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Chapter 3

KINETICS of WEATHERING and DIAGENESIS

Robert A. Berner

INTRODUCTION

Most solid materials found near the surface of the earth are not thermodynamically stable there. Some outstanding examples are: unweathered igneous feldspars, semi-amorphous "clay" (instead of well-crystallized phyllosilicates), and fine-grained goethite (instead of hematite) in soils, and undecomposed organic matter, aragonite (instead of calcite), and opaline silica (instead of quartz) in marine sediments. This metastability arises from fundamental causes which are physical, biological, and chemical in origin. First, igneous and metamorphic minerals, stable only at elevated temperatures, are carried into the zone of weathering by such physical processes as uplift and volcanism, and the energy necessary for this to occur is derived from within the earth. Second, because of an input of solar energy and its trapping by photosynthesis, organisms are able to biologically synthesize organic matter and other unstable substances such as aragonite and opaline silica. Finally, during weathering and diagenesis less stable minerals can form because of chemical factors which bring about the inhibition of nucleation and growth of more stable phases.

The preponderance of metastability near the earth's surface is a direct consequence of the slowness of chemical reaction rates at low temperatures. Thus, kinetics plays more of a leading role in earth surface geochemistry than it does at higher temperatures. Furthermore, we can study the rates and mechanisms of reactions by observing various stages during reaction both in the field and in the laboratory. The purpose of this chapter is to show how several different aspects of chemical kinetics can be brought to bear on the study of two major earth surface processes: weathering and diagenesis. Before proceeding directly to discussions of weathering and diagenesis, it is necessary to present some fundamental kinetic concepts which will enable the reader to better understand the discussions.

SOME FUNDAMENTAL CONCEPTS

In this paper we will be mainly concerned with the crystallization and dissolution of minerals from aqueous solution and the bacterial decomposition of organic matter. Basic principles controlling these three processes are presented in this section. Discussion is based on the following references which may be consulted for further details: Nielsen (1964) and Ohara and Reid (1973) for crystallization, Berner (1978a) for dissolution, and Berner (1980) for all three processes.

Crystallization

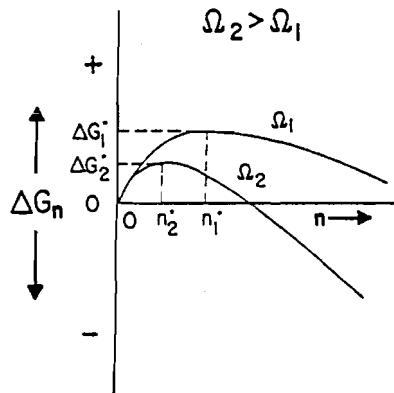


Figure 1. Plot of free energy of precipitation: ΔG_n vs crystal size illustrating nucleation and growth. The free energy change increases up to a maximum due to nucleation and then decreases due to crystal growth. The diagram is for a single crystal containing n atoms, ions or molecules. Note the effect of the degree of supersaturation Ω on the position of each curve. (Modified after Nielsen, 1964 and Berner, 1980)

The crystallization, or precipitation, of a solid substance from aqueous solution can be divided into two processes: nucleation and crystal growth. Nucleation occurs prior to growth and distinction between the two processes can be made in terms of Figure 1. As a body precipitating from solution begins to increase in size (or in the number of atoms it includes) it encounters a free energy barrier to further growth. This barrier is a consequence of the fact that an interface between the growing body and the solution forms, and this results in an increase in free energy due to the creation of the interface. At small sizes the interfacial free energy dominates over the drop in free energy accompanying the relief of supersaturation, and as a result there is a net free energy increase. The free energy increases up to a maximum where the interfacial and bulk terms balance one another. At this point the body is referred to as the *critical nucleus* and the process leading up the free energy "hill" is called nucleation. During nucleation the body is referred to as a crystal embryo.

Once the critical nucleus has formed, further increase in its size can take place spontaneously with a net decrease in free energy.

This process is referred to as crystal growth and the growing body is considered a true *crystal*. Growth (and nucleation of other crystals) continues until enough material is removed from solution that supersaturation is relieved and equilibrium is attained.

As the degree of supersaturation is increased, the ease of nucleation is increased. This is shown in Figure 1 by a decrease in the size of the critical nucleus and a decrease in the free energy of nucleation, ΔG^* as the degree of supersaturation Ω is increased. (The parameter Ω is defined as the actual ion activity product divided by the equilibrium or solubility product.) The rate of nucleation is a strong exponential function of the free energy of nucleation; consequently, at high Ω values nucleation is very fast. Since nucleation and growth compete for dissolved material, at high degrees of supersaturation the rate of nucleation may be so fast that most of the excess solute is precipitated in the form of critical nuclei with little left over for growth. Since critical nuclei are commonly in the size range 10-100 Å, such rapid crystallization can result in the formation of a very fine grained precipitate. In this way the formation of poorly crystallized minerals in nature and in the laboratory can be explained. A common example is the reddish gelatinous precipitate of $\text{Fe}(\text{OH})_3$ obtained by the mixing of concentrated solutions of ferric chloride and sodium hydroxide in the laboratory.

