Physical-Chemical Mechanisms
That Affect Regulation of Crystallization

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ABSTRACT

Minerals of biological and geological importance commonly exist as more than one polymorph or hydrate; crystallization of these minerals and polymorphs may have different pathways or mechanisms. Processes by which organisms form minerals can be complicated by the variety of mineral polymorphs and hydrates that may form, transform, and subsequently dissolve during a mineralization reaction and by the presence of the original mineral phase. Rates and mechanisms of mineral formation and transformation are regulated by conditions in solution and at the solution-mineral interface. Thermodynamic factors, such as solution pH, mineral-phase supersaturation, ionic strength, temperature, and the extent of ion association, regulate crystallization. In addition, crystallization processes also may be regulated by the kinetics of the crystallization reaction, which indicates an interfacial rate-determining step. In the example of calcium carbonate, depending on conditions, precipitation from a supersaturated solution results in a variety of mineral polymorphs and hydrates that have varying thermodynamic stabilities and reactivities. When a solution is only slightly supersaturated several common inorganic and simple organic ions decrease the calcite-seeded-crystallization rate. This rate decrease follows a Langmuir adsorption isotherm indicating that the mechanism of this process involves adsorption of these ions at growth sites on the crystal surface.

Introduction

In biological (Wheeler and Sikes 1984; Bills 1985; Lowenstam and Weiner 1985), geological (Spencer et al. 1985), environmental and technical processes (Reddy 1978) mineral crystallization has important consequences. However, an area of uncertainty in applying crystal-growth theory to processes occurring in these disciplines is that the crystallization mechanism may not be well characterized. Even though the number of possible mineral phases that will form from a supersaturated solution may be few, several different polymorphs may form, transform, and subsequently dissolve during precipitation. The potential for a variety of different solid phases forming simultaneously or consecutively from a supersaturated solution complicates the interpretation of precipitation data and the description of crystallization mechanisms. Nielsen and Christofferson (1982) propose that the most appropriate way to study and understand mineral formation in solution is by using kinetic techniques. They suggest that insight into mineral-crystallization mechanisms is best developed by a comparison of empirical rate laws and absolute reaction rates with theoretical considerations derived from well-developed hypotheses.

Nancollas (1982) has reported that mixed mineral phases may be caused by formation of one phase on another in metastable, supersaturated solutions. In other mineral systems, a sequence of unstable polymorphs form and subsequently transform in a supersaturated solution (Bills 1985; Lowenstam and Weiner 1985; Ogino et al. 1987). For example, for the precipitation of calcium phosphate minerals at ambient temperatures, different calcium phosphate phases (arranged in order of increasing solubility: hydroxyapatite, tricalcium phosphate, octacalcium phosphate, and dicalcium phosphate dihydrate) may form depending on the degree of supersaturation, ionic medium, and pH (Amjad 1987). Slow formation rates for hydroxyapatite cause the formation of less stable polymorphs, such as dicalcium phosphate dihydrate, during spontaneous precipitation of calcium phosphate minerals under physiological conditions. In the example of calcium carbonate, calcite is the stable phase at ambient temperature and pressure, but other less stable polymorphs, such as aragonite, may remain unaltered for extended intervals. Mineralization in biological systems also may involve complex organic matrix-mineral interactions that may affect mineral form and reaction kinetics (Wheeler and Sikes 1984).

Calcium carbonate is a common constituent of hard tissues of many biological organisms, geological materials and sediments in freshwater and saltwater. Because of its presence and importance in these media, the equilibria and kinetics of the heterogeneous reactions of calcium carbonate in aqueous solutions have received extensive study (see for example Reddy and Wang 1980 and references therein). However, many kinetic studies have used solutions of much greater supersaturation than those typical of biological or geological environments; therefore results from such investigations may not be directly applicable to natural mineralization reactions.

