[AMERICAN JOURNAL OF SCIENCE, VOL. 288, JUNE, 1988, P. 537–560]

American Journal of Science

JUNE 1988

OSTWALD PROCESSES AND MINERAL PARAGENESIS IN SEDIMENTS

JOHN W. MORSE* and WILLIAM H. CASEY**

ABSTRACT. The sequential formation in time (paragenesis) of minerals in sediments frequently results in the formation of phases not predicted by equilibrium thermodynamics. For several important groups of minerals paragenesis follows the qualitative Ostwald step rule for sequential reactions, and in some cases (silica) the process of Ostwald ripening is intimately associated with such diagenetic sequences.

The persistence of relatively unstable minerals can be understood in terms of standard kinetic theory, where the most rapid of a given sequence of parallel reactions controls the overall rate. For many cases, the most rapid rate proceeds via metastable intermediates which convert at vanishingly slow rates to the thermodynamically favored phase. Contrary to previous treatments, the initial formation of metastable intermediates is not predicted from thermodynamics.

Kinetic theories of grain coarsening provide considerable insight into the growth of minerals during diagenesis. These models predict: (1) that properly scaled, the distribution of crystal sizes becomes constant with time; (2) that the mean grain size increases as the cube root of time; and (3) that the total number of crystals decreases inversely with time. Because the time during diagenesis often translates into sediment depth, these relations provide a way to test the importance of Ostwald ripening as a major process of diagenesis.

INTRODUCTION

Sediments and, to a lesser extent, sedimentary rocks often contain assemblages of minerals quite different from those that would be predicted from equilibrium thermodynamics. Much of the current effort in the examination of sediment geochemistry is devoted to furthering our understanding of the processes responsible for the formation and paragenesis of minerals in these nonequilibrium systems. Studies have largely (and necessarily) focused on specific mechanisms and pathways using generally ad hoc methods to interpret the results.

These interpretations of observations have often been made using equilibrium thermodynamics as the frame of reference. Systems whose behavior does not conform to predictions based on equilibrium thermodynamics have been characterized as "badly behaved." Qualitative

* Department of Oceanography, Texas A&M University, College Station, Texas 77843

** Division 1543, Sandia National Laboratory, Albuquerque, New Mexico 87185

observational rules such as the Ostwald (1897) Step Rule for successive reactions:

> *If a reaction can result in several products, it is not the stablest state with the least amount of free energy that is initially obtained, but the least stable one, lying nearest to the original state in free energy.*

and the "simplexity principle" for "ease" of crystallization (Goldsmith, 1953):

> *In general, the highest simplexity or most disordered phases should form from a random system; where simplexity is some measure of the complexity of the distribution of individual or particular atoms or atomic groups in a phase, irrespective of space group symmetry.*

have been invoked as explanations. However, they are simply qualitative statements of tendencies that do not provide an understanding in a true thermodynamic sense or offer a framework for eventually understanding these processes in a quantitative and, hence, more predictive manner. The proper approach to chemical processes taking place in sediments is through the application of chemical kinetics.

In this paper we shall briefly summarize the behavior of several major classes of sedimentary minerals that do not conform to equilibrium thermodynamic theory. Then, relevant aspects of irreversible thermodynamic theory will be examined for their ability to predict Ostwald step rule behavior of minerals. Finally, factors favoring the formation of nuclei of metastable phases and the important, but complex, process of Ostwald ripening will be discussed.

PARAGENESIS OF SEDIMENTARY MINERALS

Carbonates.—Sedimentary carbonates are probably the most widely recognized and studied "badly behaved" sedimentary minerals. It is not uncommon to find high magnesian calcites, calcite, and aragonite all coexisting in the same sediment, with perhaps even a little protodolomite present. Clearly, this is a nonequilibrium situation. Much of this material is of biogenic origin. However, aragonite and high magnesian calcite cements and ööids, and protodolomite are probably not formed directly by organisms. In addition, when seawater becomes sufficiently supersaturated for precipitation to occur, aragonite, not the more stable calcite or dolomite, precipitates. These phenomena are also exemplified by the precipitation of $CaCO_3$ in the laboratory. When higher than room temperatures (60°–90°C) and relatively concentrated reactants are used, a metastable phase (vaterite or aragonite) is precipitated. In such cases, interferences by other ions such as magnesium cannot be invoked to explain the observed behavior.

Even though dolomite is the most stable carbonate mineral under conditions found in most recent marine sediments, its formation is relatively rare, and, even then, it appears in a poorly crystalline and nonstoichiometric form generally referred to as "protodolomite." This protodolomite shares many characteristics, such as poor structural ordering and excess calcium content, with dolomites grown in the

laboratory under less than hydrothermal conditions. Ordering and composition approach those of "ideality" for dolomite with age and the elevated temperatures and pressures associated with burial conditions. Under such conditions reaction rates are enhanced, and the dolomite can transform to a more stable form.

The fact that carbonate minerals behave in a manner incompatible with the precepts of equilibrium thermodynamics has resulted in extensive study of their reaction kinetics (see Morse, 1983 for summary) and of the behavior of metastable phases such as magnesian calcites (see Mackenzie and others, 1983 for summary). Sedimentary carbonates also serve as some of the best examples of aggrading neomorphism in which phase transformations do not occur, but fine-grained carbonates are replaced by a coarser (sparry, for example, see Folk, 1965, Bathurst, 1975) material. This process is closely akin to that of Ostwald ripening. A discussion of recrystallization processes and their relation to the Ostwald step rule will be presented later in this paper.

Silica.—Sedimentary silica minerals also represent a group of minerals whose paragenesis has been noted to follow the Ostwald step rule. Williams, Parks, and Crerar (1985) and Williams and Crerar (1985) have recently summarized much of what is known about the diagenetic controls and mechanisms for silica diagenesis. Again, as for the sedimentary carbonate minerals, the initial solid formed is often of biogenic origin (opal-A), although cements composed of similar material (opal-A′) are also common. The opal-A (or A′) is X-ray amorphous with a broad peak centered around 4.1 Å.

Opal-A can transform during diagenesis (see fig. 1 for summary) to poorly ordered opal-CT; the CT denoting the presence of cristobalite and tridymite X-ray diffraction peaks. Initially, the crystallinity of the opal-CT may be poor, but as diagenesis progresses the ordering, as observed through X-ray diffraction, becomes more ideal (Williams and Crerar, 1985). Further diagenesis can lead to the formation of cryptocrystalline quartz or chalcedony which eventually may transform to microcrystalline quartz. This process is accomplished through a dissolution reprecipitation pathway discussed in detail in the above cited papers by Williams and her associates. The increases in crystallinity in the opal-CT (and possibly opal-A) and quartz sequences are interesting, because they appear to be intimately associated with phase transition processes. Thus, silica paragenesis can involve closely associated Ostwald step rule and ripening behavior.

Iron and manganese oxides.—The oxides and oxyhydroxides of iron and manganese are common components of marine sediments and are often encountered as nodules or encrustations. Often, these minerals occur as very fine grained mixtures of different phases, with iron and manganese oxides intimately associated. Debates over their relative stabilities and the reaction pathways by which they form have resulted in a vast literature. Many of the more recent articles on sedimentary manganese oxides have been well reviewed by Burns and Burns (1979),

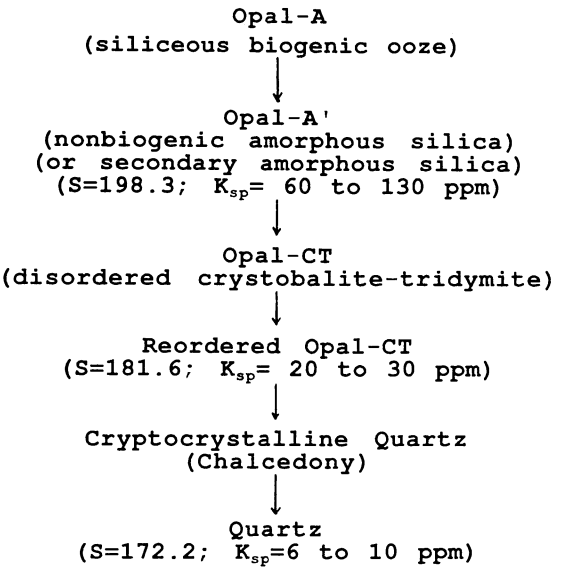

Fig. 1. Sequence of silica mineral diagenesis. Thermodynamic data from Williams, Parks, and Crerar (1985).

while the literature on iron oxides was reviewed by Murray (1979). Here we will summarize briefly only the most salient aspects of these investigations, which pertain directly to our interest in Ostwald processes.

