

Journal of Crystal Growth 41 (1977) 287-295
 © North-Holland Publishing Company

CRYSTALLIZATION OF CALCIUM CARBONATE IN THE PRESENCE OF TRACE CONCENTRATIONS OF PHOSPHORUS-CONTAINING ANIONS

I. Inhibition by phosphate and glycerophosphate ions at pH 8.8 and 25°C

Michael M. REDDY

Division of Laboratories and Research, New York State Department of Health, Albany, New York 12201, USA

Received 7 April 1977; manuscript received in final form 10 June 1977

Addition of glycerophosphate ion or orthophosphate ion to a metastable supersaturated calcium carbonate solution greatly reduced the rate of calcite seeded crystal growth at 25°C. Crystallization rate constants were decreased to half their value in pure solutions by a glycerophosphate concentration of 1.6×10^{-5} M or an orthophosphate concentration of 2×10^{-6} M. A relationship between the crystallization rate constant and the additive ion concentration of either ion follows an expression based on a simple Langmuir-type adsorption model. This relationship suggests that calcite growth inhibition by phosphorus-containing anions involves blockage of crystal growth sites on the calcite surface.

I. Introduction

Inhibition of calcium carbonate crystallization in supersaturated solutions by phosphorus-containing ions has been the subject of several studies [1-4], but until recently little detailed work has been done to characterize the inhibition mechanism for this geochemically important mineral.

The role of a number of ions in the heterogeneous reactions of calcium carbonate, i.e. crystallization, polymorphic transformation and dissolution, has been examined [5-8]. In several investigations nucleation and crystallization were studied simultaneously. In others, a less stable calcium carbonate polymorph dissolved, leading eventually to the formation of a more stable phase. Several investigators have monitored concentration changes accompanying spontaneous precipitation of calcium carbonate, with the assumption that homogeneous nucleation takes place in the supersaturated solutions. It is impossible, however, to eliminate heterogeneous nucleation in such systems. To avoid this problem the present work has been based on the growth of seed crystals in supersaturated solutions. By precise control of experimental conditions, metastable supersaturated solutions

can be prepared. After inoculation with well-characterized seed crystals, the rate of growth can be determined by measuring the concentration of lattice ions in solution as a function of time.

This experimental approach, unlike those employing spontaneous precipitation, allows reliable measurement of the crystal growth rate in the presence and absence of additives [9,10]. An additional advantage of utilizing the seeded growth procedure is that crystallization occurs on a well-defined surface. Surface characteristics during spontaneous precipitation experiments are not well known and may change markedly during the course of the reaction. Such changes make a quantitative interpretation of the nucleation and growth process difficult [9,10].

In the investigation reported here, a dilute electrolyte solution was used, making possible a chemical thermodynamic approach for description of the solution-phase composition [9-12]. Two additive ions were chosen for examination of calcite growth inhibition: glycerophosphate (a model for organic phosphates) and orthophosphate. Previous studies have been conducted employing polyphosphates [8], phosphonic acid derivatives [6] and glycerophosphate [7].

Published values of the equilibrium constants for

calcium-additive ion complexes [13,14] allowed calculation of the extent of phosphorus-containing ion pair formation in the experimental solutions.

2. Experimental

Reagent grade chemicals; distilled, deionized, filtered (0.22 μm Millipore filter) water; and grade A glassware were used in all experiments.

Supersaturated calcium carbonate solutions were prepared by the dropwise addition of 200 ml of a calcium chloride solution (5.0×10^{-4} M) to 200 ml of a sodium bicarbonate (8.0×10^{-3} M)–sodium carbonate (4.0×10^{-4} M) solution in a thermostated ($25.00 \pm 0.02^\circ\text{C}$) double-walled Pyrex glass vessel used for the growth experiments. Additive ions, when used, were added dropwise as a small volume (typically less than 10 ml) of a stock solution immediately after preparation of the supersaturated solution. Stability of each supersaturated solution was verified by the constancy of the solution pH and total calcium concentration for at least one hour. Additional experiments have shown that the supersaturated solutions employed in this study are stable up to one day.

Continuous monitoring of pH and separation of supersaturated solution from seed suspension were performed as described previously [6,15,16]. Analysis for total calcium and carbonate concentrations, and preparation and characterization of seed crystals have been described elsewhere [7].