This paper presents descriptions of the mechanisms that regulate mineral crystallization and illustrate these mechanisms using specific examples from studies of calcium carbonate. The focus of the experimental results presented will be on mineral-reaction kinetic data obtained in the author's laboratory. A brief discussion of the procedures used to characterize solution composition is presented based on a thermodynamic-solution model. Precipitation reactions in moderately supersaturated and supersaturated solutions, the mechanism of calcium carbonate (calcite) seeded crystallization from a metastable solution, and the effect of inhibitor ions on the rates and mechanism of calcite growth onto seed-crystal surfaces will be reviewed.

Factors Affecting Crystallization Mechanisms

Lattice-ion concentrations in solution substantially affect crystallization mechanisms. The lattice-ion concentrations typically are calculated from measured total-solution concentrations taking into account ion-association and acid-dissociation reactions, and activity-coefficient terms. Typical thermodynamic data used in the calculation of solution composition are presented in Table 1 for the solubility of calcite at 25 degrees Celsius, the solubility of carbon dioxide in water, the dissociation of carbonic acid, the dissociation of calcium carbonate and calcium bicarbonate ion pairs, and the dissociation of water. In the quantitative analysis of data from crystal growth experiments and calculation of supersaturation values, it is important to consider ion pairs as well as unassociated ions. For example,

a calcite-seeded-growth experiment containing a total calcium concentration of 2.6×10^{-4} mole per liter and a total inorganic carbon concentration of 42×10^{-4} mole per liter has substantial concentrations of the calcium carbonate (0.308×10^{-4} moles per liter) and the calcium bicarbonate (0.122×10^{-4} moles per liter) ion pairs (Reddy 1977).

Table 1. Thermodynamic constants at $25°$ Celcius for the sytem $CaCO_3 - CO_2 - H_2O$

Reaction	log K	Source
$CaCO_3$ (Calcite) $= Ca^{2+} + CO_3^{2-}$	-8.475	Jacobson and Langmuir (1974)
$CO_2 + H_2O = H_2CO_3^*$	-1.466	Harned and Davis (1943)
$H_2CO_3^* = H^+ + HCO_3^-$	-6.351	Harned and Davis (1943)
$HCO_3^- = H^+ + CO_3^{2-}$	-10.330	Harned and Scholes (1941)
$CaHCO_3^+ = Ca^{2+} + HCO_3^-$	-1.015	Jacobson and Langmuir (1974)
$CaCO_3^0 = Ca^{2+} + CO_3^{2-}$	-3.135	Reardon and Langmuir (1974)
$H_2O = H^+ + OH^-$	-14.000	Helgeson (1969)

Solution Supersaturation

Mineral solubility (in convenient units of concentration) plotted as a function of temperature may be divided into zones that are above and below the saturation-concentration curve. In this
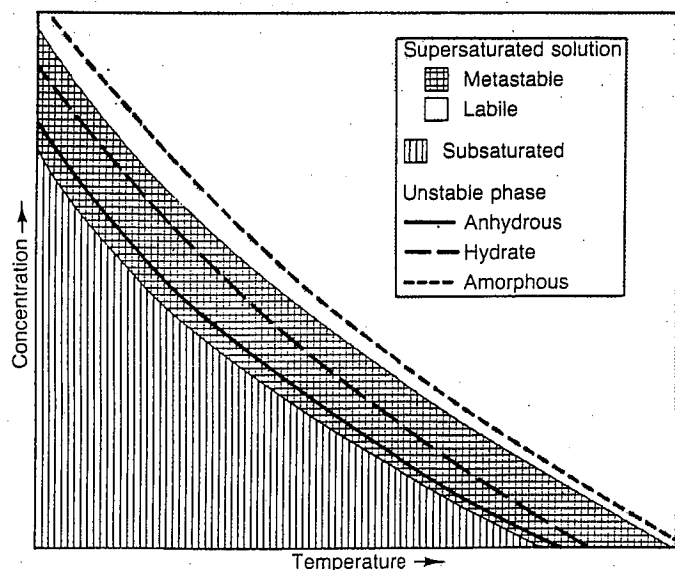

