Effect of Magnesium Ions on Calcium Carbonate Nucleation and Crystal Growth in Dilute Aqueous Solutions at 25°C

By MICHAEL M. REDDY, U.S. Geological Survey, Box 25046, Denver Federal Center,
MS 407, Denver, Colorado 80225

CONTENTS

FIGURES

TABLES

Abstract

Calcium carbonate formation has been examined within a range of solution supersaturations and magnesium-to-calcium ratios. Potentiometry, turbidimetry, and chemical analysis were used to monitor changes in solution composition; solid phases were characterized by optical and scanning electron microscopy, specific surface area measurements, and X-ray diffractometry. Nucleation rates, particle numbers, precipitate composition, and crystal morphology were found to be a function of supersaturation level, solution hydrodynamics, and magnesium ion concentration. The crystallization of calcite from metastable supersaturated solutions was studied using a seeded-growth technique. Under all conditions, calcite crystallization rates were proportional to the square of relative supersaturation and were controlled by a surface reaction. Kinetic analysis demonstrated that the observed reduction in the rate of calcite crystallization in the presence of magnesium ion resulted from a decrease in the reaction rate constant. This observed reduction was consistent with a Langmuir adsorption model, implying that the inhibition mechanism involved reversible adsorption of magnesium ions at growth sites on the calcite crystal surface. The formation of an epitaxial magnesium-rich surface phase was not significant. Crystallization experiments generally did not reach calcite equilibrium. Supersaturation at the termination of these experiments depended on the initial magnesium ion concentration and seed crystal-to-solution ratio, demonstrating a kinetically controlled reaction.

INTRODUCTION

Rates and mechanisms of carbonate mineral reactions in surface and subsurface waters are of considerable interest in low-temperature aqueous geochemistry and are important aspects of diagenesis in sedimentary rocks. Heterogeneous reactions of calcium carbonate have been studied extensively (Reddy, 1978, and references therein). Several investigators have demonstrated the importance of kinetic factors in the approach of carbonate minerals to equilibrium and the influence of kinetic inhibitors on the formation and dissolution of carbonate minerals. Magnesium ion has commonly been cited as a mediator of calcium carbonate mineral kinetics. For example, Thorstenson and Plummer (1977, 1978) and Berner (1978) examined the influence of magnesium ion on the formation of calcium carbonate over a range of natural and experimental conditions; however, relatively little is known about the reaction rates or mechanistic details of this inhibitory process.

Calcite-seeded growth in moderately supersaturated solutions follows a parabolic rate equation in both the presence and absence of magnesium ion (Reddy, 1978). In these experiments, magnesium ion reduced the rate of calcite crystallization by a mechanism involving the blockage of growth sites on the crystal surface. No evidence was obtained to support the hypothesis that a magnesium-rich surface phase formed during crystallization. Reddy and Nancollas (1976) reported that high concentrations of dissolved magnesium ion markedly influenced the formation of calcium carbonate by spontaneous precipitation.

In the present study, the formation of calcium carbonate has been characterized by chemical analysis, potentiometry, X-ray diffraction, and optical and electron microscopic methods over a wide range of supersaturation and solid/solution ratios in the presence and absence of magnesium ion. Supersaturation, Ω_c, is herein defined as the calcium carbonate ion activity product (IAP) divided by the calcite thermodynamic solubility product, (K_{sp}), that is, $\Omega_c = IAP/K_{sp}$.

Supersaturation values are commonly divided into two classes: labile solutions and metastable solutions. This differentiation is based on the time required to form a precipitate in the solution. Labile solutions have high supersaturations; nucleation occurs within a brief (typically a few seconds) interval after solution preparation. Metastable solutions, on the other hand, have intermediate supersaturations; nucleation follows a specific well-defined interval, t_i (referred to as the induction interval), typically from a minimum of several minutes to several hours. Designation of supersaturation values for each class is dependent on the mineral being studied and the experimental conditions. For calcium carbonate, labile solutions have supersaturations greater than 100, and metastable solutions have supersaturations less than 100. Metastable solutions can be prepared with low supersaturation values (5–7), which do not nucleate within 24 hours. These metastable solutions are used for seeded-growth experiments.

MATERIALS AND METHODS

Grade-A glassware, reagent-grade chemicals, and deionized, distilled water filtered through Millipore[1] filters were used in all experiments. Prior to each experiment, reagent solutions were filtered through prewashed 0.22-μm Millipore filters to minimize the presence of heteronuclei.

Details of the nucleation experiments in labile-supersaturated solutions have been presented elsewhere (Reddy and Nancollas, 1976). These solutions were prepared by mixing thermostated sodium carbonate and calcium chloride solutions in a large reaction vessel as rapidly as possible. The progress of the precipitation reaction was followed by the analyses of filtered samples withdrawn from the reaction cell. The calcium concentration in the filtered aliquots was determined by ethylene-diamine tetraacetic acid (EDTA) titration with a micrometer buret in the presence of a Calcine indicator.

---

[1] Use of trade and company names is for descriptive purposes only and does not imply endorsement by the U. S. Geological Survey.

Magnesium ion analyses were performed in the same manner (by difference) with the appropriate indicator (Eriochrome Black T). Total carbonate concentrations in solution were calculated from dilution of stock solution and separately from titration of the filtrate with 0.01 *N* sulfuric acid.

pH was measured at 25.00 ± 0.02°C with a Corning Model 12 pH meter, a Sargent Combination Electrode, and a Sargent Model SP recorder. Electrodes were calibrated prior to and following each experiment with National Bureau of Standards standard buffer solutions at pH 6.865 (0.025 *M* potassium dihydrogen phosphate, 0.025 *M* disodium hydrogen phosphate) and pH 9.18 (0.01 *M* sodium borate) at 25°C.

The preparation of metastable supersaturated solutions has been described previously (Reddy, 1978). Calcium, magnesium, and total carbonate concentrations determined by analysis of the metastable solution shortly after preparation agreed with the concentration values calculated from the dilution of stock solution. Solution pH was monitored continuously, and turbidity was determined by a light-scattering technique on aliquots withdrawn from time to time during the nucleation experiments. Estimates of the length of the induction period from pH and turbidity measurements agreed within 5 percent for the same experiment.

Precipitates for chemical and X-ray diffraction analysis and for optical and electron microscopy were obtained by filtering 10 to 500 milliliters of the growth suspension through a 0.22-μm Millipore filter, followed by air-drying. Precipitates on the filter surface were coated with carbon and gold and examined by scanning electron microscopy (SEM) using an ETEC Autoscan instrument. Dried precipitates for optical microscopy were slurried in a small amount of ethylene glycol and examined with a Zeiss RA microscope. Specific surface areas of calcium carbonate precipitates were determined with a Quantachrome Monosorb surface-area analyzer. X-ray diffraction (XRD) analyses were done using Ni-filtered CuKα radiation with a Siemens diffractometer or with a Debye-Scherrer powder camera with a Norelco X-ray generator.

Seeded-growth experiments began by inoculating a stirred supersaturated solution with a known weight of calcite seed at seed concentrations of 0.05 to 0.5 g/L for magnesium-free solutions. Inasmuch as the rate of formation of calcite in solutions containing magnesium ion can be considerably slower than in magnesium-free solutions, two modifications of this laboratory scheme were adopted for selected experiments. Several runs used seed crystal concentrations greater than 0.5 g/L to enhance calcite formation and the approach to equilibrium. Other runs were reinoculated with calcite seeds after a specific growth interval, and the subsequent reaction was followed to completion.

Several measurements of the crystallization rate in seeding solutions employed a constant pH of 9 using the Radiometer pH stat system: TTT2 titrator, titrograph, ABU 12 autoburet, a closed reaction cell with stirrer, and separate pH and reference electrodes.