Much of the interest in the relative stabilities of different iron oxides phases and their reaction pathways in sediments has centered around goethite and hematite. It has been argued that the hydrous iron oxide goethite (α-FeOOH) is the first to form, and that it can transform slowly, in common sedimentary environments, to hematite (α-Fe_2O_3). This concept was supported by the experimental work of Berner (1969) which indicated that all FeOOH polymorphs are unstable relative to hematite. However, subsequent work by Langmuir (1971) indicated that particle size may play an important role in determining the relative thermodynamic stabilities of these minerals (see discussion later in this paper).

Murray (1979 and papers cited therein) has emphasized the role of reaction kinetics and solution chemistry in controlling the formation of different iron oxide phases observed in sediments. The complexity of the problem is illustrated by the fact that fine-grained goethite is easily precipitated but metastable relative to coarse-grained hematite, which can be grown only very slowly from solution. Recent studies by Schwertmann and Murad (1983) indicate that the possible reason for this is that goethite can precipitate directly from solution, whereas hematite must form by internal rearrangement and dehydration within precursor ferrihydrite aggregates.

The transformation of fine-grained goethite to coarse-grained hematite occurs in sediments. This happens even though coarse-grained hematite is metastable relative to coarse-grained goethite. However, coarse-grained hematite can persist in sediments for hundreds of millions of years. Murray (1979) also noted that agaganéite (β-FeOOH) is the first iron oxide phase to form from chloride-rich solutions such as seawater. It is metastable and may rapidly convert to more stable goethite.

Burns and Burns (1979) have emphasized the role of adsorbed or coprecipitated Co, Cu, and Ni in influencing the behavior manganese oxides, which may be highly heterogeneous and are often too fine grained for positive identification of the polymorphs present. The primary minerals present in the marine environment are todorokite, vernadite, and birnessite. They are often intimately intermixed, and it is often questionable if they are true phases, by conventional definition. All these "phases" are probably metastable, and their formation appears to be dominated by complex kinetic factors. A good example of the complexities involved in the formation of manganese oxide phases and of the importance of precursor phases and nonequilibrium processes is given by the work of Hem and Lind (1983).

Thus, the iron and manganese oxides observed in sediments and sedimentary rocks are dominated by kinetic and particle size related phenomena, not simple equilibrium thermodynamics.

Iron sulfides.—Sedimentary iron sulfide minerals undergo a series of diagenetic reactions which may range from an initial "amorphous-FeS" phase to pyrite or marcasite. Several reaction pathways have been proposed (Berner, 1970; see fig. 2 for summary). It is often not possible to identify directly any minerals other than pyrite and occasionally greigite in recent sediments. (Morse and Cornwell, 1987). However, the presence of other metastable iron sulfide minerals is generally inferred from sediment color, chemical leaching techniques, and infrequently from pore water chemistry. Whereas organisms are important for the formation of iron sulfide minerals in sediments through the reduction of sulfate to hydrogen sulfide and, perhaps, the solubilization of iron, the current consensus of opinion is that sedimentary iron sulfide minerals are not formed by direct biogenic processes. (See Morse and others, 1987, for extensive review and discussion of this topic.)

The paragenesis of iron sulfide minerals follows Ostwald's step rule, since minerals of increasing stability are formed with time. The pathway is, however, complicated by the fact that elemental sulfur (possibly through polysulfide compounds) is involved in the precipitation of greigite and pyrite. However, in terms of the equilibrium HS^- activity for a given Fe^{2+} activity, the paragenetic pattern is generally consistent with Ostwald step rule requirements. Also, it appears probable that the amorphous-FeS to mackinawite transition represents a coarsening phenomenon similar to Ostwald ripening.

Phosphates.—Phosphate mineral behavior is complex, both under laboratory conditions and in natural systems. It has been extensively

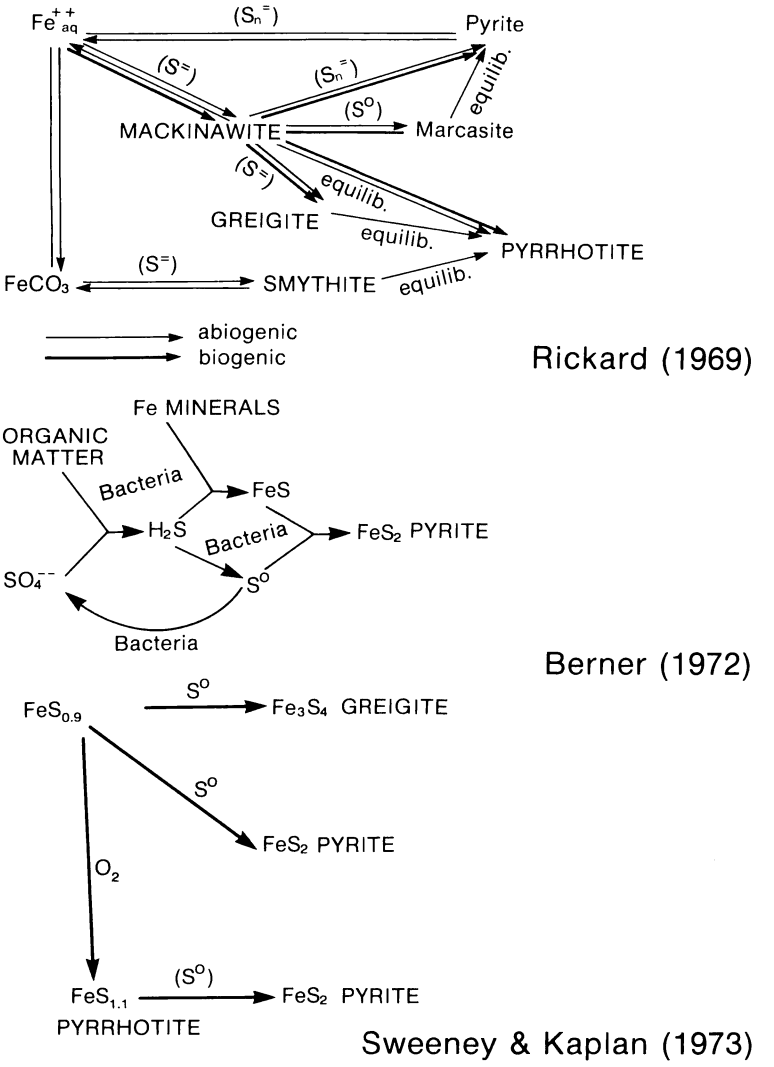

Fig. 2. Summary of hypothesized reaction paths for sedimentary sulfide mineral formation.

studied in association with bone and tooth formation. Also, aquatic systems have been investigated because of the economic importance of phosphorite deposits and the impact of phosphate as a nutrient on ecologic systems.

While some form of apatite is usually the end product of such processes in organisms and sediments, the reaction pathway can be

extremely complex, and numerous precursor calcium phosphate phases have been observed. Nancollas, Amjad, and Koutsoukos (1979) have summarized much of the literature on this topic in non-marine environments. The phases observed in ascending order of stability (see Manheim and Gulbrandsen, 1979) are nonstoichiometric amorphous calcium phosphate, dicalcium phosphate dihydrate (brushite, $CaHPO_4 \cdot 2H_2O$), anhydrous dicalcium phosphate (monetite, $CaHPO_4$), octacalcium phosphate ($Ca_4H(PO_4)_3 \cdot 2.5\ H_2O$), tricalcium phosphate (whitlockite, $Ca_3(PO_4)_2$), and hydroxyapatite ($Ca_5(PO_4)_3OH$) or dahllite ($Ca_{10}(PO_4)_6(OH)_2$).