Figure 1. Schematic diagram of dissolved mineral concentration and saturation concentration plotted as a function of temperature (modified from Nancollas and Reddy 1974). Mineral subsaturated- and supersaturated-solution zones in this diagram are defined by the mineral saturation concentration curve. Steady-state solubility saturation concentration curves are shown for three thermodynamically unstable phases of the mineral. The supersaturated-solution zone is further divided into subzones of metastable and labile supersaturated solutions, determined by the induction interval as described in the text.

type of plot (Figure 1), the equilibrium concentration (i.e., the solubility), the subsaturated-solution zone and the supersaturated-solution zone of a thermodynamically stable mineral can be schematically shown as a function of temperature. The solubility of other thermodynamically less stable and, hence, more soluble polymorphic forms of the mineral also can be shown on such a plot. As shown in Figure 1, the polymorphic solubilities decrease as follows: thermodynamically stable phase $<$ unstable anhydrous phase $<$ unstable hydrate phase $<$ unstable amorphous phase.

In the example of calcium carbonate, the thermodynamically stable phase is calcite, and there are two unstable anhydrous phases – aragonite and vaterite. In addition, there are two unstable hydrate phases – calcium carbonate monohydrate and calcium carbonate hexahydrate – and one reported amorphous phase.

Below the saturation-concentration curve in Figure 1 solutions are subsaturated solutions; that is, mineral crystals placed in solutions of this composition will dissolve. Solutions that have a composition on the saturation-concentration curve are in equilibrium, and mineral crystals placed in this solution remain unchanged. If the solution composition is above the saturation-concentration curve shown in Figure 1, the composition is within the supersaturated-solution zone, and mineral will eventually form on crystals placed in this solution.

Supersaturation, Ω_c, is defined as the ion-activity product (i.e. IAP) of the lattice ions of the mineral divided by the thermodynamic solubility product of the mineral (i.e., K_{sp}):

$$\Omega_c = IAP/K_{sp}. \qquad (1)$$

Supersaturation values are of major importance in defining the pathway or mechanism of precipitation reactions in the absence of a solid mineral.

The solution-supersaturation zone is divided into two operational subzones that reflect the time interval required to form a solid phase in solution. These two subzones consist of: 1) metastable supersaturated solutions, and 2) labile supersaturated solutions (Figure 1). In metastable supersaturated solutions, which have supersaturation values less than about 10 in the case of calcium carbonate, nucleation, in the absence of seed crystals, of the stable phase does not occur for extended time intervals (as long as several days in some instances). In labile supersaturated solutions, which have supersaturation values greater than about 20 in the case of calcium carbonate, nucleation occurs within a well-defined time interval during solution formation or shortly thereafter. This well-defined time interval, t_i, is called the induction interval, which can vary from a few seconds to a few hours.

Metastable supersaturated solutions of calcium carbonate can be prepared with small supersaturation values; these solutions are stable for 24 hours or longer. As illustrated in Figure 2 for a metastable supersaturated solution, crystal growth will not commence unless seed crystals are added. In the absence of inhibiting ions, labile supersaturated solutions of calcium carbonate with supersaturation values greater than 100 nucleate within a few seconds, usually during the time of mixing.