RESULTS AND DISCUSSION

Nucleation in labile solutions

Ionic concentrations and supersaturations were calculated from the measured pH and from the total calcium and carbonate concentrations by using mass-action and mass-balance equations (Reddy, 1978) (table 1). The solubility product of calcite and the stability constants of $CaCO_3$ and $CaHCO_3^+$ were taken from Jacobson and Langmuir (1974). Supersaturation dropped rapidly in continuously stirred labile solutions; visible onset of precipitation occurred within 2–10 seconds of mixing (fig. 1). Initial pHs of 10.4 decreased to 9.5

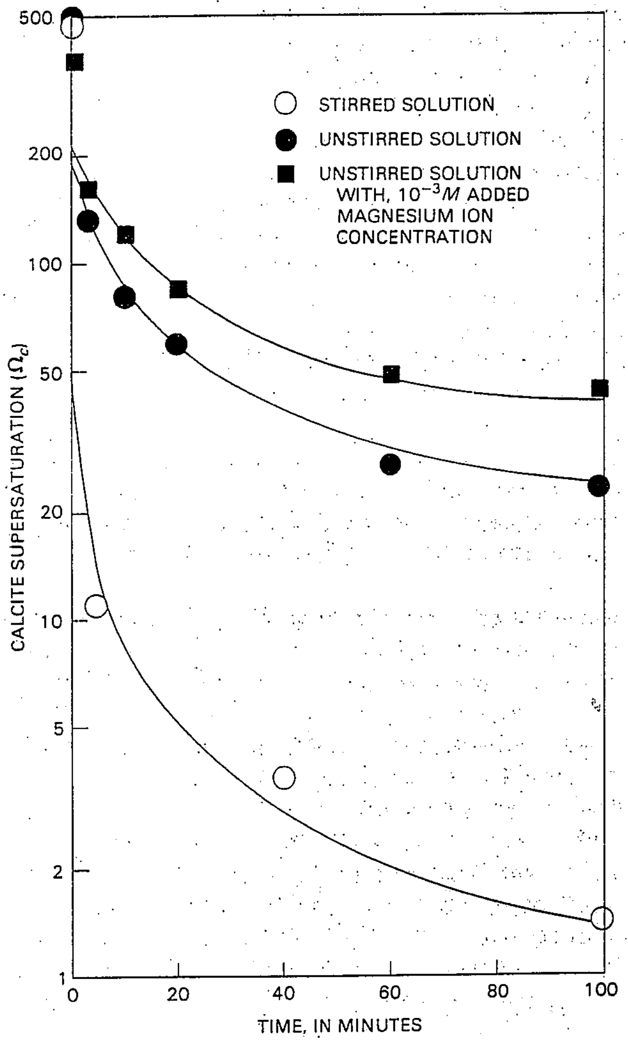


Figure 1. Calcite supersaturation (Ω_c) versus time for calcium carbonate nucleation from stirred and quiescent labile solutions.

Table 1. Initial solution concentrations and calcite supersaturation values (Ω_c) for calcium carbonate nucleation from labile-supersaturated solutions at pH 10.3

[Total carbonate concentration 5×10^{-3} *M* at 25°C. Leaders (---) indicate no added magnesium ion; Ω_c, supersaturation]

Experiment	Initial concentration (moles per liter x 10^4)					
	Total					
	Ca^{2+}	Mg^{2+}	Ca^{2+}	CO_3^{2-}	$CaCO_3°$	Ω_c
[1]3	50	---	26.83	17.16	21.82	462
[1]5	54	1	28.83	16.81	22.47	476
7	54	---	29.57	16.16	22.25	471
8	55	10	31.16	16.42	22.13	468
9	53	1	30.25	16.05	22.45	475
11	53	---	29.65	16.12	22.30	472
12	46	10	24.63	20.30	17.54	371
13	58	---	33.72	15.63	23.97	508

[1] Experiments 3 and 5 were stirred continuously during precipitation; all other experiments were quiescent after intial mixing.

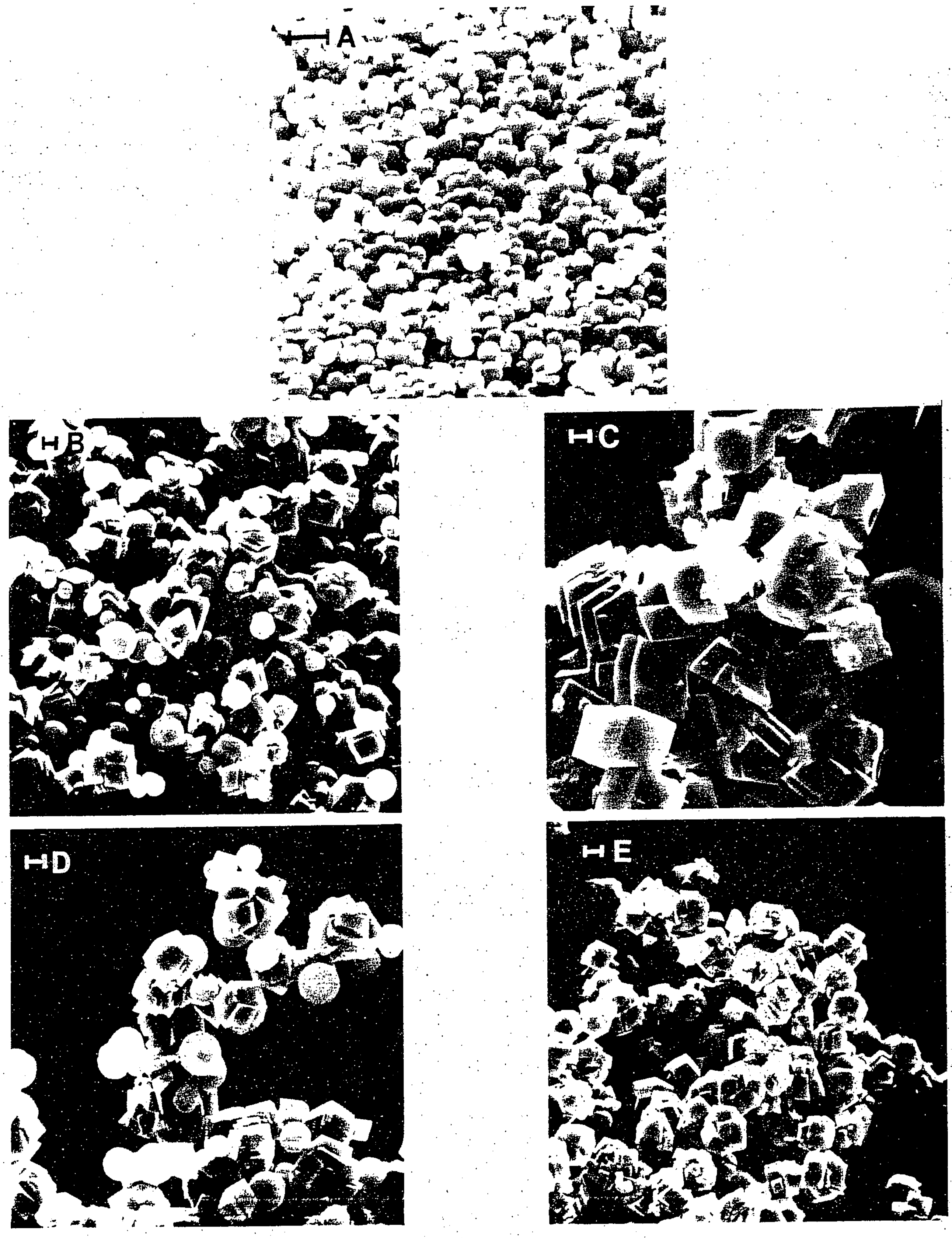
during the first 10 minutes of reaction and to 8.6 during the first 100 minutes. Long-term solution pH's approached 8.2. The total calcium concentration dropped from 5×10^{-3} *M* to a steady-state value of less than 1×10^{-3} *M* within 5 minutes of mixing and solutions rapidly approached calcite equilibrium. In unstirred experiments, the calcium concentration dropped more slowly with time; the experiments approached a steady-state calcium carbonate IAP significantly greater than that for calcite equilibrium (fig. 1). IAP's during this phase of the precipitation reaction may correspond to the steady-state values of the initially formed precipitate.