Low levels of supersaturation, by contrast, can result in good crystallinity. This comes about because the nucleation rate is so slow that most excess dissolved material is consumed by crystal growth on a limited number of critical nuclei. Most minerals which exhibit some degree of crystallinity from their x-ray diffraction patterns fall in this category. Thus, the rest of the discussion of crystallization will be devoted to crystal growth.

Crystal growth involves the transport of dissolved species to and from the surface of a crystal and various chemical reactions occurring at the surface. The latter includes adsorption, ion exchange, dehydration of ions, formation of two-dimensional nuclei on the surface, diffusion along the surface, ion pair formation, etc. The rate of growth is limited by the slowest step within a whole chain of processes and the nature of the rate-limiting step is not usually known. However, as a first approximation, the rate of crystal growth can be

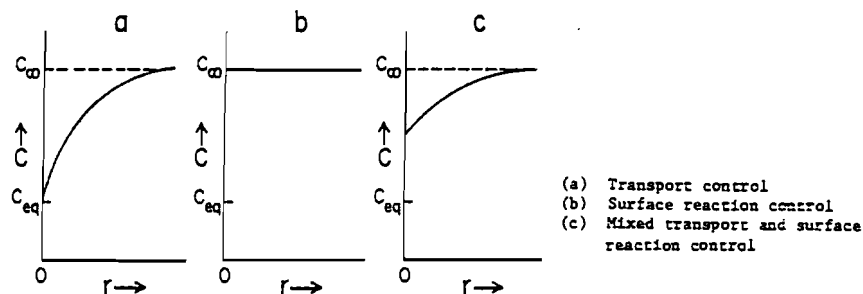


Figure 2. Schematic representation of concentration in solution C as a function of radial distance r , from the surface of a growing crystal. C_{eq} = saturation concentration, C_{∞} = concentration out in solution. (After Berner, 1980)

characterized as being controlled either by transport of ions to the surface (transport-controlled), by reactions at the surface (surface-reaction controlled), or by a combination of both processes. A comparison of the three mechanisms is shown in Figure 2.

In pure transport-controlled growth (Fig. 2-a) ions (atoms, molecules) are added to the surface of the crystal so rapidly that migration of ions in solution to take their place cannot keep pace. As a result concentrations in solution adjacent to the crystal surface fall until they almost reach the equilibrium or saturation level. Further growth is limited by the rate at which additional ions can be transported to the crystal surface and the slowest process is that of molecular (ionic) diffusion. Transport to the surface can be accelerated by bulk flow of solution past the growing crystal or by stirring. Thus, transport-controlled growth is a strong function of the hydrodynamic state of the solution.

In pure surface-reaction controlled growth (Fig. 2-b) ion attachment to the surface is so slow that replenishment of ions in solution near the surface is easily accomplished by molecular diffusion and other transport processes. Concentrations in the near-surface zone are little different than those in the bulk solution, and growth rate is not affected by the hydrodynamic state of the solution.

Intermediate situations (Fig. 2-c) arise where ion attachment is sufficiently rapid that concentrations in the near-surface region are lower than they are in the bulk solution but not rapid enough to bring about a lowering to the saturation value. In this case the rate of growth is controlled by both transport and surface reactions.

Discernment of whether the rate of crystal growth of a given mineral is controlled by transport or surface-reaction can be accomplished by comparing measured rates of growth (from laboratory experiments or, preferably, from field methods) with those calculated for growth via molecular diffusion. Molecular diffusion is the slowest process by which crystals can grow and still have their rate controlled by transport. Faster measured rates indicate (advective) transport control whereas slower measured rates point to control by surface chemical reactions. Calculation of the approximate rate of growth via molecular diffusion is normally done using the expression (Nielsen, 1964):

$$\frac{dr_c}{dt} = \frac{vD_s(C_\infty - C_{eq})}{r_c} \quad (1)$$

where: r_c = average radius of the crystals,
 v = molar volume of the crystalline substance,
 D_s = coefficient of molecular diffusion in aqueous solution,
 C_∞ = concentration in solution away from the crystal surface,
 C_{eq} = equilibrium concentration adjacent to the crystal surface,
 t = time.

For constant C_∞ (appropriate to an open system), equation (1) can be integrated to:

$$r_c = [2vD_s(C_\infty - C_{eq})t]^{\frac{1}{2}} \quad (2)$$

(Note that equations (1) and (2) are most correct when applied to equi-sized, equidimensional (i.e., cubes, spheres, etc.) crystals separated by at least five diameters.)