Nucleation

Nucleation processes illustrated in Figure 2 generally occur when supersaturation values are greater than about 20. Characteristic values of supersaturation that can be used to measure induction intervals vary among minerals; for calcium carbonate, induction intervals can be measured for supersaturation values that range from about 20 to about 80. A summary of data for calcium carbonate nucleation experiments is shown in Figure 3; particle number, the number of particles formed in
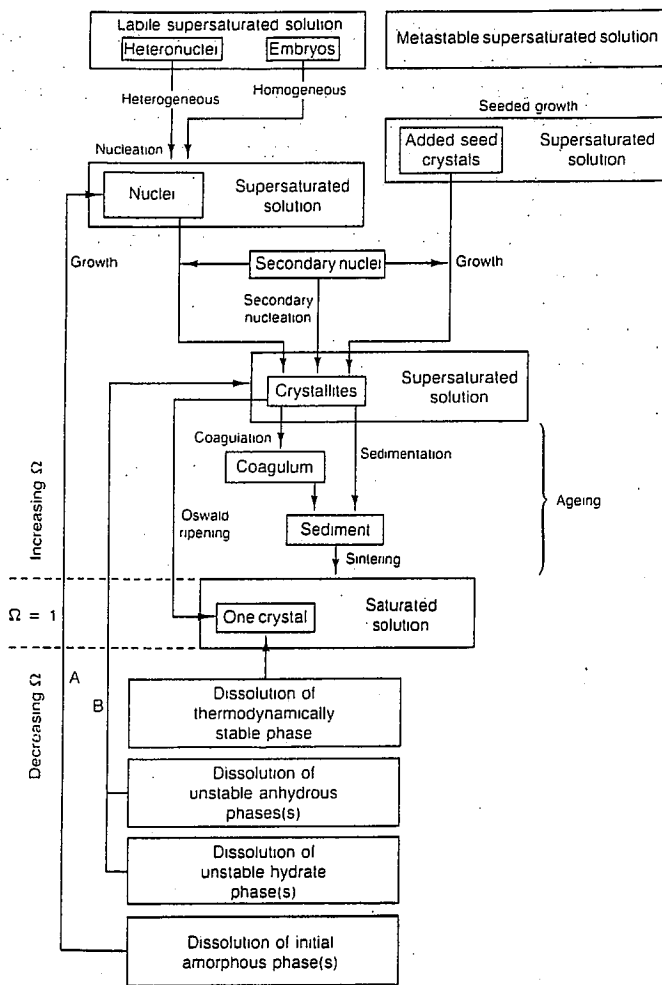
Figure 2. Pathways of mineral formation, transformation, and dissolution in aqueous solutions (modified from Nancollas and Reddy 1974). This diagram is for a hypothetical thermodynamically stable mineral that has three unstable phases that increase in solubility as follows (1) anhydrous phase, (2) hydrate phase, and (3) amorphous phase. As shown in Figure 1, the solubility of the unstable amorphous phase is within the labile-supersaturated-solution subzone; thus, nucleation of the stable phase can occur in solutions containing this phase. The unstable anhydrous and hydrate phases have lesser solubility than the amorphous phase; thus, nucleation of the stable phase does not occur readily in solutions containing these phases.

each milliliter of solution (Figure 3A), and induction interval, in minutes (Figure 3B), are plotted as a function of supersaturation. Scatter in the particle-number and induction-interval results is caused by heterogeneous nucleation on the walls of the reaction vessel and on submicrometer size particulates present in solution. Nucleation rates, expressed as the number of particles produced per milliliter per minute also can be used to evaluate calcium carbonate formation. At less than a critical supersaturation value (a supersaturation value of about 10 for the data shown in Figure 3) nucleation rates are slow.