The initial precipitate had characteristics of a noncrystalline or microcrystalline material. X-ray diffraction patterns had only a few broad peaks, and examination by optical microscopy showed submicrometer, isotropic particles. In many experiments, however, vaterite and calcite were identified in the XRD pattern, and under the microscope the samples consisted of a mixture of birefringent crystals in a submicrometer-size, optically isotropic matrix. By SEM, most of these initial precipitates were seen to consist of uniform, submicrometer-size, spherical particles that displayed no euhedral character (fig. 2). Specific surface areas calculated for these initial precipitates agreed well with the measured value of 15 m^2/g.

The formation of calcium carbonate polymorphs and their subsequent transformation and incorporation of magnesium ion differed between the stirred and unstirred solutions, suggesting that the processes occurring during or shortly after calcium carbonate nucleation from highly supersaturated solutions were influenced by solution hydrodynamics. For example, both the change in total calcium concentration and the nucleation particles number (the number of particles formed in the supersaturated solution) differed between the stirred and unstirred solutions. Particle number differences were most pronounced for calcite rhombs and vaterite spheres. The precipitates that formed in stirred solutions did not appear to have a noncrystalline component (figs. 2*B* and 2*D*), presumably because of the rapid transformation of any such material that did form. Scanning electron micrographs of precipitates collected on filters showed that in stirred solutions, containing low concentrations of magnesium ion, calcite rhombs and vaterite spheres formed in nearly equal numbers. The recrystallization of what may have initially been noncrystalline material and unstable polymorphs of $CaCO_3$ yielded calcite with a uniform, twinned-rhombohedral morphology and a narrow size distribution (figs. 2*C* and 2*E*). XRD, optical microscopy, and SEM demonstrated that for concentrations of dissolved magnesium ion at or less than 10^{-4} *M*, the final crystalline product was calcite. Sufficiently high concentrations of magnesium ion (10^{-3} *M*) caused the percentage of vaterite spheres to increase relative to calcite rhombs.

The degree of incorporation of magnesium ion in the precipitate varied with the presence or absence of stirring and with the initial magnesium concentration. Initial total concentrations of magnesium ion were selected to eliminate the formation of magnesium carbonate phases. Magnesium-to-calcium ratios thus were low, ranging from 0.2 to 0.02 in the initial solution. The calcium ion concentration decreased markedly during precipitation, whereas the magnesium ion concentration changed only slightly. Thus, as the precipitation experiment approached equilibrium the magnesium-to-calcium ratio in the solution increased. For an initial unstirred solution containing 1×10^{-3} *M* total concentration of magnesium ion, the precipitate contained about 1 percent magnesium. Experiment 12 (table 1) yielded a precipitate containing 1 mole percent magnesium ion 3 minutes after the onset of nucleation. Four subsequent analyses of the precipitate at intervals over the next 100 minutes showed that the mole percent magnesium decreased to 0.7 percent. Precipitation from a similar solution that had an initial concentration of magnesium ion of 5×10^{-4} *M* showed 0.7 mole percent magnesium in the precipitate 3 minutes after nucleation, whereas after 10 minutes the magnesium

Figure 2 (facing page). Scanning electron micrographs of calcium carbonate precipitates from stirred and unstirred solutions. *A*, unstirred solution, 3 minutes after nucleation. $T_{Mg} = 5 \times 10^{-4}$ *M*. *B*, stirred solution, 5 minutes after nucleation, no added magnesium ion. *C*, as in *B* but 1 day after nucleation. *D*, stirred solution, 5 minutes after nucleation. $T_{Mg} = 1 \times 10^{-4}$ *M*. *E*, as in *D* but 1 day following nucleation. Bar marker is one micrometer long.


A
B
C
D
E

content of the precipitate had decreased slightly to 0.6 mole percent.

Continuous stirring following nucleation yielded precipitates with somewhat higher magnesium ion contents. Experiment 2, which was equivalent to experiment 12 except that it was unstirred, produced an initial precipitate that contained 2.3 mole percent magnesium 5 minutes after nucleation. The magnesium content of the precipitate decreased to 1.6 mole percent within the first 100 minutes of reaction.

In each nucleation experiment (stirred and unstirred) that was sampled successively during the reaction, the magnesium content of the initial precipitate was at a maximum. As the precipitate aged, its magnesium content decreased, typically several tenths of 1 percent over the course of the experiment. In contrast, the precipitates that formed in the sealed-bottle experiments showed higher magnesium contents at the termination of the reaction. Inasmuch as copius amounts of calcium carbonate precipitated in the first few minutes of the reaction, changes in the magnesium ion content of the precipitate were probably due in large part to transformation and recrystallization processes.

The variation in the magnesium content of the precipitate during the formation of $CaCO_3$ may be due to a number of factors. The reaction rate is important because at high rates of precipitation (at the start of reaction) more magnesium was incorporated in the precipitate than later in the reaction when the reaction rates were significantly lower. This observation is in agreement with that of Berner (1978), who reported that experiments at high supersaturation and high precipitation rates produced calcites richer in magnesium. The incorporation of magnesium during the precipitation of calcium carbonate may have involved polymorphs other than calcite which have dissimilar magnesium ion distribution coefficients, thus leading to a variation in the distribution coefficient with changing polymorph composition.

Long-term experiments involved the recrystallization of the calcium carbonate precipitate in a solution having a magnesium-to-calcium ratio significantly higher than that at the initiation of the precipitation. Thus, because of the higher ratio, magnesium ion may have been incorporated into the precipitate either via a solid state exchange of surface magnesium or by the formation of a magnesium-rich surface phase.

Table 2. Calcium carbonate nucleation without and with magnesium ion at 25°C

[Leaders (---) indicate no added magnesium ion; Ω_c, supersaturation; t_I induction interval, in seconds]

Experi-ment	Total initial concentration (moles per liter) X 10^4					
	Ca^{2+}	Mg^{2+}	$CO_3{}^{2-}$	pH	Ω_c	t_I
3	26.64	---	41.39	8.565	27.8	480
4	13.32	---	41.39	8.567	15.5	2,100
6	33.30	---	41.39	8.502	29.2	420
7	13.32	---	41.39	8.654	18.6	1,500
8	26.64	---	41.39	8.505	24.5	660
9	33.30	---	41.38	8.545	32.0	300
12	46.62	---	41.38	8.448	33.9	300
13	6.66	---	41.38	8.832	14.2	4,500
16	19.98	---	41.38	8.647	26.1	720
M2	40.05	3.214	41.64	8.585	39.9	300
M3	26.70	2.142	41.64	8.665	34.2	450
M4	13.35	1.071	41.64	8.830	25.6	960
M12	43.74	15.01	41.55	8.419	28.7	1,050
M14	26.05	25.91	41.64	8.523	22.4	1,740
M17	52.09	51.82	41.64	8.302	22.6	1,680
M22	6.34	12.75	41.69	8.725	13.9	8,640
M25	50.00	252.09	41.71	8.135	10.7	15,120
M27	72.67	385.34	41.71	8.025	10.8	15,600

Nucleation in metastable solutions

The nucleation and subsequent crystallization of calcium carbonate in stirred, metastable-supersaturated solutions (table 2) formed less complex precipitates than those that formed from labile-supersaturated solutions. Lower initial supersaturations in metastable solutions reduced the amount of initial noncrystalline precipitate and led to smaller amounts of unstable polymorphs. Direct nucleation (that is, crystal formation from an initially supersaturated solution without intervention of an antecedent) appeared to be important in the development of the ultimate crystal assemblage.

The predominate crystalline components of the precipitate, over a range of magnesium ion concentrations and supersaturations, were vaterite and aragonite. The formation of calcite from the metastable solutions was retarded. Some aged solutions, containing low concentrations of magnesium ion, developed calcite as a final precipitate. In these experiments, initially formed vaterite transformed to calcite during the course of the experiment. Precipitates from solutions containing high concentrations of magnesium ion were aragonite.