Magnesium has long been recognized to have a major inhibiting influence on the precipitation of calcium phosphates, with its influence increasing with decreasing solubility of the phase (see Salimi, Heughebaert, and Nancollas, 1985 for recent summary). This has been of particular concern in the diagenesis of marine phosphorites. Early laboratory work (Martens and Harriss, 1970) indicated that only amorphous calcium phosphate could be precipitated from seawater because of interference from magnesium ions. Even after 9 months no recrystallization to apatite was observed. More recently, Gulbrandsen, Roherson, and Neil (1984) found that a period of 10 yrs was required for recrystallization of amorphous precipitates to "marine apatite." Interestingly, an unstable magnesium phosphate phase, details of which were not presented, developed prior (after 20 months) to formation of the apatite.

Clay minerals.—Clay mineral formation and paragenesis is more complex than the previously discussed groups of minerals. However, there is reasonable evidence suggesting that in many cases these processes may also follow the Ostwald step rule and ripening. They tend with time to more ordered or complex structures.

Tazaki (1986) has used high resolution transmission electron microscopy to study clay formation on microcline. His observations indicate that "primitive" precursors, which are poorly ordered (diffuse electron diffraction patterns) and hydrated, form prior to the development of normal crystalline clays (meta-halloysite and gibbsite) during feldspar weathering. The diagenesis of clay minerals also often follows the general pattern predicted by the Ostwald step rule. A possible example of this is the transformation of smectites to illite during burial diagenesis (Perry and Hower, 1970). In fact, there is substantial evidence that smectites are metastable and may not represent true phases even at the unit cell level, because of their inherently heterogeneous and variable nature (see May and others, 1986 for extensive discussion).

Zeolites.—Zeolite minerals are relatively rare in sediments, with a major exception being in sediments rich in volcanic glasses, which are transformed, during diagenesis, to zeolite minerals. Phillipsite is the most common zeolite in relatively young sediments, but climoptilolite and analcite become more abundant with increasing geologic age while

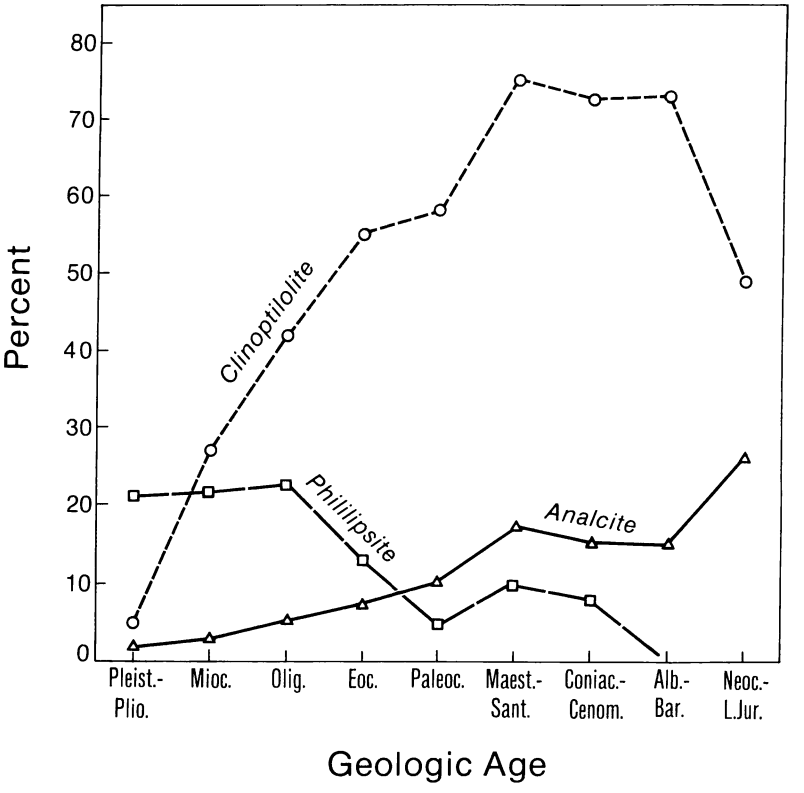

Fig. 3. Changes in frequencies of phillipsite, clinoptilolite, and analcite occurrences with age of deep-sea sediments. From Kastner (1979a).

phillipsite decreases (see fig. 3). Kastner (1979a) suggested the rapid growth and subsequent dissolution of phillipsite indicate its formation is kinetically controlled and phillipsite is not thermodynamically stable in the marine environment. Although most of the experimental studies of zeolite mineral formation have been performed necessarily under hydrothermal conditions, their behavior has been found to follow the Ostwald step rule (see Barrer, 1982 for detailed discussion of zeolite chemistry). In fact, their behavior was the inspiration for the first paper to attempt to put the Ostwald step rule on an irreversible thermodynamic basis (van Santen, 1984, to be discussed later).

IRREVERSIBLE THERMODYNAMICS

The nature of the Ostwald Step Rule.—In the previous section we discussed examples of mineral paragenesis in sediments. We argued that these paragenetic pathways involve thermodynamically unfavored

phases. Thus, sediment diagenesis may proceed as a disequilibrium process similar to that described by Ostwald (1897), who observed that crystallization from solution may proceed via thermodynamically unfavored phases. We also note that the reaction pathways are complex and poorly understood.

In this section, we examine the causes of this phenomenon. By an analysis in terms of standard kinetic theory we show that the observation of intermediates is controlled by the relative rates along each reaction path. We furthermore show that to the extent the problem can be examined with a linear theory of irreversible thermodynamics there exists no *a priori* reason for a reacting system to proceed via intermediate compounds. Thus the observation of reaction intermediates is solely controlled by the reaction rates of the direct and indirect process.

To illustrate this point, consider two paths for the formation of a product, D, from the reactant, A: (1) direct formation without intermediates; and (2) formation via two intermediates, B and C. A general reaction scheme is shown in figure 4, and we have written simple rate laws to describe the process:

$$\frac{dA}{dt} = k_{-1}D + k_{-2}B - A(k_1 + k_2) \tag{1}$$

$$\frac{dB}{dt} = k_2A + k_{-3}C - B(k_{-2} + k_3) \tag{2}$$

$$\frac{dC}{dt} = k_3B + k_{-4}D - C(k_{-3} + k_4) \tag{3}$$

$$\frac{dD}{dt} = k_1A + k_4C - D(k_{-4} + k_{-1}) \tag{4}$$

We solved this system of equations to calculate the relative concentration of the reactants and products for two sets of arbitrarily chosen rate constants. The results are shown in figure 5. In figure 5A, values were used that resulted in high concentrations of the intermediates, B

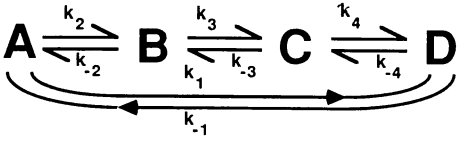

Fig. 4. Schematic representation of sequential reaction paths.