Calcium carbonate nucleation experiments may not clearly identify processes (that is a direct path in Figure 2 from the supersaturated solution to the solution at equilibrium) that regulate crystal growth. This is difficult because there commonly are one or more unstable phases that form in the initial supersaturated solutions. For calcium carbonate precipitation several investigators (Reddy and Nancollas 1976; Reddy 1986; Ogino et al. 1987) have examined the initially formed calcium carbonate precipitate. Scanning-electron-microscopic examination of the initial
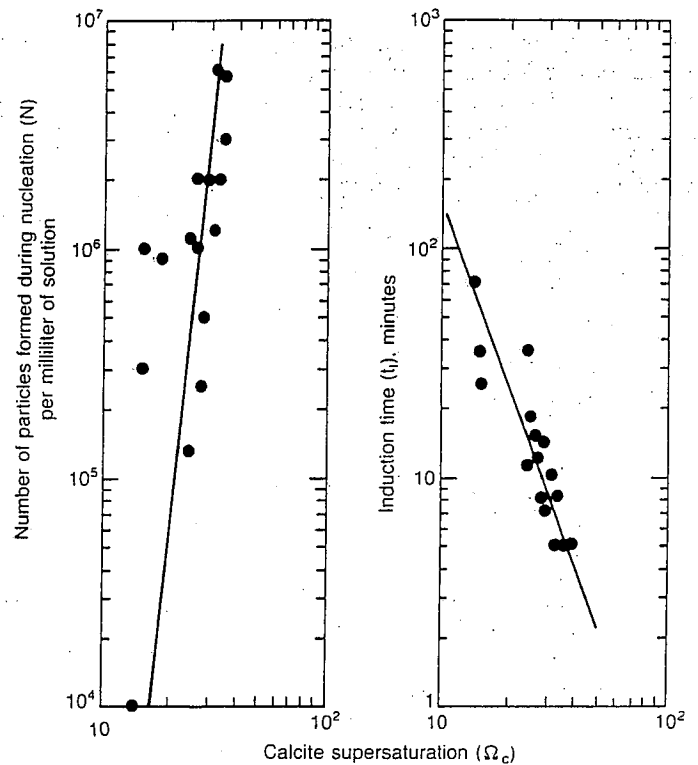

Figure 3. Calcium carbonate nucleation expressed as: A, the number of particles formed during nucleation per mililiter of solution plotted as a function of the supersaturation values of calcite; and B, the induction interval, in minutes, plotted as a function of supersaturation values of calcite (Reddy 1986).

precipitate indicates spherical particles with diameters that range from several tenths of a micrometer to as much as 1 micrometer (Reddy 1986). X-ray diffraction and optical-microscopy measurements indicate that this material is amorphous calcium carbonate.

Ogino et al. (1987) recently have published a careful investigation of calcium carbonate precipitation processes in supersaturated solutions. They have identified an amorphous calcium carbonate, that has a solubility product of approximately 10^{-6} (mole per liter)^2, which forms during rapid precipitation from supersaturated solutions and subsequently transforms to a mixture of crystalline polymorphs within minutes. Specifically, this amorphous calcium carbonate transforms either to the unstable polymorphs of vaterite (at low temperatures) and aragonite (at high temperatures) or to calcite; both polymorphs transform to calcite through a dissolution-reprecipitation mechanism. The rate determining step in the dissolution-reprecipitation process is the growth of calcite crystals.

Crystallization

In contrast to spontaneous precipitation experiments, which investigate nucleation and crystal-growth mechanisms in combination (Figure 2), the crystallization mechanism alone can be studied using a seeded-crystal-growth technique (Reddy 1983). During a seeded-growth-experiment, seed crystals are placed in a metastable supersaturated solution. These seed crystals grow at a rate defined by the solution composition. Spontaneous precipitation in solution is avoided; the incorporation of growth units on a crystal surface and the effect of additive ions on the reaction rate can be reproducibly measured.

Calcite seed crystals used in selected seeded-crystal-growth experiments are about 10 micrometers on the edge, and are aged in a seed suspension prior to use (Reddy and Gaillard 1981). Most calcite seed crystals used in experiments described here have uniform surfaces, and are free of irregularities. After addition of the seed crystals to the supersaturated solution, there are changes in the surface morphology of the seed crystals that correspond to new crystal growth (Reddy and Gaillard 1981).

Seeded-crystal-growth experiments can be used to identify interfacial-rate-determining processes, and the effect of additive substances on the crystallization mechanisms. Conditions for a typical calcite seeded-crystal-growth experiment discussed here were: temperature, 25 degrees Celsius; pH, 8.72; total calcium concentration, about 2.6×10^{-4} mole per liter; total carbonate concentration, 42×10^{-4} mole per liter. A relatively small quantity of total carbonate was present as free carbonate ions at this solution pH, and the supersaturation value was 4.6 with respect to calcite.