An abrupt change in solution pH and turbidity was used to identify calcium carbonate nucleation. The time required to initiate this change after the component solutions were mixed was considered to be the induction interval (t_I). At low supersaturations, changes in the solution pH and turbidity during nucleation were less pronounced. Induction intervals and the number of particles formed during nucleation (particles per milliliter) exhibited little systematic variation with changing magnesium ion concentration (fig. 3).

Both the induction interval and the number of particles per milliliter followed a log-log linear relationship with calcite supersaturation; the best-fit line for solutions containing magnesium ion lay slightly above that for the magnesium-free solution (fig. 3). The presence of magnesium ion in the supersaturated solutions lengthened the induction interval and led to a larger number of nucleation particles. Nucleation rates, defined as N/t_I, were thus used to identify the metastable region of calcium carbonate supersaturation and to quantify the influence of magnesium ion on this region (fig. 4).

As discussed previously, metastable solutions can be divided into two groups: (1) those having a very small nucleation rate, and (2) those having a measurable nucleation rate, with subsequent crystalline phase formation in a specific time interval t_I. A rate of 50 particles per cubic centimeter per second has been chosen as the boundary between these two regions. For the experiments shown in figure 4, the calcium carbonate metastable region extends from $\Omega_c = 1$ to $\Omega_c = 10$. Inasmuch as the presence of magnesium ion increased both the induction interval and the nucleation particle number in roughly the same proportion, magnesium ion did not appear to have altered the calcium carbonate nucleation rate appreciably.

Calcite-seeded crystallization

The initial conditions for calcite-seeded growth experiments are given in table 3. Typical plots of the concentration of calcium in solution and pH against time for calcite growth in the presence and absence of magnesium ion illustrate that seed crystals induced immediate crystal growth. Total calcium concentrations and solution pH's demonstrate that magnesium ions did not prevent crystallization, but that they reduced the calcite crystallization rate markedly. The role of magnesium ions is most clearly shown with the second addition of seed crystal to solutions with the high magnesium-ion concentration. Initially, the concentration of calcium in solution decreased only slightly, but if more seeds were added the growth rate nearly equaled that of the magnesium-free control reaction. The formation of calcite from supersaturated solutions with a high concentration of magnesium ions was thus kinetically inhibited and proceeded only when sufficient reactive surfaces were available. Magnesium exhibited no marked changes in solution concentration during the course of the reaction. The crystallization rates followed an expression found to hold in earlier work (Reddy, 1978):

$$dN/dt = ksN^2 , \qquad (1)$$

where N is the amount of calcium carbonate in moles per liter at time t (from the start of the reaction by addition of seed crystal) in minutes to be precipitated to reach (calcite) equilibrium; dN/dt is the calcite crystallization reaction rate; k in [(moles per liter) × minutes × milligrams of seed crystal per liter]$^{-1}$ is the crystal growth-rate constant; and s in milligrams of seed per liter is the added seed concentration and is proportional to the surface area available for growth.

Analysis of the data for the seeded crystallization experiments was facilitated by use of an integrated form of equation 1:

$$N^{-1} - N_0^{-1} = kst , \qquad (2)$$

where N_0 (the initial theoretical crystal yield) is calcite (moles per liter) to be precipitated from the stable supersaturated solution at the time of seed inoculation. Linear plots of $N^{-1} - N_0^{-1}$ versus time demonstrate the validity of equation 2 (Reddy, 1978) for interpreting the experimental results. Rate constants for calcite crystallization in solutions with and without magnesium ion are listed in table 3. The parabolic dependence of the crystal growth rate (the N^2 term in equation 1) is consistent with a calcite crystallization mechanism involving a rate-limiting surface reaction step at the crystal face (Reddy, 1978).

Equation 2 enables a quantitative description to be made of the influence of magnesium ion on calcite crystallization kinetics. Plots of $N^{-1} - N_0^{-1}$ versus time showed a decrease in slope (ks from equation 2) with increasing magnesium ion concentration. The influence of magnesium ion on the calcite crystallization rate was compared for different experiments by plotting the reduced reaction-rate constant, k/k_0 (where k is for solutions containing magnesium ion and k_0 is for magnesium-free control experiments), as a function of the magnesium ion concentration (fig. 5). This plot presents the data shown in table 3 as well as two sets of published data. The good agreement of the four independent sets of experimental results is evidence of the reliability of the seeded-growth technique. Rate-constant reduction occurred at magnesium ion concentrations of 10^{-5} M; pronounced decrease in the rate constant was evident above 2×10^{-4} M. Previous investigations have shown that calcite growth-rate reduction follows a Langmuir-type adsorption model (Reddy, 1978). If this treatment is appropriate, the crystallization rate constant in the presence and absence of magnesium ion is

$$k_0/(k_0 - k) = 1 + k_2(k_1 T_{\mathrm{Mg}^{2+}})^{-1} , \qquad (3)$$

where k_1 and k_2 are the adsorption and desorption rate constants, respectively, for magnesium ion at the growth sites on the crystal surface, and $T_{\mathrm{Mg}^{2+}}$ is the total concentration of dissolved magnesium ion. A linear relationship between $k_0/(k_0 - k)$ and the reciprocal of the total magnesium ion concentration (fig. 6) demonstrates that the Langmuir adsorption isotherm model described the inhibition satisfactorily. This agreement over a wide range of solid to solution ratios implies that inhibition of calcite growth was due to the adsorption of magnesium ion at growth sites on the crystal surface.

