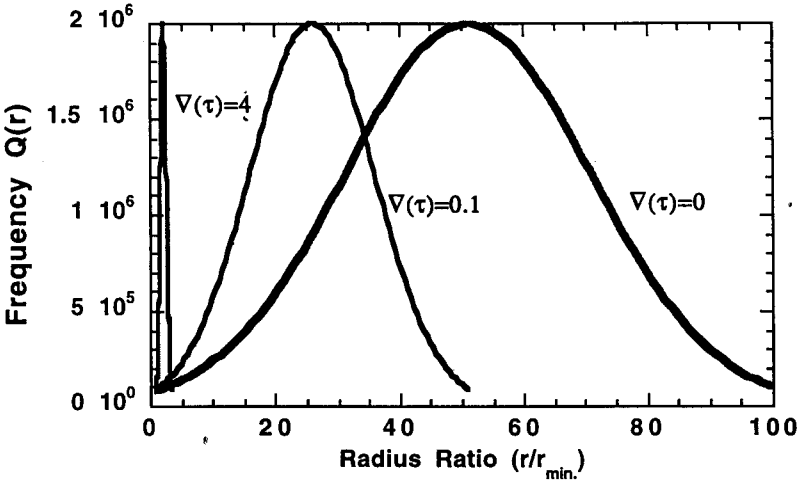

Fig. 6. Grain size frequency distribution [Q(r)] versus grain radius ratio for transport controlled growth at *different extents of reaction, Δ(t).*

may take place at close to constant supersaturation which is maintained by near equilibrium between pore waters and a metastable precursor phase. Because the supersaturation of the fluid is constant the rate of nucleation and crystal growth can also be reasonably expected to remain close to constant until near the end of the transformation process.

A major difference in this situation from the previously described case is that instead of having a constant number of grains in the system there is a constantly increasing number of grains in the system. The rate of this increase in the number of grains is determined by the nucleation rate (U). U is exponentially dependent on the saturation state of the solution which is above that required for critical nucleation of the more stable phase.

The theoretical basis and associated mathematical models for homogeneous nucleation kinetics are well developed and will be used here. However, it should be noted that in most natural systems and almost certainly in sediments the dominant mode of nucleation is via the heterogeneous mechanism where nucleation takes place on preexisting solid surfaces. A major difference between heterogeneous and homogeneous nucleation is that substantially lower degrees of supersaturation are needed for nucleation to take place via heterogeneous reactions. Unfortunately, the heterogeneous nucleation mechanism is complex, depending on, among other factors, surface free energy differences, structural similarity, and defect density. It is not therefore readily modeled in a general manner. Although we use a homogeneous model for nucleation, the general resulting concepts regarding subsequent grain growth at a close to constant nucleation rate are still valid.

According to classical nucleation theory (Nielsen, 1964)

$$U = \alpha \exp\left[\frac{\Psi}{(\ln \Omega)^2}\right] \tag{17}$$

where α is constant on the order of 10^{30} (cm^{-3} sec^{-1}), and $\Psi = -(16\pi/3)[\sigma^3 v^2/(kT)^3]$. Between time τ and $\tau + d\tau$, the number of crystals formed (dN) is

$$dN = U d\tau. \tag{18}$$

Consequently, the grain size frequency distribution is

$$Q(r) = \frac{dN}{dr} = U\left(\frac{d\tau}{dr}\right). \tag{19}$$

At time t, the size of crystals nucleated at time τ, for surface reaction-controlled growth and assuming that the critical radius is much less than the grain radius, is approximately (based on eq 14)

$$r = r_c + k\int_\tau^t (\Omega - 1)^n dt \cong k\int_\tau^t (\Omega - 1)^n dt. \tag{20}$$

As new nuclei are continuously added to the system the total surface area in the system (A_{tot}) on which growth can take place steadily increases with time so the net precipitation rate (J_{tot}) should accelerate. This can be quantified for the case used here where the nucleation rate and precipitation rates per unit surface area are constant at constant supersaturation. At time t, the surface area of crystals formed between time τ and $\tau + d\tau$ is

$$dA(\tau) = 4\pi r^2 dN = 4\pi\left[\int_\tau^t R d\tau\right]^2 U d\tau = 4\pi[R(t-\tau)]^2 U d\tau. \quad (21)$$

The total surface area at time t is then

$$A_{tot} = \int_0^t dA(\tau) = \left(\frac{4\pi}{3}\right) U R^2 t^3, \quad (22)$$

and, consequently, if the net precipitation rate is proportional to total surface area, the rate will be

$$J_{tot} = \left(\frac{4\pi}{3}\right) U R^3 t^3. \quad (23)$$

From this equation it is apparent that the reaction rate should accelerate in proportion to the cube of reaction time until the precursor phase is nearly dissolved and can no longer buffer the pore water at a constant composition close to its solubility. At the point where the dissolution rate of the precursor phase becomes less than the precipitation rate of the phase that is forming, the saturation state of the solution with respect to the new phase will decline and at some time reach a point where the nucleation rate becomes negligible (fig. 7). [and] The growth rate rapidly declines with further reaction due to the decreasing degree of supersaturation in the pore waters until the reaction stops at equilibrium.

During the period when the nucleation and growth rates are constant, the grain size distribution should be uniform (the number of grains of each size up to the maximum size will be the same for any incremental size unit). The maximum grain size will increase with reaction time until equilibrium is reached. However, after nucleation significantly decreases and stops, all grains will continue to grow at the same radial velocity, and although the absolute difference in grain size between different grains remains constant, the relative size difference will decrease. For example, if the smallest grain considered was 0.XX μm, and the largest grain was 5 μm when nucleation stopped, and all grains increased by 1 μm before final equilibrium was reached, the final range in grain size would be 1.XX to 6 μm (fig. 8) and would be the appearance of a small range in grain size.