Solution phase phosphorus analysis was performed using an aliquot of the filtered supersaturated solution according to the method of Murphy and Riley [17].

3. Results and discussion

Typical plots of solution calcium concentration and pH against time for the growth of calcium carbonate in the absence of additive ions are shown in fig. 1. Addition of inoculating seed crystals to the stable supersaturated solution at time zero induces immediate crystal growth.

As shown in fig. 2, for a fixed set of solution phase conditions, the crystallization rate varies as a function of the amount of inoculating seed crystal added at the start of the experiment.

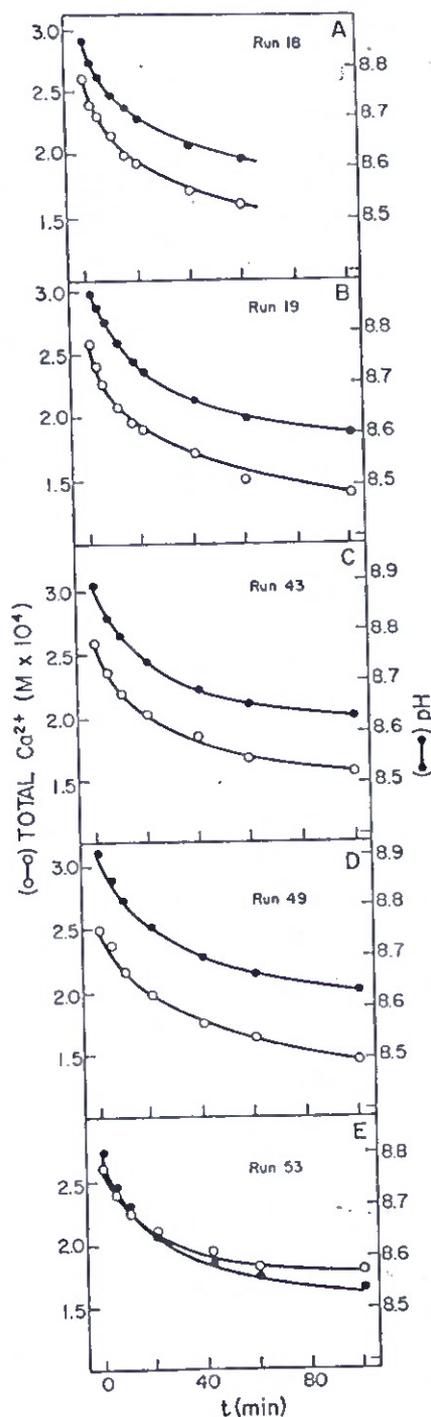


Fig. 1. pH and total calcium concentration as a function of time in the absence of additive ions: (A) run 18; (B) run 19; (C) run 43; (D) run 49; (E) run 53.



Fig. 2. To the absence concentration seed/l; (o)

Concentration calculated calcium action at

Table 1
Equations
1 atm a)

Equation

Mass action

- (1) $[\text{H}^+][\text{HCO}_3^-] = K_1[\text{H}_2\text{CO}_3^*]$
- (2) $[\text{H}^+][\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-]$
- (3) $[\text{H}^+][\text{C}^{z-}] = K_3[\text{HC}^{z-}]$
- (4) $[\text{CaCO}_3] = K_4[\text{Ca}^{2+}][\text{CO}_3^{2-}]$
- (5) $[\text{CaHCO}_3] = K_5[\text{Ca}^{2+}][\text{HCO}_3^-]$
- (6) $[\text{CaOH}^+] = K_6[\text{Ca}^{2+}][\text{OH}^-]$
- (7) $[\text{Ca}^{2+}] = K_7[\text{CaCO}_3] + K_8[\text{CaHCO}_3] + K_9[\text{CaOH}^+]$

Mass balance

- (8) $T_{\text{Ca}} = [\text{Ca}^{2+}] + [\text{CaHCO}_3] + [\text{CaOH}^+] + [\text{CaCO}_3]$
- (9) $T_{\text{CO}_3} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CaCO}_3]$

a) Bracket notation.