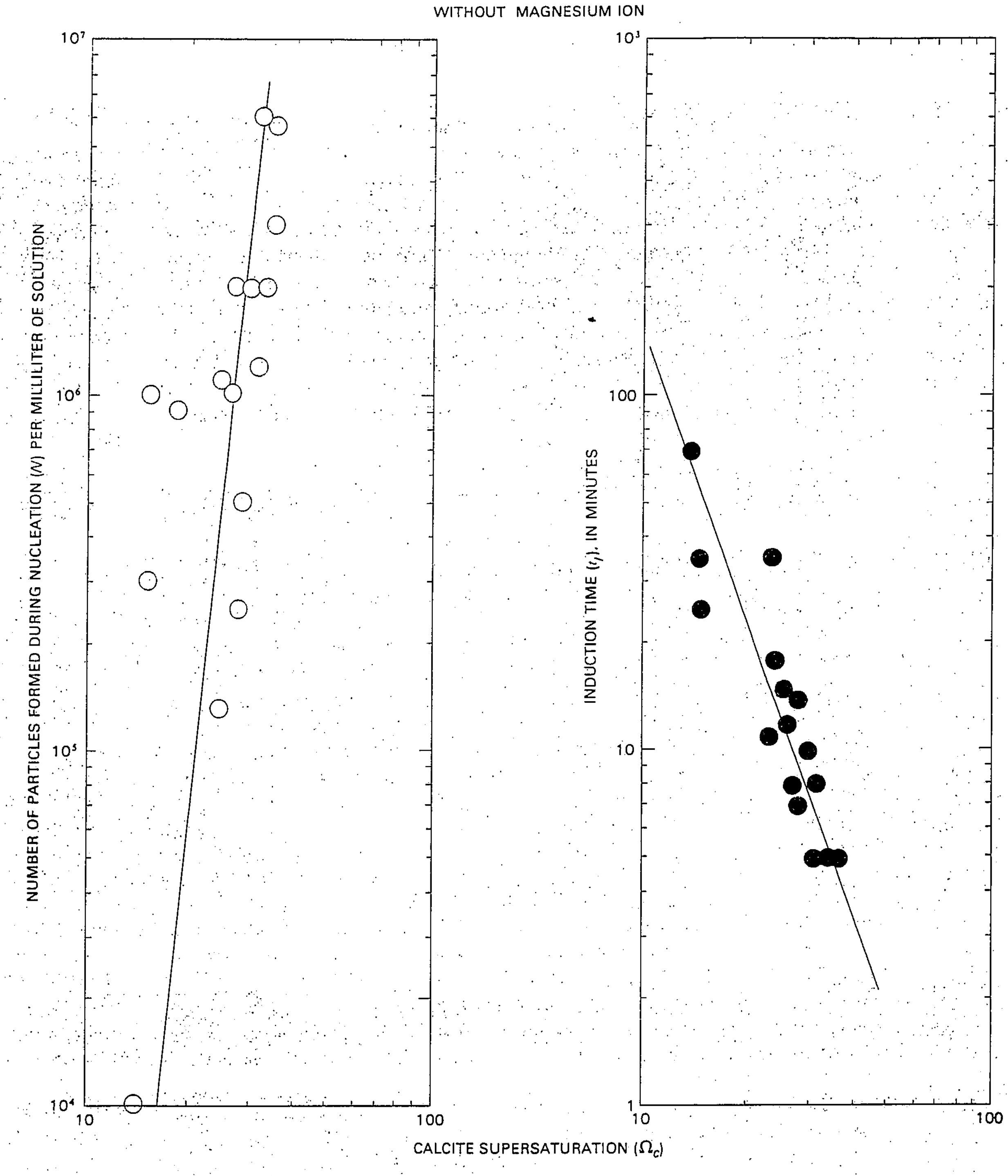
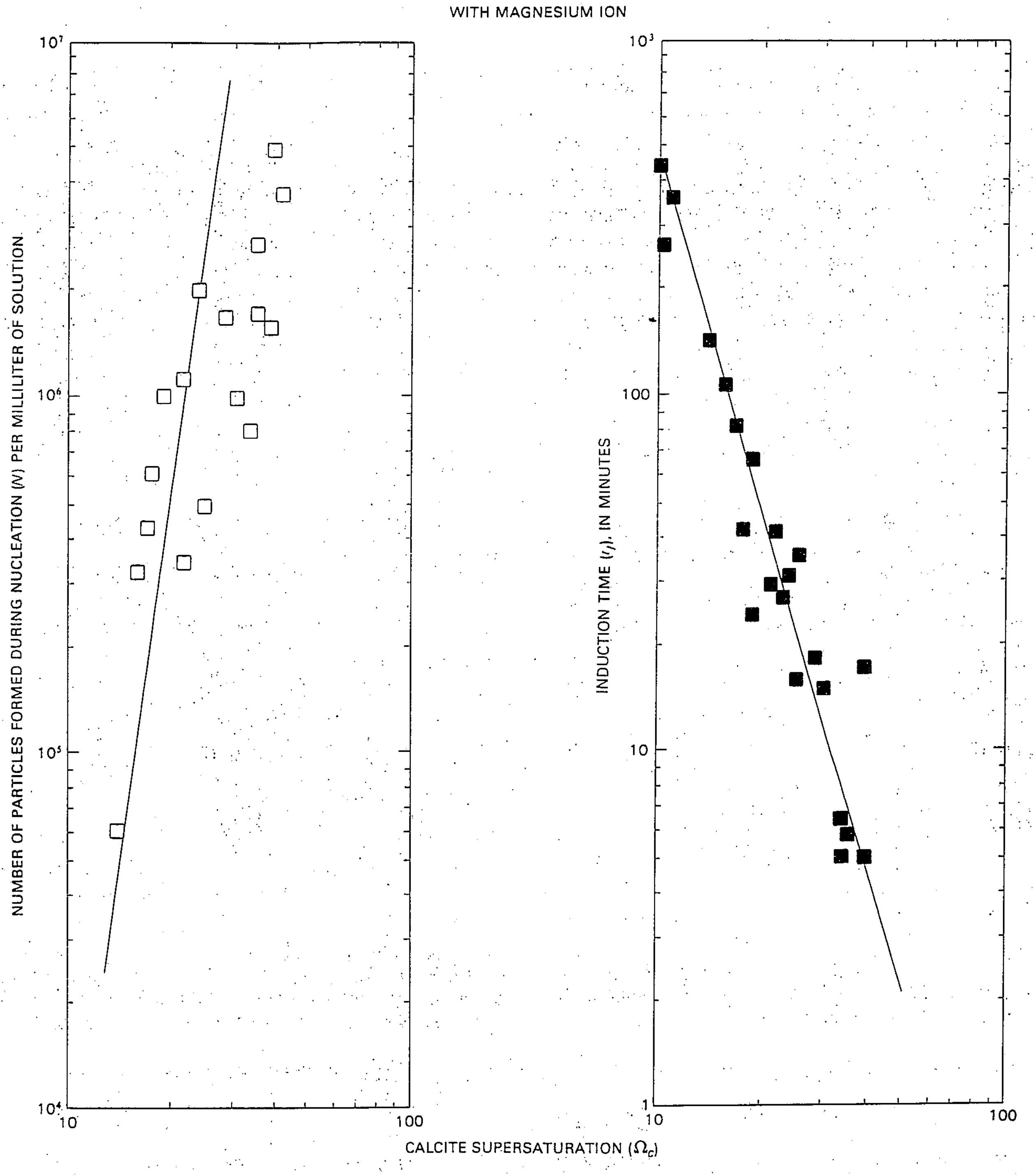


Figure 3 (above and facing page). Number of nucleation particles and induction interval versus calcite supersaturation for precipitation without and with magensium ions.

Approach to calcite equilibrium

Whereas an adsorption mechanism is compatible with calcite growth-rate inhibition by magnesium ion during most of the reaction, equation 1 does not describe the crystallization process near equilibrium. In the absence of magnesium ion, and at an intermediate seed-crystal concentration, calcite equilibrium was attained within 100 minutes of reaction. In the presence of magnesium ion, even with significantly higher seed concentration, the crystallization did not reach calcite equilibrium (fig. 7). In several experiments, the solution composition after extended reaction time changed only slightly and appeared to approach steady-state calcite supersaturations



significantly greater than equilibrium. This steady-state calcite supersaturation value was related to both the initial magnesium ion concentration and the seed-crystal concentration (fig. 8). Changes in the concentration of magnesium ion during calcite growth were not statistically significant over the initial phase of the reaction. Long-term equilibration and successive seed additions, however, led to the loss of magnesium ion from solution.

Steady-state supersaturation, the saturation value approached in solutions at long reaction times, was clearly related to magnesium-ion concentration (fig. 7). At higher magnesium-ion concentrations, steady-state supersaturation was higher. With a second addition of seeds, new steady-state supersaturations were reached which were closer to calcite equilibrium. Steady-state supersaturation values for several replicate experiments at intermediate seed concentrations were in good agreement. Crystallization experiments, at similar seed-crystal concentrations, exhibited steady-state supersaturation, which was a function of the log magnesium ion concentration (fig. 8). This

Table 3. Experimental conditions, seed crystal concentrations (*s*), and rate constants (*k*) for calcite growth in the presence and absence of magnesium ion

[*s* in milligrams per liter; rate constant (*k*) in (moles per liter)·(minutes)·(milligrams of seed per liter)]

Experiment	Initial concentration of ions in solution (moles per liter) x 10^4							
	Total							
	Ca^{2+}	Mg^{2+}	CO_3^{2-}	Ca^{2+}	CO_3^{2-}	pH	s	k
SC-1	2.258	0	40.97	1.874	2.307	9.01	248	1.40
SC-2	2.238	0	40.97	1.848	2.357	9.02	24.8	1.42
SM-1	2.315	10.979	40.97	1.924	2.393	9.00	1247	0.0124
SM-2	2.172	10.979	40.97	1.837	2.394	9.00	1247	0.0084
SM-3	2.078	5.227	38.62	1.749	2.279	9.02	2327	0.020
SM-4	2.243	2.233	40.97	1.875	2.288	9.00	249	0.162
SM-5	2.197	5.723	40.97	1.828	2.382	9.01	248	0.037
36	1.862	0	41.86	1.679	1.035	8.638	249	1.49
38	2.297	13.08	42.30	2.031	1.385	8.736	1370	0.0012
40	2.165	6.066	39.86	1.938	1.262	8.736	2410	0.025