THE UPPER SIZE LIMIT

Reasonable theoretical explanations can be found for the observation that the lower size limit for many authigenic minerals is often on the

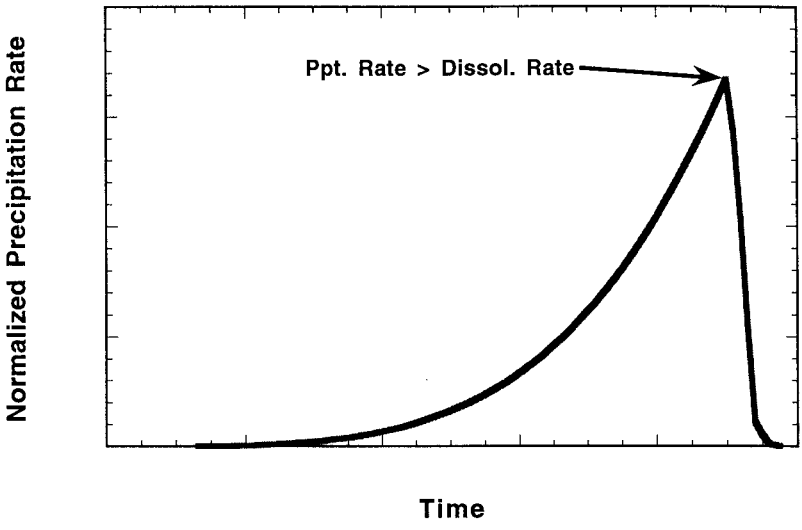

Fig. 7. Schematic representation of normalized (initial rate = 1) precipitation rate with time in arbitrary units.

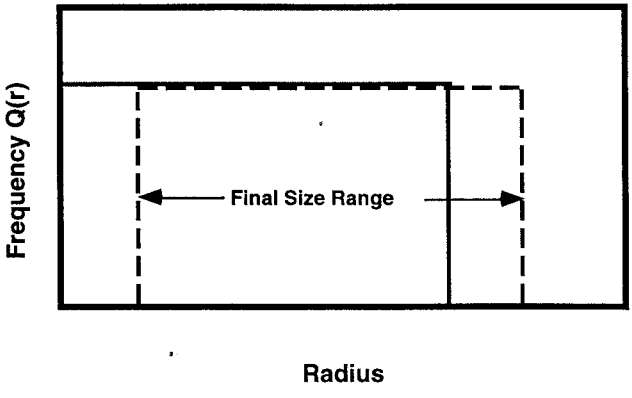

Fig. 8. Size frequency distribution versus grain radius. Solid line is for growth during constant nucleation and dashed line is for distribution after nucleation stops and reaction goes to completion at equilibrium.

order of several tenths of a micron or larger (see preceding discussion). However, it is not obvious from crystal growth theory why the upper limit for minerals formed during early diagenesis and in many cases even during burial diagenesis is often at most only a few tens of microns. The potential for formation of much larger (macroscopic) crystals is demonstrated by their occurrence in some ancient sedimentary rocks.

We suggest three possible factors that may play a role in limiting the upper size range of authigenic minerals. The first is simply the ratio of the number of growing nuclei versus the available supply of reactant. Depending on the concentration of reactants and how "open" the sediment is considered, it is possible to calculate what the total concentration of an authigenic mineral can be. The observation that reactant and authigenic mineral concentrations often co-vary indicates that diagenetic processes must also often be strongly coupled in generally similar manners (for example, see Morse and Berner, 1995, for discussion of the relationship between diagenetic processes and the burial ratio of sedimentary organic-carbon and reduced sulfur). If there is a relatively large number of nuclei compared to the potential concentration of an authigenic mineral, then small crystals will result.

Over the geologically short periods of time when authigenic mineral formation is most intense during early diagenesis, transport processes also may play an important role in limiting size. Nordeng and Sibley's (1996) analysis of cathodoluminescent growth zones in authigenic dolomites indicated that their growth rate is flux-limited and that increasing crystal size reflected increases in flux rates. When many small crystals are present their relatively close proximity will limit the "sphere of influence" over which they effectively compete for dissolved reactants. This can in turn lead to limitations in their size.

Finally, there is the possibility that pressure resulting from crystal growth may exert an influence on the upper size of authigenic mineral grains by raising the solubility of larger grains when they exceed the characteristic pore size. This pressure results from the growing crystal pushing against other grains as it expands. An example of this influence on early authigenic mineral formation is possibly the tendency of pyrite-framboid formation to be favored in the relatively large open spaces in biogenic (for example Foraminifera) tests. However, it is likely that the force of crystallization may play a significant role in lithified sediments where much higher growth pressures can be generated than in unconsolidated sediments.

SUMMARY

The relatively narrow range in grain size of authigenic minerals often observed in sediments can be understood via models for crystal growth that do not demand close to simultaneous nucleation and growth of the crystals. The models presented in this paper indicate that different grain size distributions should result if the rate of precipitation is transport or surface-controlled.

In an initially steady-state system, where the solution composition is buffered by a metastable precursor phase and rates of nucleation and surface-controlled growth are constant, the net growth rate increases as the cube of time (reaction progress) leading to "quenching" of the system and a relatively narrow and close to uniform distribution of grain size.

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