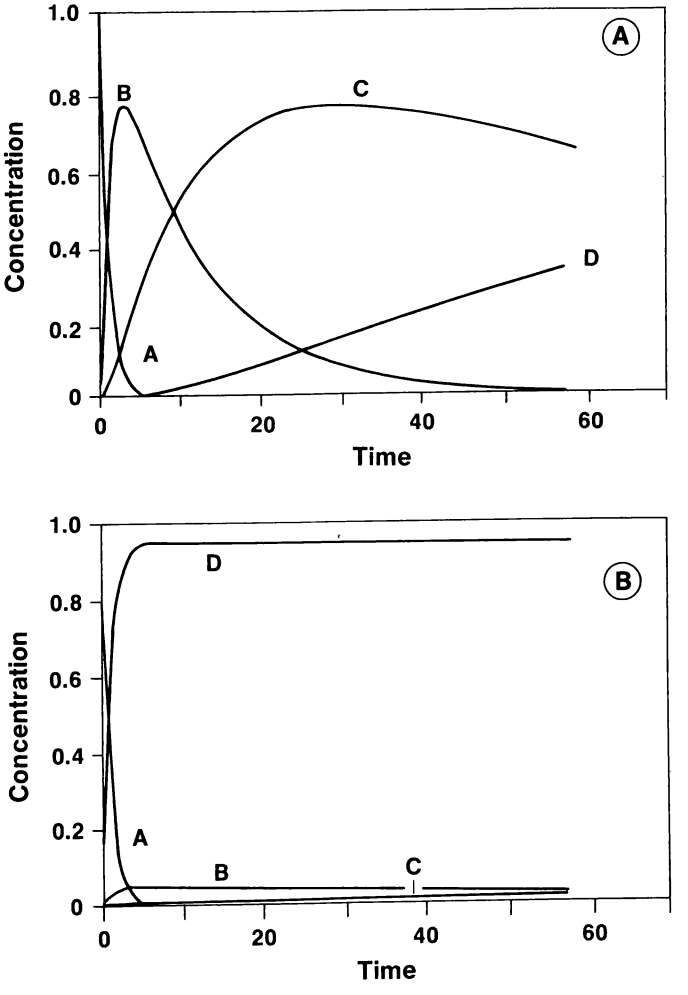

Fig. 5. Distribution of reactants and products with time for case 1 (A) and case 2 (B). See text for discussion.

and C, relative to the stable product for an extended period of time. In figure 5B, values were chosen that resulted in relative fast formation of the stable product, D, and very low concentrations of the intermediates. For the example we use the initial conditions: A(0) = 1.0, B(0) = C(0) = D(0) = 0. Time and concentration are presented in arbitrary, dimensionless units. The rate constants used to generate these figures are compiled in table 1.

For the first case (fig. 5A), A reacts rapidly to form B, which then slowly reacts to form C. The stable product, D, forms slowly. Note that

TABLE 1

Rate constants used in eqs 1 to 4

Constant→	k_1	k_{-1}	k_2	k_{-2}	k_3	k_{-3}	k_4	k_{-4}
Case 1	9×10^{-4}	9×10^{-7}	0.9	9×10^{-7}	0.09	9×10^{-7}	0.009	9×10^{-7}
Case 2	0.942	9×10^{-7}	0.047	9×10^{-7}	0.009	9×10^{-7}	9×10^{-4}	9×10^{-7}

there exists a relatively lengthy period of time when the intermediates constitute virtually all the major products. For this case, one concludes that the reaction to form the stable C product obeys the Ostwald Step Rule; that is, the reaction first forms a less-stable intermediate.

In the second case (fig. 5B), we have changed the rate constants so that the stable product, D, forms rapidly from A. The less-favored intermediates (B and C) are consistently present only as minor phases. For this case, one would conclude that the step rule is violated. That is, the stable product forms directly and rapidly.

These simple examples illustrate the important point that, given parallel reaction paths, the character of the products at any one time is controlled by the relative reaction rates. A second, self-apparent, point is that each possible pathway contributes to the overall reaction rate. These points become important in the next section when we analyze Ostwald's step rule in terms of disequilibrium thermodynamics.

Irreversible thermodynamics and the Ostwald Step Rule.—The abundance of metastable reaction products, along with the certainty implied in Ostwald's original statement, led workers to try and place Ostwald's Step Rule on a rigorous thermodynamics base (van Santen, 1984). In this section we demonstrate that, to within the limits of linear irreversible thermodynamics, there is no generality to the Ostwald Step Rule. The true nature of this rule lies in the relation of structural chemistry to precipitation and growth rates.

The logical starting point for this discussion is the concept of entropy production. From the second law of thermodynamics, we know that entropy is produced by any irreversible process, such as by mineral diagenesis. The local entropy production, σ, is the *rate* of entropy produced in a volume element of the reacting, disequilibrium system.

Prigogine (1967) showed that some disequilibrium systems tend to evolve toward a minimum in rates of entropy production. This minimum corresponds to a stable steady state, which, for an isolated system represents equilibrium. For open systems, a unique disequilibrium steady state is maintained by conditions at the system boundary, such as fixed chemical affinities. The criteria of minimum entropy production thus provides a measure of stability of a disequilibrium system. An additional, critical point to note about the linear theory of irreversible thermodynamics is that only a *single* steady state exists for a given disequilibrium configuration. Thus there exists a unique rate of entropy

production consistent with the reaction pathways and boundary conditions.

With manipulation it can be shown that the rate of entropy production is proportional to a linear series of terms relating a flux (J_i) to the thermodynamic force (X_i) driving that flux (see Fisher and Lasaga, 1981; Katchalsky and Curran, 1974):

$$\sigma = \sum_{i}^{n} J_i X_i \tag{5}$$

Included in (5) are forces and fluxes required to describe the system thermodynamically. Thus for a system with a heterogeneous distribution of temperature and chemical affinity, terms must be included to describe the transport of heat and mass as well as the chemical reactions. Additional terms are added if the system is in mechanical disequilibrium (see deGroot and Mazur, 1962), such as would be caused by the ebullation of gases.

For our purposes we consider only a system undergoing chemical reaction. For this case, forces and fluxes in eq (5) correspond to chemical affinities and reaction rates, respectively.

$$\sigma = \sum_{i}^{n} J_i \frac{A_i}{T} \tag{6}$$

where T is temperature. We develop our argument by expanding eq (6) into two parts, corresponding to direct and indirect parallel reaction paths:

$$\sigma = \sum_{i}^{n} \frac{A_i}{T} (J_i + J_{id}) \tag{7}$$

and by remembering that chemical affinity is a state function; that is, independent of the reaction path. As long as the overall reaction rate is constant ($J = J_d + J_{id}$), the relative velocities of the direct and indirect reaction paths are immaterial to entropy production. Thus, to the extent that linear irreversible thermodynamics can be applied to this problem, no thermodynamic benefit is derived *a priori* from the abundant number of steps in an indirect reaction path.

Correct interpretation of Ostwald's statement emphasizes structural chemistry, not entropy production. As we showed in the preceding section, the most rapid of parallel reaction paths controls the observed distribution of products. Metastable intermediates appear where they are *sterically* favored to form rapidly. Thus Ostwald's statement is not an invariant rule but an observation that metastable reaction products with simple structures form more rapidly than complicated, although thermodynamically stable, minerals. Simple ionic solids such as NaCl, for example, precipitate directly from solution whereas complicated structures, such as aluminosilicates, form slowly and via simpler interme-

diates. It is for this reason that Goldsmith (1953) emphasizes crystal chemistry in laying out the simplexity principle.

Metastable "hangups".—One possible consequence of a reaction series is that a metastable phase that can effectively terminate the reaction sequence may form. In this case, precursor phases may initially form at a faster rate than the most stable phase but lead to a metastable phase of very low reactivity. Thus, the pathway effectively leads to a terminal phase quite different from that predicted from equilibrium thermodynamic considerations. This phenomenon is easily understood by examining figure 5A and imagining the case where time is in units of hundreds of millions of years. The conversion rate of intermediate C to the stable product D is then effectively immeasurably slow in geologic time.

Many sedimentary minerals, such as silicates, have reaction rates that, for practical purposes, approximate zero under Earth surface conditions. Consequently, they are able to persist in sediments with little discernible alteration for tens of millions of years. When they are formed during a sequence of reactions, they may effectively stop the progression of the reaction before the most stable phase is reached. During burial diagenesis P-T conditions may change sufficiently to cause the reaction to proceed at a faster rate, resulting in further advancement along the reaction sequence. It is important to recognize that these transitions between metastable and metastable or metastable and stable phases are distinctly different from equilibrium phase transitions, since the transitions involving the metastable phases are solely the result of reaction kinetics.

Silica (fig. 6) and clay minerals are among the best examples of this type of behavior. Although factors other than temperature and pressure such as composition of solutions are recognized to influence opal-A to opal-CT and opal-CT to quartz transformations, it is clear that temperature is a major influence (see Williams, Parks, and Crerar, 1985, and references therein). Based on a compilation of data from 37 DSDP volumes (Kastner, 1979b) established the following relationships for formation of opal-CT in deep sea sediments (ϕ = time in millions of years, t = °C)

$$\phi = 80 - 2t + 0.01t^2 \tag{8}$$

$$\phi = 83 - 4.15t + 0.1t^2 - 0.001t^3 \tag{9}$$

Kastner was prevented by a scarcity of data from establishing a similar relation for formation of quartz.