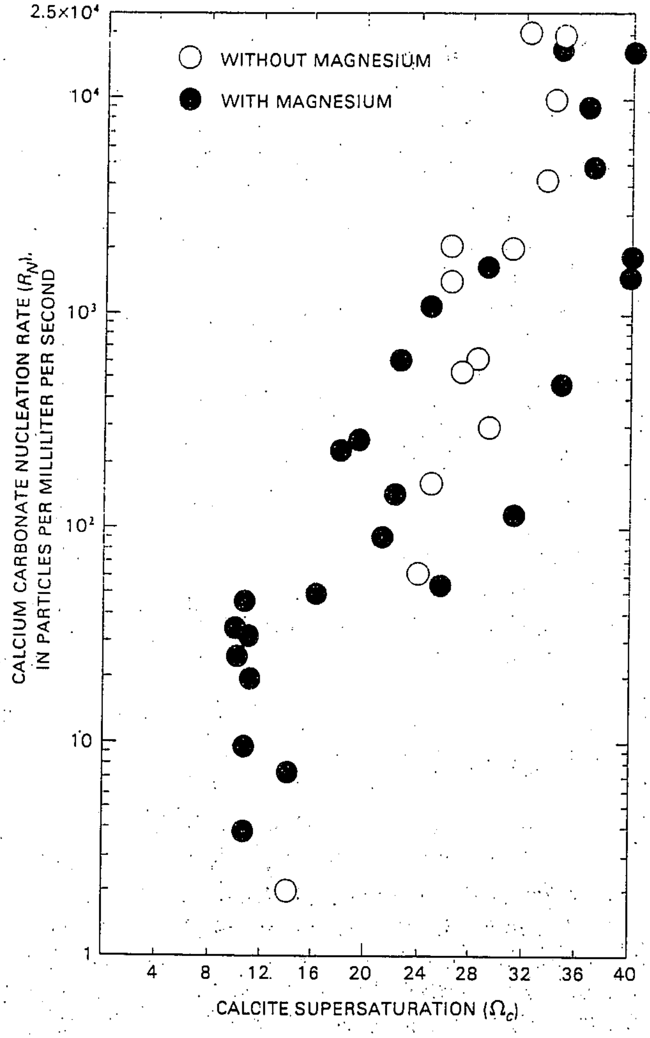


Figure 4. Calcium carbonate nucleation rate versus calcite supersaturation in solutions without and with magnesium ions.

situation may have arisen because of irreversible adsorption of magnesium ion on the calcite surface forming localized areas of a magnesium-rich phase. This explanation is consistent with the suggestion of Fajans (1931) that an ionic species is strongly adsorbed on a crystalline solid if that species forms an insoluble compound with opposite charged ions of the crystal structure. A quantitative description of this process is difficult to develop on a theoretical basis, because the incorporation of magnesium ion during growth led to changing surface properties with time. The incorporation of magnesium ion (or subsequent exclusion from a growth phase) may have been a function of growth rate. During rapid crystallization, ions may be incorporated in a crystal by a process that does not correspond to simple adsorption (Adamson, 1960). Such adsorption would be accompanied by surface exchange. In the present experiments, magnesium ions may have been continually taken up or released as each growth layer came into exchange equilibrium with the substrate crystal and the solution. The final steady-state supersaturation value decreased linearly (fig. 8) with increasing log of the seed concentration.

Other authors have emphasized the kinetic restrictions associated with the heterogenous reactions of aqueous calcium carbonate in the presence of magnesium ion. For example, Thorstenson and Plummer (1977, 1978) termed the steady-state solution composition in such systems "stochiometric saturation." The solid phase in contact with this solution remains invariant, even though it may be part of a continuous compositional series. They proposed that the magnesium content of solid calcium carbonate should be governed primarily by the activity product of calcium and carbonate ions in solution. From the thermodynamic requirements of stoichiometric saturation, the solution magnesium-to-calcium ratio should not be a major regulating factor in determining

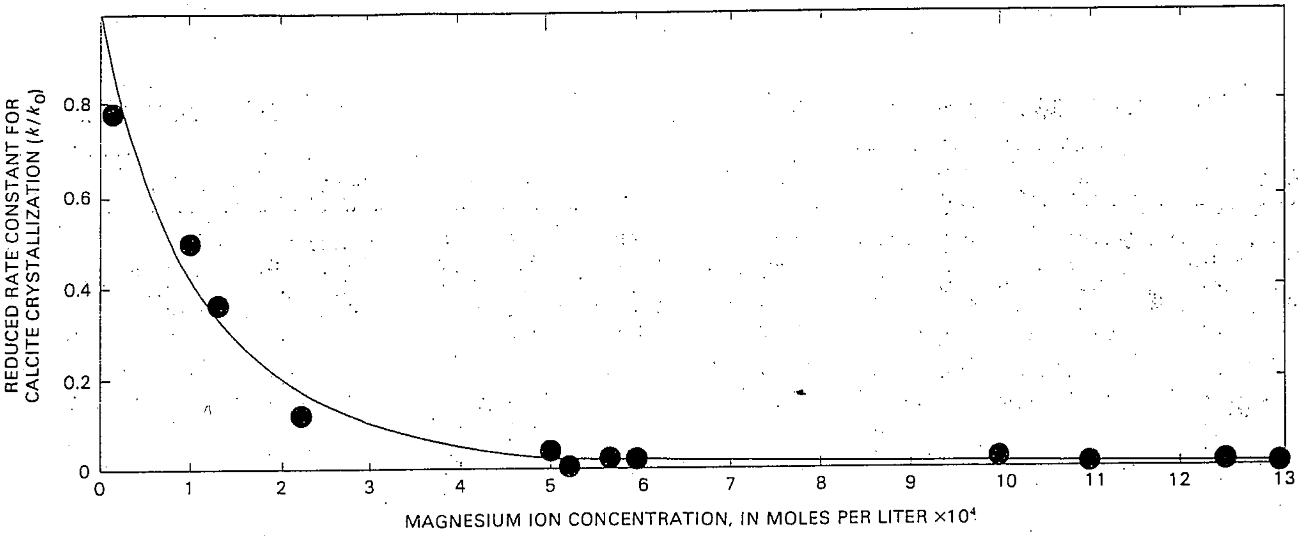


Figure 5. Calcite crystallization reduced-rate constant (k/k_0) as a function of the concentration of magnesium ion in solution.

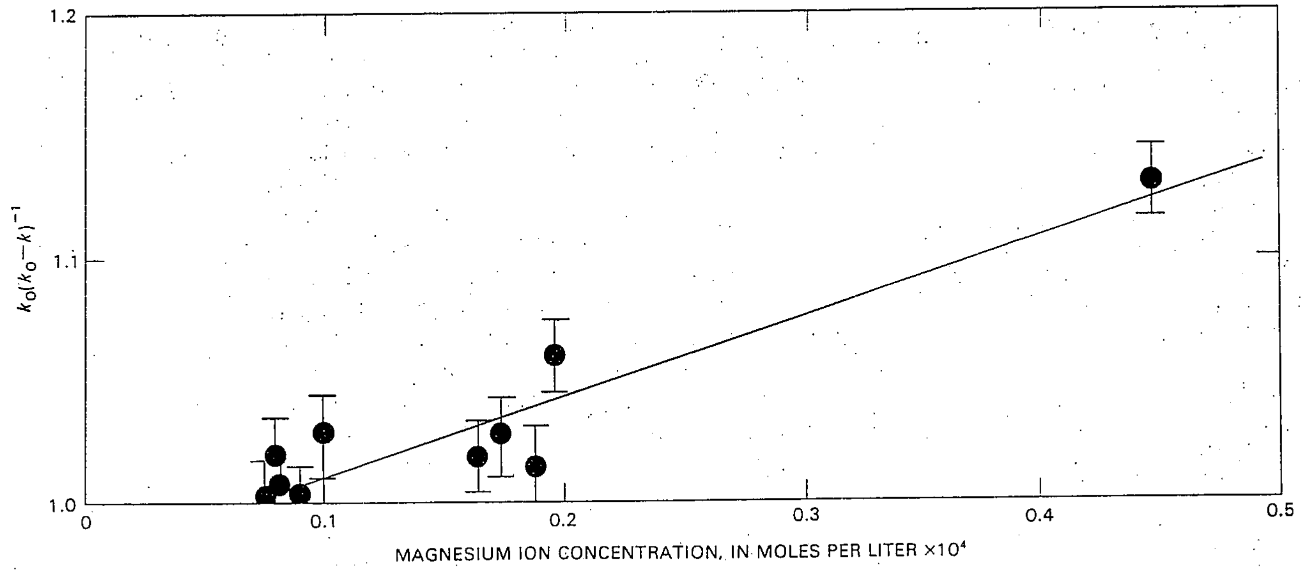


Figure 6. Langmuir isotherm plot of $k_0/(k_0 - k)$ versus the reciprocal of the magnesium ion concentration.