b) The term charge z

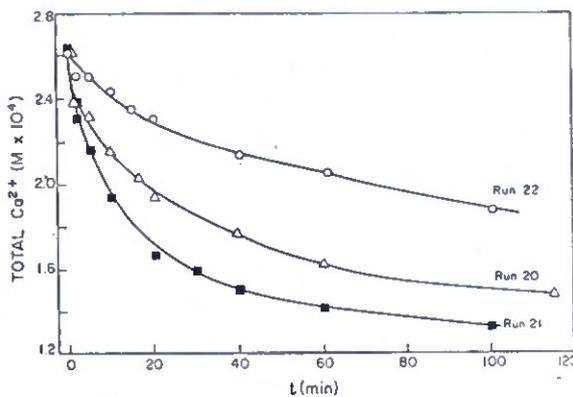


Fig. 2. Total calcium concentration as a function of time in the absence of added ion for three different calcite seed concentrations: (Δ) run 20, 94.0 mg seed/l; (\blacksquare) run 21, 185.6 mg seed/l; (\circ) run 22, 37.9 mg seed/l.

Concentrations of ionic species in solution were calculated from measured solution pH and from total calcium and carbonate concentrations using the mass action and mass balance equations in table 1. This

Table 1
Equations used for calculation of ionic species at 25°C and 1 atm^a

Equation	Reference for constant
Mass action	
(1) $[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 10^{-6.35}$	[23]
(2) $[\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 10^{-10.33}$	[24]
(3) $[\text{H}^+][\text{OH}^-] = 10^{-14.00}$	[25]
(4) $[\text{CaCO}_3]/[\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{3.2}$	[26]
(5) $[\text{CaHCO}_3^+]/[\text{Ca}^{2+}][\text{HCO}_3^-] = 10^{1.4}$	[27]
(6) $[\text{CaOH}^+]/[\text{Ca}^{2+}][\text{OH}^-] = 10^{1.4}$	[12]
(7) $([\text{Ca}^{2+}][\text{CO}_3^{2-}])_{\text{calcite}} = 10^{-8.4}$	[29]
Mass balance ^b	
(8) $T_{\text{Ca}} = [\text{Ca}^{2+}]/f_2 + [\text{CaOH}^+]/f_1 + [\text{CaHCO}_3^+]/f_1 + [\text{CaCO}_3]/f_0$	
(9) $T_{\text{CO}_3} = [\text{CO}_3^{2-}]/f_2 + [\text{HCO}_3^-]/f_1 + [\text{H}_2\text{CO}_3]/f_0 + [\text{CaHCO}_3^+]/f_1$	

^a) Bracketed terms denote thermodynamic activities in solution.

^b) The term f_z denotes the activity coefficient for ion of charge z .

involved successive approximations for ionic strength, I [12], and was done with a Wang 720C programmable calculator. Ionic activity coefficients were obtained from the modification of the Debye-Hückel equation proposed by Davies

$$\log_{10} f_z = -Az^2 \frac{I^{1/2}}{1 + I^{1/2}} - 0.3I, \quad (1)$$

where f_z is the activity coefficient for ion of charge z and A is a constant [11].

The predominant carbonate species in the experimental solutions is bicarbonate ion, comprising more than 95% of the total carbonate concentration. Concentrations of calcium carbonate and calcium bicarbonate ion pairs were significant (table 2) and were considered in solubility calculations.

The crystallization rate data illustrated in figs. 1 and 2 follow an expression of the form found to hold in a previous study [7]

$$dN/dt = -k_s N^2, \quad (2)$$

where N is calcium carbonate (in mol/l) at time t (in min) to be precipitated from solution before equilibrium is reached; k (in $[(\text{mol/l})(\text{min})(\text{mg seed/l})]^{-1}$) is the crystal growth rate constant; and s (in mg seed/l) is the seed crystal concentration, which is proportional to the surface area available for growth. s is determined by dilution of a standard stock suspension of seed crystal and is checked by a complexometric titration of an acidified sample of seeded supersaturated solution or by a standard particle-counting technique employing an inverted microscope. N is calculated from the measured total calcium concentration at each time

$$N = T_{\text{Ca}}(t) - T_{\text{Ca}}(\infty), \quad (3)$$

where $T_{\text{Ca}}(t)$ equals the total molar concentration of all dissolved species containing calcium at time t . The equilibrium total calcium concentration, $T_{\text{Ca}}(\infty)$, is obtained from the solubility product of calcite, the solution pH and the total carbonate concentration at time t .