Perry and Hower (1970) studied the diagenesis of clay minerals in oil wells. They observed that temperature rather than depth of burial appeared to be the dominant factor. For the montmorillonite to illite transition they noted a regular decrease in montmorillonite over the temperature range of 55° to 95°C and then an abrupt decrease to a near constant value at temperatures between 95° and ~100°C.

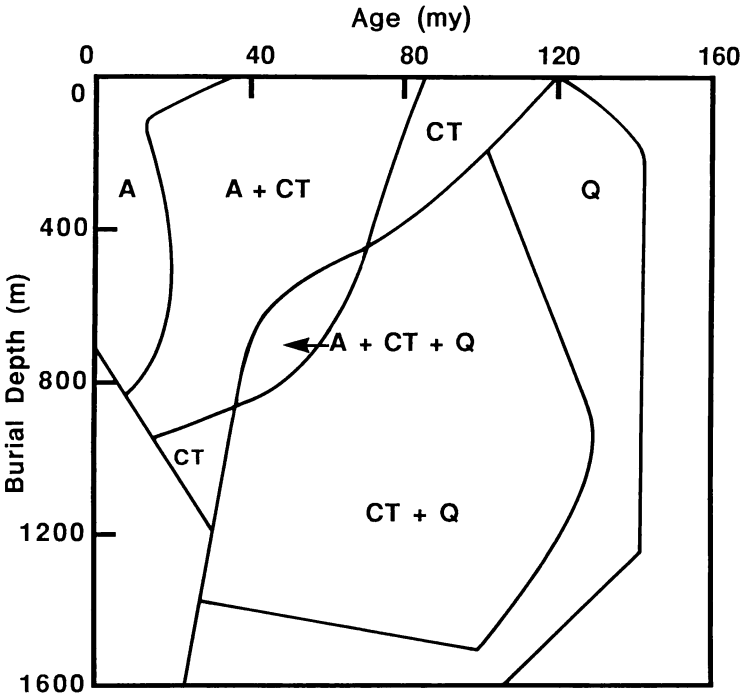

Fig. 6. Distribution of silica phases in Atlantic Ocean sediments with respect to burial depth and time (after Calvert, 1983). A = opal, CT = opal-CT, Q = quartz.

THE ROLE OF NUCLEATION PROCESSES

Nucleation processes play a critical role in determining both what phase is initially formed and potential grain size. In Ostwald Step Rule behavior, the kinetics of nucleation are probably often at least as important as those of crystal growth. It is, consequently, important to examine the factors that can lead to nucleation of metastable phases. An associated question is what controls the number of nuclei formed, since if many nuclei are produced the resulting precipitate will tend to have a small grain size.

Modern nucleation theory (Walton, 1967) indicates that at high supersaturations the critical nucleus may be extremely small; so small in fact that it can be less than a unit cell (see fig. 7). Under these conditions all possible product phases have identical nucleation rates with respect to the initial state of the system. The structural path taken by such a nucleus will be dependent on whether or not there exist barriers to its structural rearrangement during growth, and it is likely to grow into the simplest structure encountered at a later stage. Morris (1970), through a statistical mechanical treatment of this problem, demonstrated that Ostwald Step Rule behavior under such conditions can be extremely

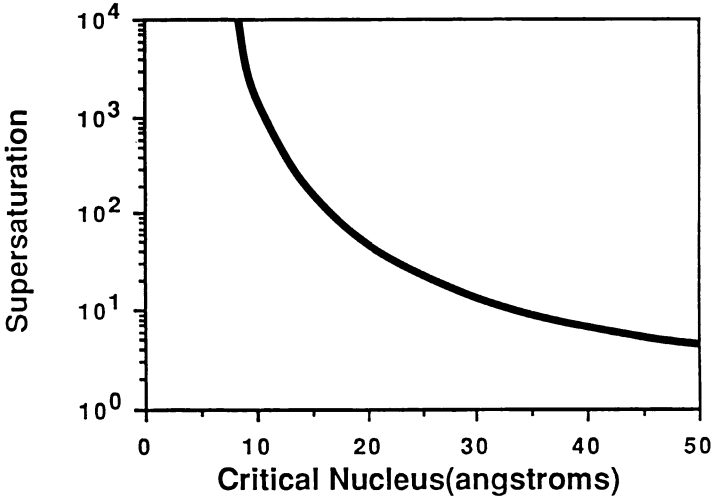

Fig. 7. The size of a critical nucleus as a function of supersaturation for calcite with a surface free energy of 85 ergs cm^{-2}.

complex. These concepts have been applied by Feenstra and de Bruyn (1981) to the formation of nonstoichiometric amorphous calcium phosphate.

It is also important to consider that within the size range of particles associated with nucleation processes surface free energy contributes substantially to the total free energy for the reaction. It is, therefore, possible for the relation of ΔG_r values between two phases to be the opposite for nuclei or fine particles from those based on "bulk" or "ideal" ΔG_r values. Under such conditions, the nuclei of the "metastable" phase are the thermodynamically more stable nuclei, and, consequently, their formation and the subsequent growth of the metastable phase are favored. This type of behavior appears to be of central importance for sedimentary minerals such as iron oxides (Murray, 1979).

A simple example of this concept for the formation of different $CaCO_3$ phases is given in figure 8. There a plot is presented of the equilibrium nuclei size versus difference in surface free energy for calcite, aragonite, and vaterite $CaCO_3$ phases. It is interesting to note that, considering surface free energies are typically on the order of ~100 ergs cm^{-2}, only about a 5 to 10 percent difference between the surface free energy of calcite and aragonite is necessary to control which phase is nucleated. It, therefore, becomes obvious why surface chemistry plays such an important role in determining the phase that is nucleated.

A major difficulty in understanding nucleation processes in sediments arises from the fact that most nucleation probably is heteroge-

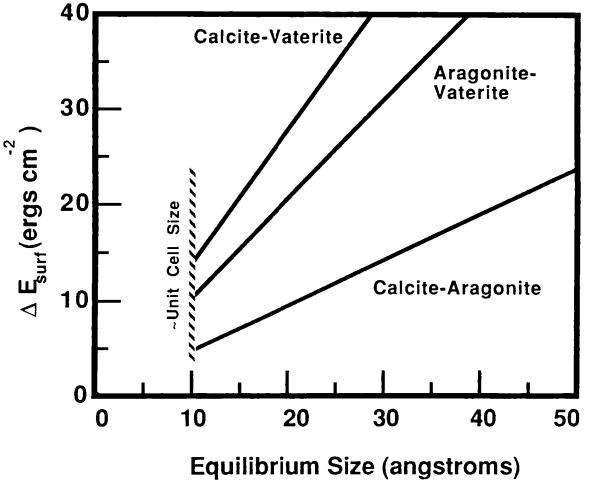

Fig. 8. Equilibrium size for different carbonate phases versus differences in surface free energies.

neous. In heterogeneous nucleation, a different phase of the same substance or an entirely different mineral can serve as a site for nucleation. When this takes place epitaxy can play a major role in controlling the phase nucleated and can effectively override the previously discussed controls on nucleation. Our knowledge of heterogeneous nucleation phenomena associated with mineral diagenesis is, unfortunately, very limited at present. However, heterogeneous nucleation may be responsible for Ostwald Step Rule behavior for minerals such as those associated with silica, since the next most stable phase is often more structurally similar to the precursor phase than a thermodynamically more stable phase.

The general relation between nucleation and solution composition is that as supersaturation increases, both the rate of nucleation and the number of nuclei produced increase. When more nuclei are produced, the resulting precipitate tends to be finer grained. This relationship is complicated by the observation that the nucleation rate, for a given degree of supersaturation, is proportional to a salt's solubility. It is consequently possible to obtain highly supersaturated solutions of sparingly soluble salts (see Boistelle, 1982). This can lead to Ostwald Step Rule behavior if a more soluble form of the salt (or mineral) can nucleate most rapidly. If rapidity of nucleation is often the controlling factor in the paragenic formation of sedimentary minerals, it may in part explain the tendency of intermediate phases to often be fine-grained.