Other ways of deducing overall growth mechanisms are through the use of different temperatures and different stirring rates in laboratory crystallization experiments. A stronger temperature dependence than that predicted for aqueous diffusion-controlled growth indicates a surface-reaction mechanism whereas a dependence on stirring rate, as discussed above, indicates transport control.

Actual mechanisms offered to explain surface-reaction controlled growth are varied and numerous. The two most commonly cited ones are surface nucleation control and dislocation control. In the former, rates of ion attachment are limited by the rate at which a new two-

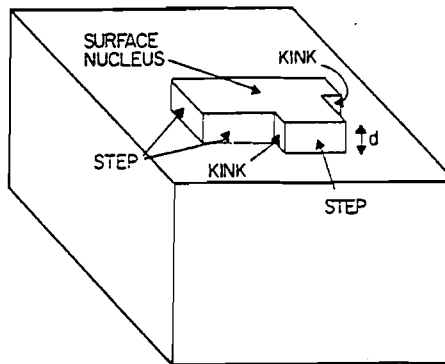


Figure 3. Idealized representation of the surface of a crystal. Dimension d represents one atom, molecule, unit cell, etc. On the flat crystal surface a "two-dimensional" surface nucleus is present which exhibits non-atomic steps and kinks. (After Berner, 1980)

dimensional nucleus is formed on an otherwise atomically flat crystal face. The new nucleus is needed to provide unit-cell-sized steps and kinks on the surface which are energetically favored points of attachment. This is shown in Figure 3. In dislocation-controlled growth, built-in steps and kinks are provided by the intersection of screw

dislocations with the crystal surface. By this mechanism the energy of surface nucleation is already provided by dislocation outcrops

and growth spirals emanating from them, and, as a result, growth may occur at very low degrees of supersaturation. Although dislocation-controlled growth has been studied considerably, further discussion is beyond the scope of this paper, and the reader is referred to the book by Ohara and Reid (1973) or the classic work of Burton, Cabrera and Frank (1951) for additional details.

An important process, so far unmentioned, which can appreciably affect the rate of growth (and nucleation) of crystals from aqueous solution, is the adsorption of ions, molecules, etc., from solution onto the crystal surface (see Chapter 1). Natural waters contain many dissolved constituents which readily adsorb onto growing crystals, and some of these can serve as growth inhibitors. If normally available growth sites, such as kinks, are blocked by strongly adsorbed ions, then overall rates of growth can be greatly diminished. Also, preferential adsorption of such "poisons" onto certain crystal faces can result in the deceleration of their growth and a consequent alteration in crystal habit. Octahedral halite grown in the presence of urea is a classical example. The adsorption of inhibitors can so alter growth rates that normal rate dependences on supersaturation, as given for example by the usual models for dislocation-controlled growth (Burton *et al.*, 1951), are not obeyed (*e.g.*, see Ohara and Reid, 1973).

Dissolution

Like crystallization the overall process of dissolution of solids by an aqueous solution is controlled either by transport or by surface chemical reactions. The classification scheme shown in Figure 2 can also be applied to dissolution with the only difference being that concentrations adjacent to the crystal surface, for transport-controlled dissolution, are higher than they are in the bulk solution. Obviously, dissolution occurs only where undersaturation of the bulk solution is present, in other words, where $\Omega < 1$.

Methods for the discernment of the rate-controlling mechanism of dissolution are similar to those for crystallization. The rate of diffusion-controlled dissolution can also be obtained from equation (1). Note in this case that dr_c/dt is negative because C_{eq} is greater than C_∞ . Comparison of measured rates of dissolution with that calculated for diffusion control, via equation (1), enables elucidation of the overall rate-controlling mechanism. Determination of the effects of temperature variation and stirring in the laboratory can also be used for the same purpose.

Dissolution is dissimilar to crystallization in one important respect. It is that three-dimensional nucleation is not necessary in dissolution since the dissolving crystals are already present. In fact, observations of partially-dissolved crystals can be used as an additional method for deducing the dissolution rate-controlling mechanism. In the case of rate control by surface reaction, slow partial dissolution of the surface results in the formation of crystallographically controlled features, such as large, well-developed etch pits. This arises from the fact that major dissolution originates only at points of excess energy on the surface such as dislocation outcrops. In the case of transport-controlled dissolution, attack of the surface is so rapid and non-specific that etching occurs virtually everywhere, and, as a consequence, only general rounding results. A comparison of morphological features produced by each mechanism for the same mineral, calcite, is shown in Figure 4.