the composition of the solid phase. Results obtained in the seeded-crystallization experiments are consistent with the hypothesis of Thorstenson and Plummer, because calcite containing little or no magnesium ion formed over the range of experimental conditions used.

Berner (1978), in discussing the magnesium content of calcite precipitated from seawater, emphasized that the composition of the solid phase is controlled by kinetic factors, and that it does not represent exchange equilibrium of calcium and magnesium ions between seawater and calcite. Morse and others (1979) observed a magnesium calcite growth onto a calcite crystal suspended in seawater. This incorporation of magnesium in the growth phase in the seawater experiments differs from the dilute solution results presented in this paper. The differences may be due in part to the higher ionic strength of the seawater medium or to naturally occurring calcite-growth inhibitors present in seawater, which could have facilitated the formation of magnesium calcite. Additional work on the comparison of laboratory and field calcium carbonate formation kinetics seems needed.

CONCLUSIONS

Diagenetic transformations of sedimentary carbonate minerals arise from numerous processes including calcium carbonate nucleation and crystal growth. Results obtained in this study demonstrate that calcium carbonate mineral formation was characterized reliably and reproducibly over a range of magnesium ion concentrations. Both magnesium ion distribution and calcium carbonate

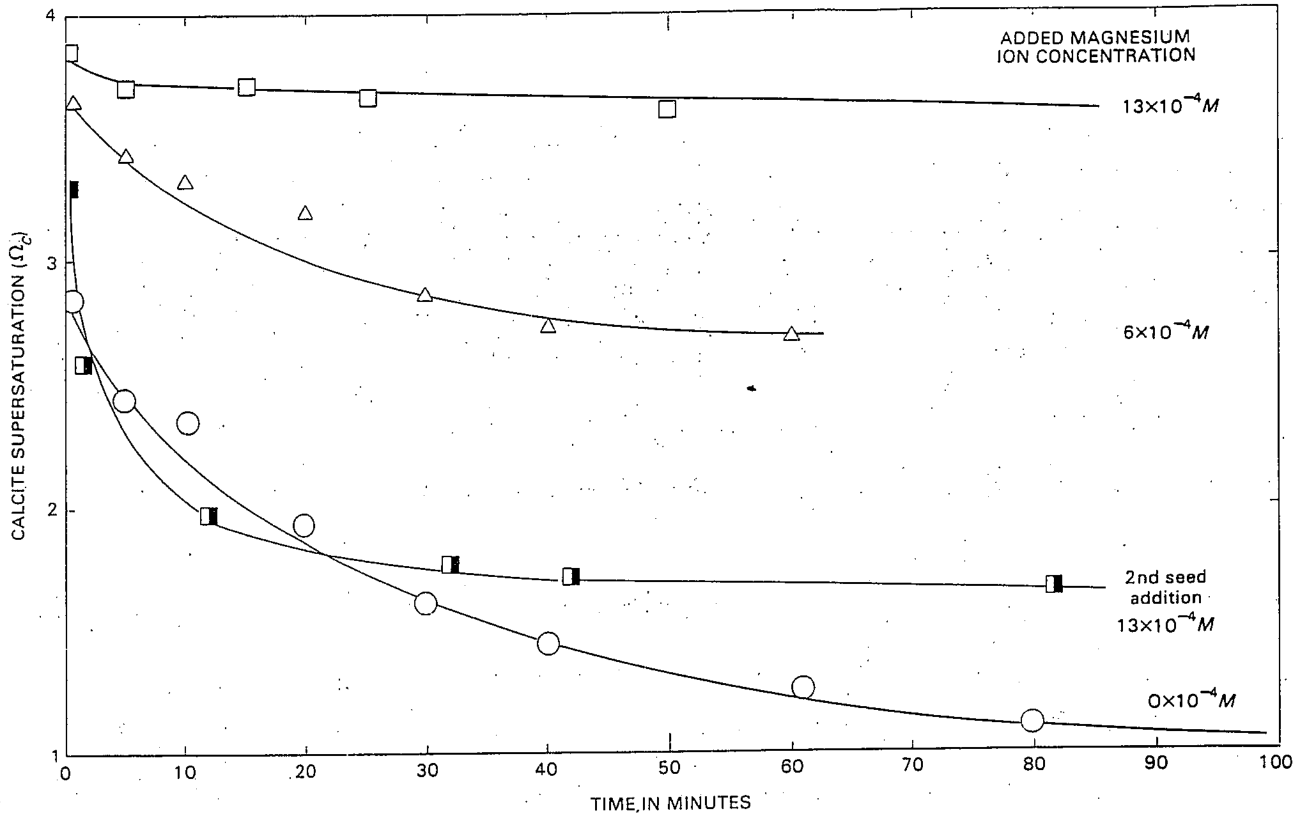


Figure 7. Calcite supersaturation versus time for calcite-seeded crystallization without and with magnesium ions.

formation exhibited systematic variations over a wide range of calcium carbonate formation rates and supersaturations.

Solution supersaturation, hydrodynamics, magnesium ion concentration, and reaction path were involved in regulating the course of calcium carbonate formation. Supersaturation level was of paramount importance in the experiments examined here. At high supersaturations nucleation proceeded rapidly, yielding an unstable and reactive initial precipitate, which rapidly transformed to more stable carbonate minerals. Solution hydrodynamics and the concentration of magnesium ion had a secondary influence on the nucleation reaction at high supersaturation.

At intermediate supersaturations (10–40) the influence of supersaturation on the precipitation reaction was also important: nucleation particle number and induction interval followed a log-log linear relationship with supersaturation. As observed at high supersaturation, magnesium-ion concentration level had a secondary influence on the rate and course of reaction. High magnesium-ion concentrations regulated the polymorphic composition of the final CaCO$_3$ precipitate.

For calcite-seeded growth from metastable solutions (supersaturations of less than 10), nucleation processes were unimportant. The growth rate followed a second-order rate equation, consistent with a surface reaction rate-determining step. Magnesium ion reduced calcite formation under these conditions by blocking growth sites on the seed crystal surface. Variation of the reaction rate constant with magnesium ion concentration is consistent with a Langmuir adsorption isotherm model. Because many sediment reactions occur in metastable solutions, the quantitative description of the influence of magnesium ion on the calcite crystallization rate may be useful in interpreting field observations. Additional support for a kinetic mechanism for the retardation of the growth rate of calcite by magnesium ion is that the steady-state supersaturation, reached at the apparent end of the crystallization experiment, was a function of the experimental solution-to-solid ratio. The formation of a magnesium-containing surface phase did not appear to be associated with the mechanism of magnesium ion inhibition of calcite crystal growth.

Bathurst (1983) pointed out several puzzling aspects of carbonate cement mineralogy which may be clarified by a fuller understanding of the chemical processes involved in calcite crystal growth. Cement formation and dissolution reactions are regulated in large measure by the solution concentration of magnesium ion; however, supersaturation levels and the presence of a reactive growth surface can be more influential than magnesium ion concentration in some situations.