In seeded-crystal-growth experiments (in the absence of growth inhibitors), crystallization of fresh mineral begins immediately after addition of the seed crystals and is accompanied by a corresponding decrease in solution concentration. Experimental results (Figure 4) illustrate that the total calcium concentration in the solution decreases from 2.6×10^{-4} mole per liter at the start of the experiment to 1×10^{-4} mole per liter at the end of the experiment. During the crystallization reaction, there is a corresponding change in pH of the solution that is plotted as a function of time, in minutes, in Figure 4. The rate of reaction is equal to the slope of the total calcium concentration as a function of time curve at any particular time.
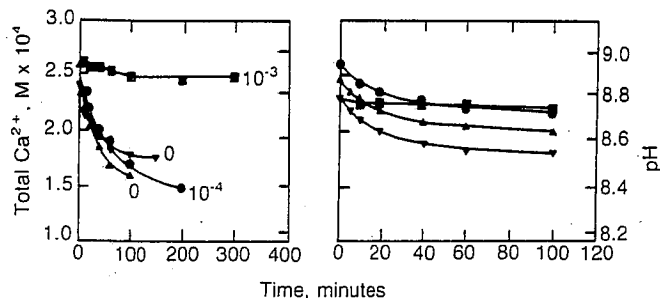

Figure 4. Total calcium concentration and pH of the supersaturated solution plotted as a function of time for seeded crystal growth in the presence and absence of added magnesium ion. Molar concentrations of added magnesium ions are indicated at the end of the curves (Reddy and Wang 1980).

Results of seeded-crystal-growth experiments can indicate the effect of additive ions, such as magnesium ions, on the crystallization process. The change in solution calcium concentration as a function of time for seeded crystallization in the presence (upper curves) and absence of magnesium ions (lower curve) is plotted in Figure 4. As magnesium ion concentration increases from 10^{-4} to 10^{-3} mole per liter, there is a concomitant decrease in the calcite-crystal-growth rate.

A number of rate equations have been proposed for the analysis of calcite crystallization kinetics (Reddy 1977; Smallwood 1977; Reddy et al. 1981; Inskeep and Bloom 1985; Compton and Daly 1987; House and Donaldson 1986; House 1987). In these mathematical expressions, the rate of crystal formation, which is the change in crystal mass with time, is related to a product of terms; each term in the rate equation corresponding to a process or factor that regulates the crystallization reaction. These terms are: (1) the crystallization rate constant k, which is a kinetic factor; (2) the surface area term, s; and (3) a term for the chemical driving force, which is related to the difference between the actual

solution concentration and the equilibrium value for the mineral being crystallized. This term for the chemical driving force is raised to a power greater than unity (to the second power in the example of a parabolic rate law, Nielsen 1981) in crystal-growth processes that have a surface-reaction-rate determining step.

Nielsen (1987) has classified the mechanisms that control the growth rate of electrolyte crystals in aqueous solutions. Linear kinetics originate when crystal-growth rates are controlled by transport through the solution or by adsorption at the crystal surface. Conversely, parabolic kinetics originate when the crystal-growth rates are controlled by the integration of growth units at kinks on the crystal surface.

For the growth of calcite seed crystals at pH 8.8 and fixed ionic strength, the change in total calcium ion concentration with time follows a rate expression of the form:

$$dN/dt = -k s N^2 \qquad (2)$$

where N is the quantity of calcite to be precipitated from solution to reach equilibrium; k is the crystal-growth-rate constant; and s is the concentration of seed crystal that is proportional to the surface area available for growth.

Mullin (1972) has described a crystallization parameter, "theoretical crystal yield" that is equivalent to N as defined above. The experimental value of N is determined by calculating the difference between total calcium concentration in the solution and the value for that term at equilibrium calculated from the calcite solubility product, the solution pH, and the total carbonate concentration. An integrated form of equation 2 is convenient for analysis of the experimental results:

$$N^{-1} - N_o^{-1} = k s t \qquad (3)$$

where N_o is the quantity of calcite to be precipitated from the supersaturated solution at the onset of the crystallization reaction.