THE KINETICS OF OSTWALD RIPENING

In addition to noting the common formation of metastable phases, Ostwald observed that small crystals in a fresh precipitate often recrys-

tallize with time into fewer, but larger, crystals. This coarsening is referred to as Ostwald ripening and is the basic process of aggrading neomorphism (see p. 365 of Lerman, 1979). In this section we review some of the general properties of coarsening ensembles as originally presented by Lifshitz and Slyozov (1961) and Wagner (1961). The original treatment is mathematically complex, and we present only the salient features of the derivation. Readers interested in advanced treatments are referred to Voorhees (1985) and to a thesis by Marder (ms). Baronnet (1982) also presents a clear overview of coarsening and its relation to growth of the geologically important minerals, calcite and phlogopite.

The driving force for grain coarsening is the dependence of chemical potential on the interface curvature:

$$\mu = \mu^\circ + V_m \gamma \frac{\partial s}{\partial v} \tag{10}$$

where s is the surface area, v is the grain volume, μ° is the chemical potential of a molecule at a flat interface, γ is the surface tension, and V_m is the molar volume. We can rearrange eq (10) to express the concentration of a reactive solute at the boundary of a grain of radius R:

$$\log C = \log C_\infty + \frac{\alpha}{R} \tag{11}$$

where α is a parameter that depends upon temperature, the particle shape, the interfacial surface tension, and the molar volume of the crystal. C_∞ is the solubility of an infinite flat crystal. It is apparent from eq (11) that a potential for mass transfer exists between grains of different sizes. Atoms may diffuse from a small crystal, with high interfacial curvature, to larger grains. The net result with time is that small grains disappear from an ensemble as the mean grain size increases (see fig. 9). In figure 9 we review results of Baronnet (1982) who monitored the particle size distribution during experiments to grow phlogopite hydrothermally. Note that the grain size distribution becomes increasingly broad with time, and that the mean particle size increases as the assemblage ripens.

The radius of a grain, therefore, varies with time. For the diffusion-controlled case:

$$\frac{\partial R}{\partial t} \approx \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right) \tag{12}$$

where D is the degree of supersaturation ($\Delta = C - C_\infty$), and D is the diffusion coefficient for solutes. Note that for a given supersaturation there exists a grain with the critical radius in equilibrium with the solution: $R_c = \alpha/\Delta$. Grains with radii greater than R_c grow, while smaller grains dissolve. Because the critical radius depends upon the degree of

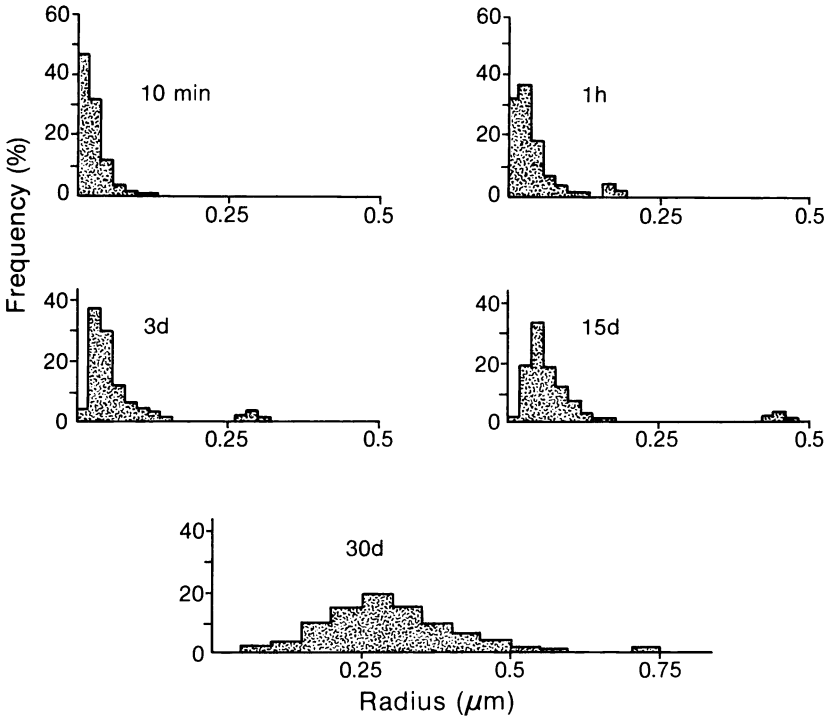

Fig. 9. Histograms of particle sizes for phlogopite at different times (after Baronnet, 1982).

supersaturation, which in a closed system decreases with time, the critical radius varies with time.

In our subsequent discussion it is useful to employ dimensionless variables. Therefore, in keeping Lifschitz and Slyozov (1961), we write Δ_o to be the initial supersaturation, R_{co} to be the initial critical grain radius, and $T = R^3/\alpha D$. The length and time variables are then scaled:

$$\rho = \frac{R}{R_{co}} \text{ and } t' = \frac{t}{T}$$

Dropping the prime on t', we rewrite the equation for the rate of crystal growth:

$$\frac{d(\rho^3)}{dt} = 3\left(\frac{\rho(t)\,\Delta(t)}{\Delta_o} - 1\right) \tag{13}$$

Lifschitz and Slyozov (1961) characterized the particles in terms of a volume distribution function, $f(\rho, t)$, where f is the number of particles

per unit volume at time t with a volume in the interval ρ^3, $\rho^3 + d\rho^3$. Note that this characterization implies that there exist enough grains to approximate the size distribution as a continuous function. The time rate of change of the particle size distribution is then given by a continuity equation:

$$\frac{\partial f}{\partial t} + \frac{\partial (f, \nu)}{\partial \rho^3} = 0 \tag{14}$$

which equals the flux of particles in the space of sizes. ν is the velocity with which grains enter and leave a particular size interval.

At this point it is useful to identify some of the simplifying assumptions. Firstly, note in eq (14) the flux is set equal to zero so there is no nucleation of new grains during ripening. Secondly, note that eq (12) for the rate of particle growth requires a steady-state distribution of solute around each grain. This assumption requires that the rate of solute migration is fast relative to grain coarsening. Thirdly, we consider a closed system (see Beenakker and Ross, 1985 for consideration of an open system), and fourthly, we employ a mean field approach. This assumption amounts to ignoring the probability that large crystals are close to other large crystals (pair correlation of sizes). Additional simplifications include the requirement of: (1) spherical grains; (2) that stress is not generated during growth; (3) that particle positions are fixed; (4) that the Gibbs-Thompson equation describes the surface energy; and (5) that the volume fraction of the minor phase is sufficiently small so that grains do not impinge upon one another. These latter assumptions simplify the mathematics and have been evaluated both in the original work by Lifschitz and Slyozov (1961) and in subsequent treatments (Voorhees, 1985; Marqusee and Ross, 1984).

To complete the analysis, Lifschitz and Slyozov (1961) write an equation to conserve mass between the solvent and the growing crystals. That is:

$$Q_o = \Delta(t) + q(t)$$

$$q = \frac{4}{3} \pi R_{co} \int_0^\infty \rho^3 f(\rho^3, t) \, d\rho^3 \tag{15}$$

where Q_o is the initial supersaturation, and q is the volume of matter held in the crystals.

The kinetic eqs (13), (14), and (15) must be solved simultaneously to determine size-distribution of growing crystals as function of time. After considerable manipulation, Lifschitz and Slyozov (1961) derived a solution for the distribution of grain sizes appropriate for the asymptotic limit of large times. We present a modified form of their result in eq (16). The result is modified to show the probability of encountering a grain *radius,* rather than a *volume,* as grain radii are most easily measured in natural settings. It is also convenient to scale the grain radii

by the critical radius, for reasons that will soon become clear. This scaling is defined: $z = R(t)/R_c(t)$. The frequency distribution is then (for $0 \leq z \leq 1.5$):

$$g(t, z) = \left(\frac{3}{2}\right)^{5/3} z^2 \left(\frac{3}{3 + z}\right)^{7/3} \left(\frac{\frac{3}{2}}{\frac{3}{2} - z}\right)^{11/3} \exp\left(\frac{-z}{\frac{3}{2} - z}\right) \qquad (16)$$

with $g(t, z) = 0$ for $z > 1.5$. The frequency distribution of reduced sizes is plotted in figure 10. We also include the distributions of crystal sizes for surface-controlled reactions (Wagner, 1961; Marqusee and Ross, 1983) in figure 10.