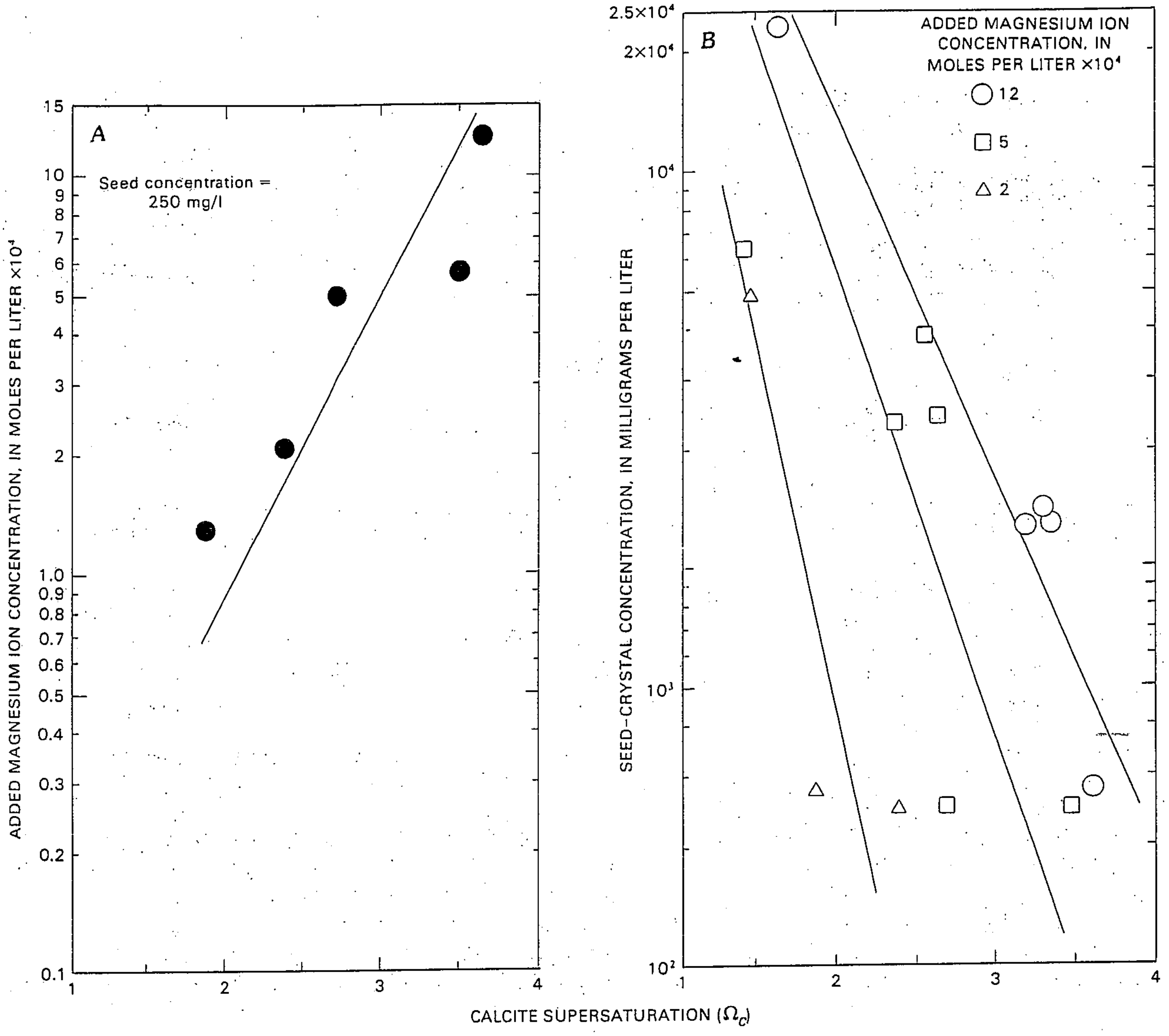


Figure 8. Steady-state calcite supersaturation versus (*A*) initial total magnesium-ion concentration and (*B*) initial seed-crystal concentration.

As an example of the application of laboratory results to a field situation, consider the formation of low-magnesian calcite from marine sediments that have been uplifted and bathed in fresh water. Mackenzie and others (1983) summarized the results of numerous investigations which showed magnesium loss and fabric retention during freshwater diagenesis of high-magnesian calcites. This reaction depends strongly on solution supersaturation level and the presence of crystallization inhibitors. Although the high-magnesian calcites are less stable than low-magnesian calcite, the transformation from the unstable phase to the stable phase was not observed until the sediment pore water changed from a marine to a freshwater composition.

It is unclear whether the rate-limiting step in the transformation is the dissolution or the crystallization process. If the crystallization reaction is rate-limiting and calcite supersaturation values are fixed by the solubility of the high-magnesian calcite, calcite will not form until the solution concentration of magnesium ion decreases to a value consistent with an appreciable calcite growth rate. If a minimum necessary rate constant is assumed to be 1 percent of the value in the absence of magnesium ion, from the data in table 3, the magnesium concentration associated with this calcite growth-rate constant is about 1–2 millimoles of magnesium ion per liter. To reduce a seawater magnesium-ion concentration to this value requires a 50-fold dilution, a value consistent with circulation of a low-magnesium fresh water in the uplifted sediment. Conversion rates would also be regulated by hydrodynamic factors, including the pore-water flushing rate.

The observed microstructure retention during the transformation implies low-solution supersaturations and low growth rates. Release of magnesium ion to the pore water during recrystallization will limit supersaturation and growth rates at the microstructure level.

The important point concerning the application of laboratory studies to carbonate-sediment diagenesis is that information about the mechanism of magnesium ion regulation of carbonate-sediment diagenetic reactions is available. Laboratory studies, such as those presented in this paper, give reliable, quantitative estimates of the influence of magnesium ion on mineralogical changes that occur in sediments. Additional work is needed to extend these results to actual sedimentary environments.

REFERENCES CITED

Adamson, A. W., 1960, Physical chemistry of surfaces: New York, Wiley-Interscience Publishers, 629 p.

Bathurst, R. G. C., 1983, Early diagenesis of carbonate sediments, *in* Parker, A., and Sellwood, B. W., eds., Sediment diagenesis: Boston, Mass., D. Reidel Publishing Company, p. 349-377.

Berner, R. A., 1978, Discussion—Equilibrium, kinetics, and the precipitation of magnesium calcite from seawater: American Journal of Science, v. 278, p. 1475-1477.

Fajans, Kasimir, 1931, Radio elements and isotopes; chemical forces and optical properties of substances: New York, McGraw-Hill, 125 p.

Jacobson, R. L., and Langmuir, D., 1974, Dissociation constants of calcite and $CaHCO_3^+$ from 0 to 50°C: Geochimica et Cosmochimica Acta, v. 38, p. 301-318.

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., Mineralogical Society of America Reviews in Mineralogy, v. 11, p. 97-144.

Morse, J. W., Mucci, A., Walter, L. M., and Kaminsky, M. S., 1979, Magnesium interaction with the surface of calcite in seawater: Science, v. 205, p. 904-905.

Reddy, M. M., 1978, Kinetic inhibition of calcium carbonate formation by wastewater constituents, *in* Rubin, A. J., ed., The chemistry of wastewater technology: Ann Arbor, Michigan, Ann Arbor Science Publishers, Inc., p. 31-58.

Reddy, M. M., and Nancollas, G. H., 1976, The crystallization of calcium carbonate—IV. The effect of magnesium, strontium and sulfate ions: Journal of Crystal Growth, v. 35, p. 33-38.

Thorstenson, D. C., and Plummer, L. N., 1977, Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—Example, the magnesium calcites: American Journal of Science, v. 277, p. 1203-1223.

______1978, Discussion:—Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase—Example, the magnesium calcites: American Journal of Science, v. 278, p. 1478-1488.