The rate function (equation 3), which is a linear function of time, can be plotted so that the slopes of the lines are proportional to the rate constant k (Figure 5). For calcite growth in presence of magnesium ions, plots of the rate function are linear with time, which is in agreement with the proposed rate law. In the absence of magnesium ions, the rate-function plot has the largest slope and, correspondingly, the largest rate constant. As the magnesium ion concentration increases, the best-fit slope values and the rate constant for crystal growth decrease.
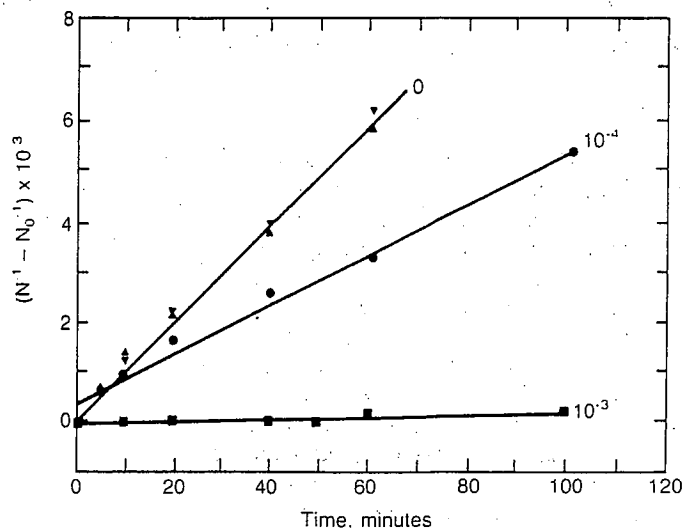

Figure 5. Plots of the integrated rate function as a function of time for growth of calcite seed crystals in the presence and absence of magnesium ions. Molar concentrations of added magnesium ions are indicated at the end of the curves (Reddy and Wang 1980).

The rate of calcite crystallization in the presence and absence of magnesium ions is consistent with equations 2 and 3, and with an interfacial rate controlling process. This indicates that the rate determining step in calcite-crystal growth involves the incorporation and dehydration of an adsorbed, partially hydrated calcium carbonate species into the crystal at a growth site on a crystal surface.

Rate constants for calcite-crystal growth for a range of magnesium ion concentrations indicate the crystal growth inhibition effect (Figure 6). There is a substantial decrease in the calcite-crystal growth-rate constant as the magnesium ion concentration increases.
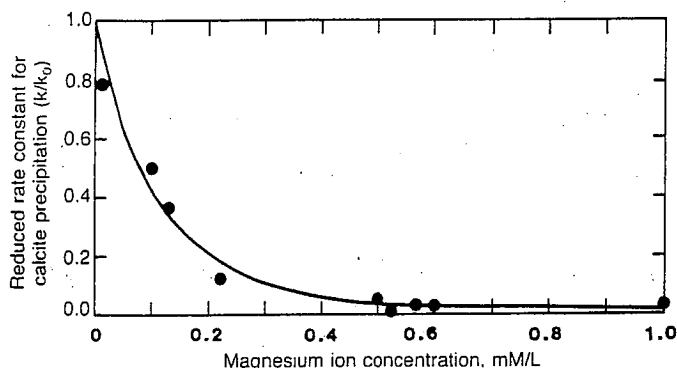

Figure 6. Calcite crystallization reduced-rate constant (k/k_o) as a function of the concentration of magnesium ions in solution (Reddy 1986).