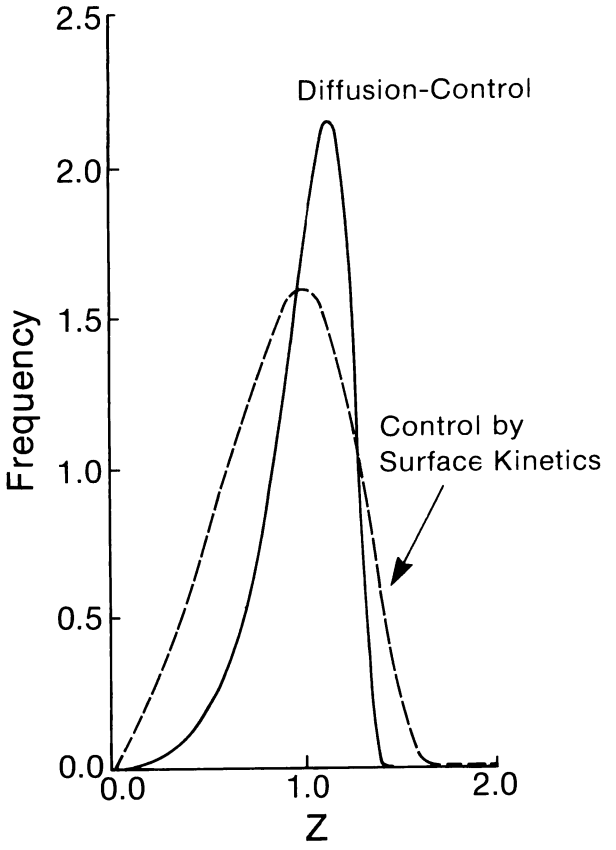

Fig. 10. Normalized grain-size distributions calculated for diffusion-controlled and surface-controlled crystal growth rates.

There are essential points to note both about eq (16) and figure 10. First, observe that the size-distribution, when scaled by the critical radius, is independent of time. That is, although the mean grain size of a coarsening ensemble consistently increases (the most stable state is adjacent crystals of each phase), the *distribution* of sizes relative to this mean is constant. This feature of a coarsening ensemble is universal and applies for reaction rates that are both diffusion-controlled, such as we model here, and surface controlled (see Marqusee and Ross, 1983). The time-independence of grain sizes only applies, however, to the degree that the initial distribution of sizes has disappeared. This requirement is, in essence, the reason that the analysis applies only for the asymptotic limit of large time. Note also that the theory predicts that reduced grain radii will not exceed 1.5 but will decrease uniformly to zero from a mode at about 1.0. In other words, with time the mode of the measured grain distribution becomes virtually identical to the critical radius.

Secondly, from an extended analysis, one can write kinetic equations to describe the evolution in measured radii for large times. The number of particles decreases inversely with time:

$$N(t) = \frac{1}{2D\alpha t} \tag{17}$$

while the critical radius increases as the cube root of time:

$$R_c^3 = (4/9)\, D\alpha t \tag{18}$$

To within a constant factor, this dependence of particle number, radius, and concentration on time is universal for ripening systems (Voorhees, 1985).

Application to diagenesis.—The theory of Ostwald ripening is developing rapidly. Workers subsequent to Lifshift and Slyozov (1961) have expanded the treatment to consider surface-controlled reactions (Wagner, 1961; Marqusee and Ross, 1983), large volume fractions of the growing phase (Voorhees and Glicksman, 1984; Marqusee and Ross, 1984), open systems (Beenakker and Ross, 1985), pair correlations between grains (Marder, 1985, 1986), and, ripening when initial conditions are important (Venzl, 1983). These improvements have confirmed the salient features of the classic theory. These are: (1) scaled, time-invariant distributions of particle sizes, (2) particle numbers that decrease as the inverse of time, and (3) critical radii nearly identical to the observed mode and that decrease as the cube root of time. In general, subsequent workers have shown that the distribution of particle sizes is broader than predicted by eq (16) and that the broadened profiles match well with the observed distribution of secondary particle sizes in a wide range of materials (Marder, 1986).

Considerable work remains if the theoretical developments are to be applied to natural sediment. Firstly, it must be shown that the rate at which initial distributions disappear is rapid enough to remove any

inherited size distributions. This step is critical. Secondly, the theory must be adapted to treat anisotropic crystals where the rate of particle growth depends upon crystal orientation. It is also not clear that pore fluids during diagenesis are sufficiently close to equilibrium with minerals for surface forces to be important relative to bulk free energy. In spite of these caveats, the mathematical treatment of ripening outlined by Lifschitz and Slyozov (1961) and subsequent workers provides a promising framework for understanding rock textures and diagenetic processes near chemical equilibrium.

There has been unfortunately little quantitative analysis of particle sizes of diagenetic minerals, in spite of the common occurrence of secondary cements. The mathematical treatment of Ostwald ripening outlined by Lifschitz and Slyozov (1961) and subsequent workers suggests that this is an area of profitable future research.

SUMMARY

The formation and diagenesis of many of the most important groups of sedimentary minerals clearly do not behave in a manner in accordance with predictions based on equilibrium thermodynamics. In this paper we have attempted to lay a framework for understanding the paragenesis of sedimentary minerals, stressing the fact that phenomenologic "rules" such as those by Ostwald have a firm basis in kinetic theory.

Both theory and data are far from being adequate for providing detailed predictions about the behavior of the extremely complex systems involved in these processes. However, considerations of irreversible thermodynamic and kinetic theory, such as those presented in this paper, are necessary if coherent progress is to be made in understanding the behavior of sedimentary minerals.

ACKNOWLEDGMENTS

We would like to thank Kathryn L. Nagy, Frank J. Millero, David Rickard, and Lynn M. Walter for their comments and encouragement. Support for this research was provided by the National Science Foundation Chemical Oceanography Program and the Texas A&M University Center for Energy and Mineral Resources.

REFERENCES

Baronnet, A., 1982, Ostwald Ripening: The case of calcite and mica: Estudios Geologie, v. 38, p. 185–198.

Barrer, R. M., FRS, 1982, Hydrothermal Chemistry of Zeolites: London, Acad. Press, 360 p.

Bathurst, R. G. C., 1975, Carbonate Sediments and Their Diagenesis: New York, Elsevier, 658 p.

Beenakker, C. W. J., and Ross, J., 1985, Theory of Ostwald Ripening for open systems: Jour. Chem. Physics, v. 83, p. 4710–4714.

Berner, R. A., 1969, Goethite stability and the origin of red beds: Geochim. et Cosmochim. Acta, v. 33, p. 267–273.

———— 1970, Sedimentary pyrite formation: Am. Jour. Sci., v. 268, p. 1–23.

———— 1972, Sulfate reduction, pyrite formation and the oceanic sulfur budget, *in* Dryssen, D., and Jagner, D., eds., Proceedings of the Nobel Symposium 20: Stockholm, Almquist and Wiskell, p. 347–361.