Analysis of calcite growth data is facilitated by the integrated form of eq. (2):

$$N^{-1} - N_0^{-1} = kst, \quad (4)$$

where N_0 is calcium carbonate (mol/l) to be precipi-

Table 2
Initial pH and solution concentrations, seed crystal concentrations (s) and rate constants (k) for calcite growth experiments at 25°C^{a)}

Expt. No.	Initial pH	Initial concentrations (mol/l × 10 ⁴)						s (mg/l)	k $\frac{1 \text{ mol}^{-1} \text{ min}^{-1}}{\text{mg seed/l}}$
		Total Ca ²⁺	Total CO ₃ ²⁻	Ca ²⁺	CO ₃ ²⁻	CaCO ₃	CaHCO ₃ ⁺		
18	8.850	2.603	41.77	2.172	1.651	0.3081	0.1223	94.5	1.21
43	8.886	2.593	41.57	2.143	1.781	0.3286	0.1200	95.2	0.82
49	8.905	2.496	41.02	2.057	1.830	0.3250	0.1135	94.3	1.20
53	8.805	2.594	40.83	2.194	1.461	0.2773	0.1219	94.3	0.790
5 ^{b)}	8.798	2.255	42.01	1.902	1.483	0.2435	0.1089	56.6	1.98
16 ^{b)}	8.895	2.274	41.97	1.871	1.837	0.2960	0.1059	74.3	2.14
17 ^{b)}	8.910	2.489	42.21	2.039	1.910	0.3339	0.1154	98.5	2.40
19	8.870	2.580	41.78	2.142	1.725	0.3173	0.1202	94.4	1.36
20	8.808	2.618	41.78	2.207	1.505	0.2856	0.1248	94.0	1.56
21	8.862	2.625	41.24	2.188	1.676	0.3150	0.1216	185.6	1.55
22	8.837	2.615	41.11	2.187	1.618	0.3034	0.1241	37.9	1.01

^{a)} Solution stirring rate, 200 rpm.

^{b)} Data from ref. [7].

tated from a supersaturated solution at zero time. The linear plot of $N^{-1} - N_0^{-1}$ as a function of time in figs. 3 and 4 confirms the validity of eq. (2) for interpretation of the experimental results. All calculations required to evaluate the integrated rate function and to perform a multiple least-squares linear regression of the integrated rate function versus time were done with a Wang 720C programmable calculator.

Fig. 4, showing data from fig. 2, demonstrates that the slopes of the integrated rate function plots (i.e. ks) are directly proportional to the seed crystal concentration, supporting the proposed rate law.

Rate constants for calcite crystallization in solutions without phosphorus-containing ions are given in table 2. These rate constants, which were determined over a period of 2 years, show that the rate does not appear to be a function of the initial pH of the supersaturated solution in the narrow range of pH employed in this study. Variations in the rate constants shown in table 2 and the corresponding rate plot slopes in fig. 3 result from recrystallization and aging of the seed suspension over a period of two years. These variations are smaller than the rate constant differences shown by calcite seed crystals with different morphologies [8]. Each series of additive experiments was accompanied by a growth experi-

ment in the absence of additive ion to give an independent measure of the growth rate in pure solution for that series of experiments.

The observed parabolic dependence of the crystal growth rate (i.e. the N^2 term in eq. (2)) supports a crystallization mechanism involving a surface reaction rate-limiting step at the crystal face [7].

Experimental data for calcium carbonate crystal growth in the presence of additive ions are presented in table 3. Total calcium concentration as a function of time during several of these experiments is plotted in fig. 5. The marked inhibition of calcium carbonate formation by both additives used in this study is clearly seen. It is noteworthy that phosphate ion appears to be effective in inhibiting crystallization at concentrations one order of magnitude smaller than glycerophosphate ion. A quantitative analysis of additive ion effect on the calcium carbonate growth process is facilitated by using the integrated rate function (eq. (4)). Plots of this function versus time (fig. 6) for experiments in the presence and absence of additive ions show clearly a decrease in slope with increasing additive concentration. Fig. 6 illustrates that the rate expression for calcite growth in pure solution is also applicable to growth in the presence of both additive ions used here.