Adsorption mechanisms commonly have been used to describe growth-rate decrease by added substances. A Langmuir adsorption isotherm model, for example, (Reddy 1977; Reddy and Wang 1980) yields equation 4, which relates the change in the crystal growth-rate constant to the additive ion concentration.

$$k_o (k_o - k)^{-1} = 1 + (A/C) \qquad (4)$$

In equation 4, the first rate constant, k_o, is that for a pure supersaturated solution. The second rate constant, k, is the rate constant in the presence of added ions. The first term, A, is a constant related to the rates of adsorption and desorption of the added ions. The second term, C, is the concentration of the added ions in solution. A plot of the Langmuir rate-function term as a function of the reciprocal of the magnesium ion concentration has a linear relation with an intercept of almost unity that supports the use of the Langmuir model to describe the inhibition effect of magnesium ions (Figure 7). This inhibition effect indicates that magnesium ions decrease the growth rate of calcite crystals through an absorption process at growth sites on the crystal surface.
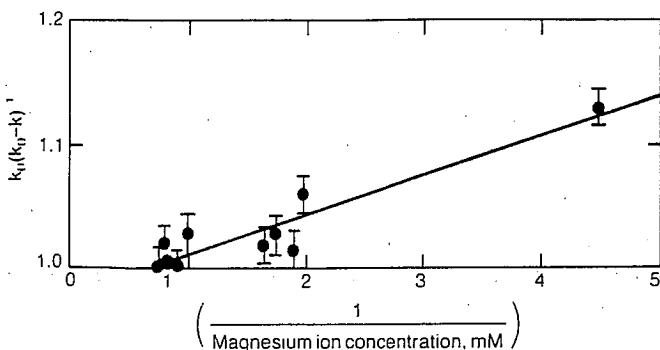

Figure 7. Langmuir isotherm plot of $k_o/(k_o-k)$ as a function of the reciprocal of the added magnesium ion concentration in solution for calcite seeded crystallization (Reddy 1986).

The surface mechanism for calcite crystallization involves incorporation of hydrated calcium species absorbed on the crystal surface at a growth site. For calcite-crystal growth in the presence of magnesium ions, a magnesium ion becomes adsorbed at the growth site. Because ionic dehydration after adsorption of the incorporating unit at a growth site is considered to be the rate determining step in calcite-crystal growth, the greater hydration energy of the magnesium ion in comparison to that for the calcium ion causes slower ion dehydration at the growth site, which decreases the overall calcite-crystal growth rate.

The effect of other ions on the calcite-crystal-growth mechanism has been studied using the seeded-growth technique. For example, glycerophosphate, a phosphorus containing ion in the terrestrial environment, and orthophosphate have been examined in detail (Reddy 1975, 1977). Glycerophosphate and phosphate ions have calcite-crystal-growth-inhibition characteristics that are consistent with the Langmuir absorption isotherm model, which indicates that calcite-crystal-growth inhibition by these ions is caused by absorption at growth sites on that crystal surface.

One of the requirements of the Langmuir absorption model is that the adsorbed ion does not incorporate into the crystal. This requirement can be tested, for example, by measuring the phosphate concentration in a supersaturated solution during a calcite-crystallization experiment. When these measurements were made in the experiments described above, the phosphorus concentration remained unchanged. Phosphorus ions were not incorporated into the growing calcite crystals in substantial quantities, rather these ions function as a surface inhibitor by blocking the calcite- crystal growth sites (Reddy 1980).

SUMMARY

Mechanisms that regulate crystallization processes, for growth onto seed crystals in a metastable supersaturated solution, have been much more clearly defined than those for spontaneous precipitation. In the instance of calcite crystallization from a seeded supersaturated solution, the rate limiting step is a surface-controlled reaction. A Langmuir absorption mechanism describes the measured calcite-crystallization-rate decrease for several additive ions discussed in this paper (magnesium, phosphate, and glycerophosphate ions). There is an absence of mineral phases other than calcite during the calcite seeded crystal growth in the presence of phosphate and magnesium ions when supersaturation values are small.

Crystallization mechanisms can vary substantially for several minerals that are involved in biomineralization. Supersaturation values, when large, cause the formation of complex mineral polymorph and hydrate mixtures that may transform or dissolve or both as the solution composition approaches equilibrium with the thermodynamically stable phase. At the present time, there is a general outline available for describing the precipitation of several biominerals (i.e., calcium carbonates and calcium phosphates). However, much additional research is needed to identify the effect of organic substances on mineral transformations in biomineralization processes.

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