Boistelle, R., 1982, Mineral crystallization from solution: Estudios Geologie, v. 38, p. 135–153.
Burns, R. G., and Burns, V. M., 1979. Manganese oxides, *in* Ribbe, P. H., ed., Marine Minerals: Washington, D.C., Mineralog. Soc. America, p. 1–46.
Calvert, S. E., 1983, Sedimentary geochemistry of silicon, *in* S. R. Aston, S. R., ed.: Silicon Geochemistry of Biogeochemistry: New York, Acad. Press, p. 143–186.
deGroot, S. R., and Mazur, P., 1962, Non-equilibrium thermodynamics: Amsterdam, North Holland Pub. Co. 510 p.
Feenstra, T. P., and de Bruyn, P. L., 1981, The Ostwald rule of stages in precipitation from highly supersaturated solutions: A model and its application to the formation of the nonstoichiometric amorphous calcium phosphate precursor phase: Jour. Colloid and Interface Sci., v. 84, p. 66–72.
Fisher, G. W., and Lasaga, A. C., 1981, Irreversible thermodynamics in petrology, *in* Lasaga, A. C., and Kirkpatrick, R. J., eds., Kinetics of Geochemical Process: Rev. in Mineralogy, v 8., p. 171–210.
Folk, R. L., 1965, Some aspects of recrystallization in ancient limestones, *in* Dolomitization and Limestone Diagenesis: A Symposium: Soc. Econ. Paleontologists Mineralogists, Spec. Pub., v. 13, p. 14–48.
Goldsmith, J. R., 1953, A "simplexity principle" and its relation to "ease" of crystallization: Jour. Geology, v. 61, p. 439–451.
Gulbrandsen, R. A., Roberson, C. E., and Neil, S. T., 1984, Time and the crystallization of apatite in seawater: Geochim. et Cosmochim. Acta, v. 48, p. 213–218.
Hem, J. D., and Lind, C. J., 1983, Nonequilibrium models for predicting forms of precipitated manganese oxides: Geochim. et Cosmochim. Acta, v. 47, p. 2037–2046.
Kastner, M., 1979a, Zeolites. In Burns, R. G., ed., Marine Minerals: Rev. Mineralogy Ser., v. 6, p. 111–122.
——— 1979b, Silica polymorphs in Marine Minerals, *in* Burns, R. G., ed., Marine Minerals: Rev. Mineralogy Ser., v. 6, p. 99–110.
Katchalsky, A., and Curran, P. F., 1974, Nonequilibrium thermodynamics in Biophysics: Cambridge, Mass., Harvard Univ. Press, 244 p.
Langmuir, D., 1971, The Gibbs free energies of substances in the system Fe-O_2-H_2O-CO_2 at 25°C: U.S. Geol. Survey Prof. Paper 650-B, p. 180–184.
Lerman, A., 1979, Geochemical Processes: Water and Sediment Environments: New York, Wiley Intersci., 481 p.
Lifshitz, I. M., and Slyozov, V. V., 1961, The kinetics of precipitation from supersaturated solid solutions: Jour. Phys. Chemistry Solids, v. 19, p. 35–50.
Mackenzie, F. T., Bischoff, W. D., Bishop, F. C., Loijens, M., Schoonmaker, J., and Wollast, R., 1983, Magnesian calcites: Low-temperature occurrence, solubility and solid-solution behavior, *in* Reeder, R. J., ed., Carbonates: Mineralogy and Chemistry: Washington, D.C., Mineralog. Soc. America, p. 97–144.
Manheim, F. T., and Gulbrandsen, R. A., 1979, Marine phosphorites, *in* Burns, R. G., ed., Marine Minerals: Rev. Mineralogy Ser., v. 6, p. 151–174.
Marder, M., 1985, Correlations and droplet growth: Physics Rev. Letters, v. 27, p. 2953–2956.
——— ms, 1986, Droplet Growth: Ph.D. thesis, Univ. California, Santa Barbara, 133 p.
Marqusee, J. A., and Ross, J., 1983, Kinetics of phase transitions: Theory of Ostwald Ripening: Jour. Chemical Physics, v. 79, p. 373–377.
——— 1984, Theory of Ostwald Ripening: Competitive Growth and its dependence on volume fraction: Jour. Chem. Physics, v. 80, p. 536–543.
Martens, C. S., and Harriss, R. C., 1970, Inhibition of apatite precipitation in the marine environment by magnesium ions: Geochim. et Cosmochim. Acta, v. 34, p. 621–625.
May, H. M., Kinniburgh, D. G., Helmke, P. A., and Jackson, M. L., 1986, Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: Kaolinite and smectites: Geochim. et Cosmochim. Acta, v. 50, p. 1667–1677.
Morris, J. W., Jr., 1970, The Ostwald step law in the rapid nucleation of structures, *in* Blocker, J. M., Chemical Vapor Deposition, Electrochem. Soc. 2d Internat. Conf., New York, p. 89–105.
——— 1983, The kinetics of calcium carbonate dissolution and precipitation, *in* Reeder, R. J., ed., Carbonates: Mineralogy and Chemistry: Washington, D.C., Mineralog. Soc. America, p. 227–264.
Morse, J. W., and Cornwell, J. C., 1987, Analysis and distribution of iron sulfide minerals in recent anoxic marine sediments: Marine Chemistry, v. 22, p. 55–69.

Morse, J. W., Millero, F. J., Cornwell, J. C., and Rickard, D., 1987, The chemistry of hydrogen sulfide and iron sulfide systems in natural waters: Earth Science Rev., v. 24, p. 1–42.
Mullin, J. W., 1972, Crystallization: London, Butterworths, 480 p.
Murray, J. W., 1979. Iron oxides, *in* Ribbe, P. H., ed., Marine Minerals, Washington, D.C., Mineralog. Soc. America, p. 47–98.
Nancollas, G. H., Amjad, Z., and Koutsoukos, P., 1979, Calcium phosphates-speciation, solubility and kinetic considerations, *in* Jenne, E. A., ed., Chemical Modelling in Aqueous Systems: Am. Chem. Soc. Symposium Ser., p. 475–498.
Ostwald, W. Z., 1897, Studien über die Bildung und Umwaldung fester Korper. 1. Abhandlung: Übersattigung and Überkaltung: Zeitschr. Physik Chemie., v. 22, p. 289–330.
Perry, E. A., and Hower, J., 1970, Burial diagenesis in Gulf pelitic sediments: Clays and Clay Minerals, v. 18, p. 165–177.
Prigogine, I., 1967, Thermodynamics of Irreversible Processes: New York, Intersci. Pub., 147 p.
Rickard, D. T., 1969, The chemistry of iron sulfide formation at low temperatures: Stockholm Contr. Geology, v. 20, p. 67–95.
Salimi, M. H., Heughebaert, J. C., and Nancollas, G. H., 1985, Crystal growth of calcium phosphates in the presence of magnesium ions: Langmuir, v. 1, p. 119.
Schwertmann, U., and Murad, E., 1983, Effect of pH on the formation of goethite and hematite from ferrihydrite: Clays and Clay Minerals, v. 31, p. 277–284.
Sweeney, R. E., and Kaplan, I. R., 1973, Pyrite framboid formation: laboratory synthesis and marine sediments: Econ. Geology, v. 68, p. 618–634.
Tazaki, K., 1986, Observation of primitive clay precursors during microcline weathering: Contr. Mineralogy Petrology, v. 92, p. 86–88.
van Santen, R. A., 1984. The Ostwald step rule: Jour. Phys. Chemistry, v. 88, p. 5768–5769.
Venzl, G., 1983, Ostwald Ripening of Precipitates I. Numerical Solution for the particle size distribution function in closed systems: Ber. Busenges. Phys. Chemistry, v. 87, p. 318–324.
Voorhees, P. W., 1985, The theory of Ostwald Ripening: Jour. Statistical Physics, v. 38, p. 231–252.
Voorhees, P. W., and Glicksman, M. E., 1984, Ostwald Ripening during liquid phase sintering—Effect of volume fraction on coarsening kinetics: Metall. Trans. A., v. 15A, p. 1081–1088.
Wagner, C., 1961, Theorie der Alterung von Neiderschlägen durch Umlösen (Ostwald Reifung): Zeitschr. Elektrochem., v. 65, p. 581–591.
Walton, A. G., 1967, The formation and Properties of Precipitates: New York, Intersci. Pub., 232 p.
Williams, L. A., and Crerar, D. A., 1985, Silica diagenesis, II, General mechanisms: Jour. Sed. Pet., v. 55, p. 312–321.
Williams, L. A., Parks, G. A., and Crerar, D. A., 1985, Silica diagenesis, I. Solubility controls: Jour. Sed. Pet., v. 55, p. 301–311.