Fig. 3. Rate function of additive ion 49; (E) run 53

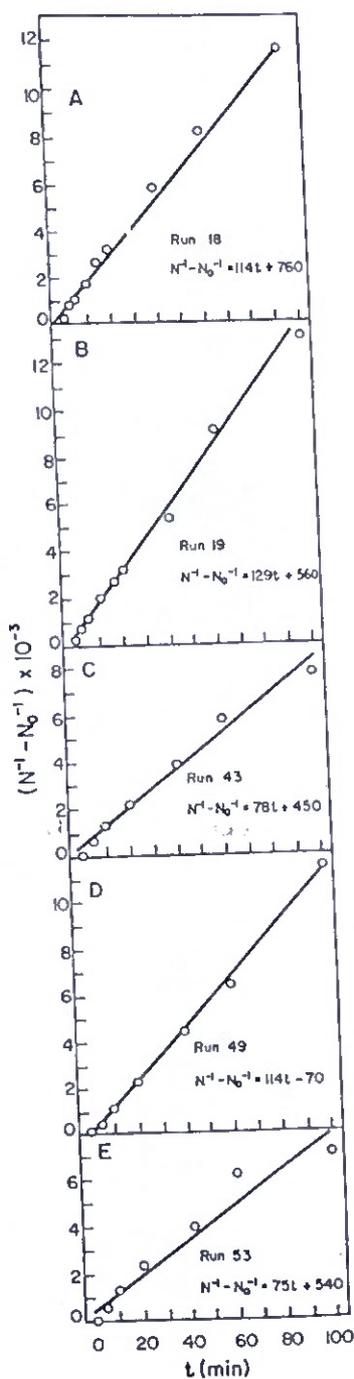


Fig. 3. Rate function $N^{-1} - N_0^{-1}$ against time in the absence of additive ions: (A) run 18; (B) run 19; (C) run 43; (D) run 49; (E) run 53.

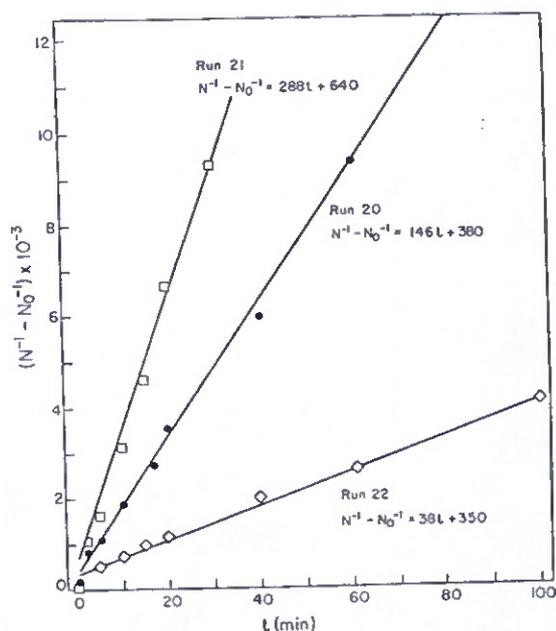


Fig. 4. Rate function $N^{-1} - N_0^{-1}$ against time in the absence of added ion for three different calcite seed concentrations: (●) run 20; (□) run 21; (○) run 22.

Rate constants for crystallization in solutions with a range of additive concentrations are given in table 3. Duplicate experiments at high additive (table 3, runs 38 and 39, and runs 54 and 55) concentrations are in moderate agreement. Growth experiments performed at the same additive concentration but within different series of experiments show good agreement at intermediate (table 3, runs 40 and 55) and low (table 3, runs 42, 48 and 57) additive concentrations.

An evaluation of the contribution of calcium glycerophosphate and calcium phosphate ion pair formation to calcite growth inhibition involves calculation of their concentrations from stability constant data [13,14]. These calculations indicate that, in the experimental supersaturated solutions at a glycerophosphate concentration of 10^{-4} M, or at a phosphate concentration of 10^{-5} M, less than 1% of the total dissolved calcium in solution is bound as a phosphorus-containing ion pair. The effect of ion pair formation on the reaction kinetics thus is negligible.