As in the case of crystallization, rates of dissolution are considerably affected by the presence of adsorbed inhibitors. Such inhibition leads to surface-reaction controlled dissolution whose rate

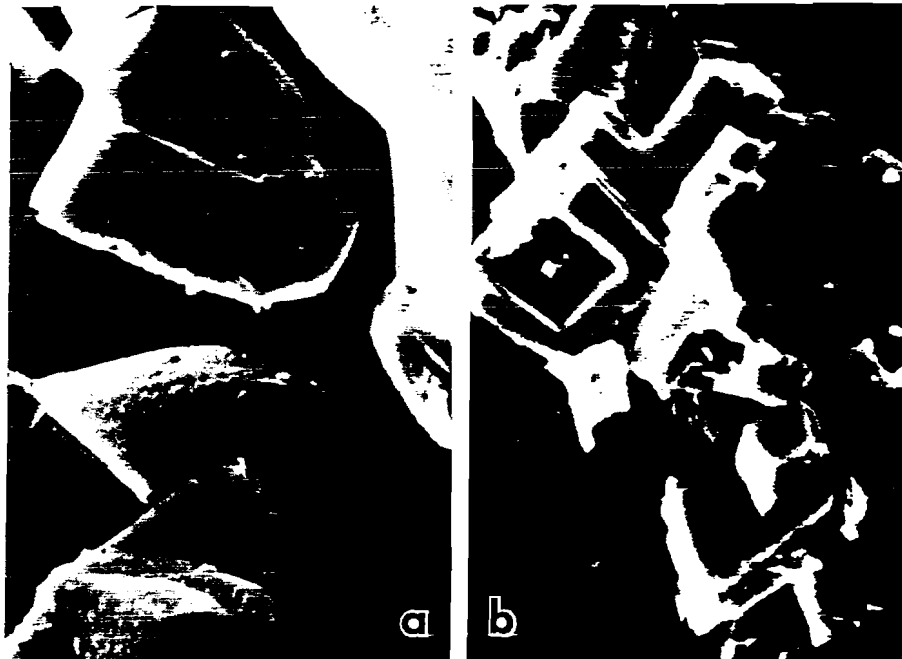


Figure 4. Electron photomicrographs of calcite which has undergone partial dissolution in seawater (X4000)

(a) Transport controlled dissolution; pH = 3.9. Note general rounding.

(b) Surface reaction controlled dissolution; pH = 6.0. Note angular, crystallographically controlled etch features.

(After Berner, 1978a, 1980 and Berner and Morse, 1974)

dependence on the degree of undersaturation is much greater than that predicted by commonly adopted theories. For example, the work of Morse (1978) and Keir (1980) has shown that calcite, under earth-surface conditions dissolves in seawater at a rate that is proportional to the fourth or fifth power of the concentration difference ($C_{eq} - C_{\infty}$). (Compare with equation (1).) This high-order kinetics is believed to be caused by the adsorption of dissolution-inhibiting phosphate ions onto the calcite surface (Berner and Morse, 1974; Morse and Berner, 1979).

Organic Matter Decomposition

Organic matter decomposition is discussed in the present paper because it exerts a major control on the chemistry and authigenic mineralogy of shallowly buried sediments. Rate laws for the decomposition of organic matter in sediments have not been well established. The model used here is that which I have used before (Berner, 1974; 1980). In it, it is assumed that the overall process of organic

decomposition (which includes a number of individual microbial steps) to CO_2 and other simple inorganic molecules, is first order with respect to the initial polymeric material undergoing decomposition. In other words:

$$\frac{dG}{dt} = -kG \quad (3)$$

where: G = concentration of organic carbon undergoing decomposition
(not total organic carbon),
 k = first-order rate constant,
 t = time.

The parameter G represents that fraction of the total organic matter actually undergoing decomposition at any given time. The reactivity, or k value, of organic compounds (*i.e.*, metabolizability) varies greatly and this is reflected by large variations in k from sediment to sediment and with depth in a single sediment (Toth and Lerman, 1977; Berner, 1978b; 1980; Jorgensen, 1978). Total organic carbon at the time of deposition is divided into various fractions, G_α , G_β , etc., according to their reactivity or k value. After deposition the most reactive compounds are destroyed first (G_α), followed by the next most reactive compounds (G_β), and so forth. As a result, sediments buried at slow rates contain only the less reactive organic compounds since the more reactive ones are destroyed at the sediment-water interface.

For each organic fraction designated as G the value of k varies with the process of decomposition. Organic matter in sediments is destroyed (microbially) by a variety of oxidizing agents in a definite succession (*e.g.*, Claypool and Kaplan, 1974). Dissolved oxygen is first used until it is entirely consumed, then dissolved nitrate until it is all gone, and then dissolved sulfate. Once all sulfate is used up there are no more inorganic oxidizing agents, and some of the organic carbon then appears as methane. Because of differences in free energy yields and metabolic pathways, decomposition of the same organic compounds by each of these processes can result in a different value of k in each case.