If the inhibition of crystal growth by additive ions is due to surface adsorption of the ions at growth sites on the crystal surface, some form of adsorption isotherm should be applicable. In terms of a simple

Table 3

Initial pH and solution concentrations, seed crystal concentrations (s) and rate constants (k) for calcite growth experiments in the presence of glycerophosphate or phosphate ions at 25°C^a

Expt. No.	Initial pH	Initial concentrations (mol/l $\times 10^4$)						s (mg/l)	k $\frac{1 \text{ mol}^{-1} \text{ min}^{-1}}{\text{mg seed/l}}$
		Additive ion ^{b)}	Additive ion	Total Ca^{2+}	Total CO_3^{2-}	Ca^{2+}	CO_3^{2-}		
23	8.852	A	0.40	2.618	41.37	2.187	1.646	93.0	0.152
24	8.847	A	0.10	2.592	41.67	2.165	1.637	93.8	0.826
25	8.853	A	0.20	2.611	41.57	2.179	1.656	93.5	0.562
26	8.832	A	0.30	2.606	41.47	2.187	1.578	93.3	0.413
27	8.855	A	1.0	2.567	39.91	2.155	1.600	91.6	0.155
38	8.963	B	1.0	2.606	40.60	2.117	2.063	88.1	0.0137
39	8.937	B	1.0	2.606	40.58	2.134	1.948	91.6	0.0051
40	8.861	B	0.50	2.569	41.07	2.143	1.667	94.0	0.0366
41	8.896	B	0.20	2.649	41.37	2.187	1.813	94.7	0.0612
42	8.885	B	0.10	2.594	41.47	2.146	1.773	95.0	0.156
44	8.896	B	0.08	2.568	41.49	2.118	1.818	95.0	0.132
45	8.971	B	0.01	2.634	40.81	2.131	2.104	95.0	0.628
46	8.959	B	0.02	2.620	40.62	2.129	2.039	94.5	0.423
47	8.982	B	0.04	2.680	40.22	2.166	2.121	93.5	0.374
48	8.972	B	0.10	2.626	39.38	2.136	2.029	90.7	0.150
54	8.803	B	0.50	2.564	40.34	2.174	1.438	93.0	0.0069
55	8.845	B	0.50	2.731	40.34	2.293	1.578	93.0	0.0344
56	8.747	B	0.20	2.611	40.62	2.239	1.277	93.8	0.0483
57	8.745	B	0.10	2.620	40.73	2.246	1.274	94.0	0.134
58	8.761	B	0.05	2.610	40.73	2.230	1.321	94.0	0.225

a) Solution stirring rate, 200 rpm.

b) A, glycerophosphate; B, orthophosphate.

Langmuir-type adsorption [7], which has been found to hold for calcium carbonate growth inhibition in the presence of phosphonate ions [6] and glycerophosphate ions [7], the rate constant in the presence and absence of additive ion yields:

$$k_0/(k_0 - k) = 1 + k_2/(k_1 [\text{additive}]), \quad (5)$$

where k_0 is the crystal growth rate constant in the absence of additive ion and k_1 and k_2 are the adsorption and desorption rate constants for these ions respectively.

In fig. 7, $k_0/(k_0 - k)$ is plotted against the reciprocal of the additive concentration. A linear relation with an intercept of unity indicates that the Langmuir isotherm satisfactorily described the inhibitory effect of the additive ions. Data shown in tables 2 and 3 as well as data for glycerophosphate inhibition published previously [7] have been used in fig. 7. All data points which have been plotted, except those

in parentheses, have been used to determine the best fit line. Support for the use of the Langmuir adsorption model is shown by the fact that two sets of glycerophosphate additive experiments, with two different k_0 values, lie on the best fit line ($k_0/(k_0 - k) = 0.944(\pm 0.041) + 0.162(\pm 0.011) \times 10^{-4} [\text{additive}]^{-1}$) and three sets of phosphate additive experiments, with three different k_0 values, lie on a second best fit line ($k_0/(k_0 - k) = 0.992(\pm 0.012) + 0.019_6(\pm 0.001) \times 10^{-4} [\text{additive}]^{-1}$). This agreement demonstrates good reproducibility and reliability for the seeded growth technique in the examination of crystallization inhibition by trace constituents. The best fit linear relation and an intercept (within experimental uncertainty) of unity strongly suggest that the mechanism of inhibition involves that proposed for the Langmuir adsorption isotherm — namely the formation of a monomolecular blocking layer of additive ions at the growth sites on the crystal surface.

TOTAL Ca^{2+} (M $\times 10^4$)

Fig. 5. Growth in the absence of a calcium concentration of glycerophosphate $0-1 \times 10^{-5}$ M. The symbols represent the additive ion.

The slope of the line in fig. 7 illustrates the linear relation between the reciprocal of the additive concentration and the rate constant. This may be expressed as

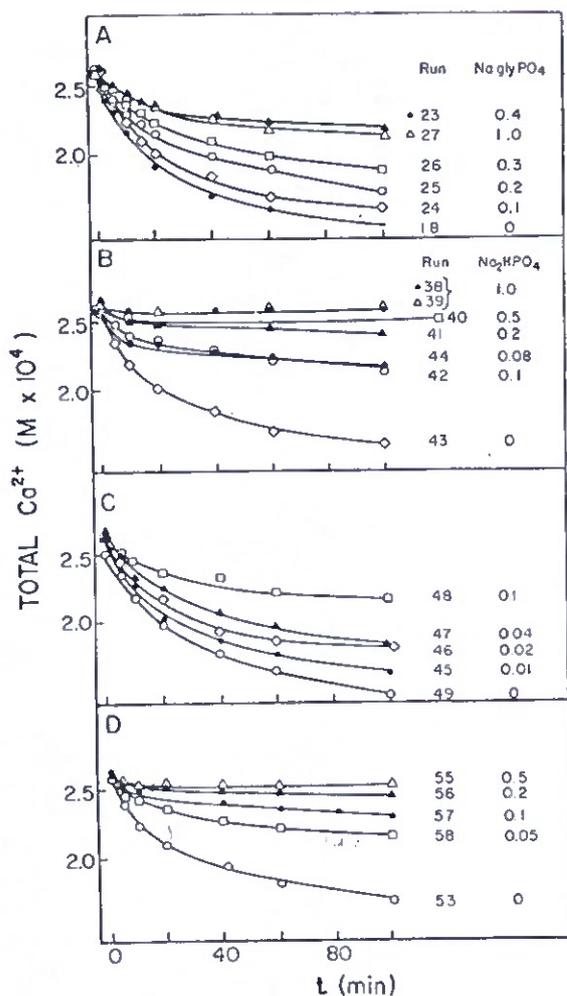


Fig. 5. Growth of calcite seed crystals in the presence and absence of additive ions, shown by the change in total calcium concentration as a function of time: (A) $0-1 \times 10^{-4}$ M glycerophosphate ion; (B) $0-1 \times 10^{-4}$ M phosphate ion; (C) $0-1 \times 10^{-5}$ M phosphate ion; (D) $0-5 \times 10^{-5}$ M phosphate ion. The symbols and the numbers beside the curves indicate the additive ion concentration $\times 10^4$.

The slopes of the Langmuir function plots shown in fig. 7 illustrate the difference in growth inhibition between glycerophosphate and phosphate ions. Comparison of slope values for glycerophosphate ($0.16_2(\pm 0.011) \times 10^{-4}$) and phosphate ion ($0.019_6(\pm 0.001) \times 10^{-4}$) indicates that 50% reduction in the rate constant occurs for phosphate at a concentration approximately 1/10 that of glycerophosphate. This may reflect stronger equilibrium adsorption of

phosphate at the interface, probably due to a reduction in k_2 , the desorption rate constant. Additional experiments are underway to examine the nature of phosphorus adsorbed on a calcium carbonate surface.

The mechanism presented for the kinetics of calcium carbonate formation is consistent with that of other studies conducted in solutions of higher alkalinities and pH [6,15,16]. Nancollas [18] has shown that the BCF theory, extended by Reich and Kahlweit [19], yields, under conditions of low supersaturation, the equation

$$-dm/dt \approx k_r(m - m_0)^2, \quad (6)$$

where m is the concentration of the solute in the supersaturated solution, m_0 the saturation concentration, dm/dt the rate of crystal growth and k_r the rate constant for the surface controlled reaction. This rate law shows a parabolic dependence on supersaturation and is similar to an equation derived by Davies and Jones [20]. The Davies-Jones approach, based on a model for crystal growth incorporating an adsorbed monolayer at the crystal surface, yields a parabolic dependence on supersaturation in solutions containing nonequivalent concentrations of the lattice ions obtained in this study (eq. (2)). Contradictions arising in the application of the adsorption layer model to solutions of non-equivalent ion concentrations indicate that the more likely mechanism of calcium carbonate growth is that of the BCF dislocation theory [21].

Calcite growth inhibition in solutions containing either glycerophosphate ion or phosphate ion is similar to that observed in supersaturated solutions containing polyphosphates [8] and phosphonic acid derivatives [6]. In experiments involving calcite inhibition by any one of these compounds there is an abrupt change in crystal growth rate over a narrow range of additive concentrations, and the additive inhibits the reaction by a reduction in growth rate — not by causing an induction period as in the case of calcium sulfate dihydrate crystal growth [22].

There is no evidence in the experiments reported here for the formation of a second phase (other than calcium carbonate) on the surface of the calcite seed crystals during growth experiments in the presence of additive ions. For example, experimental solutions containing the highest added phosphate concentrations were supersaturated with respect to hydroxy-

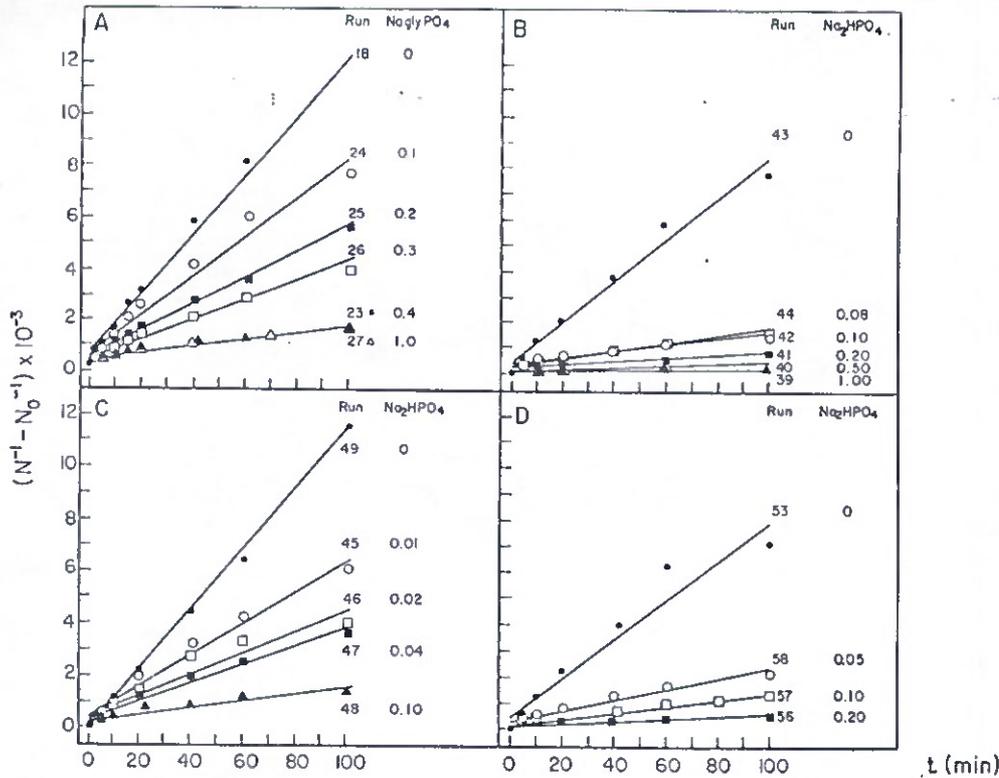


Fig. 6. Calcite crystal growth in the presence and absence of additive ions, as expressed by the rate function $N^{-1} - N_0^{-1}$ versus time. (A) $0-4 \times 10^{-4}$ M glycerophosphate ion; (B) $0-1 \times 10^{-4}$ M phosphate ion; (C) $0-1 \times 10^{-5}$ M phosphate ion; (d) $0-0.2 \times 10^{-5}$ M phosphate ion. As in fig. 5 the symbols and the numbers beside the curves indicate the additive ion concentrations $\times 10^4$.

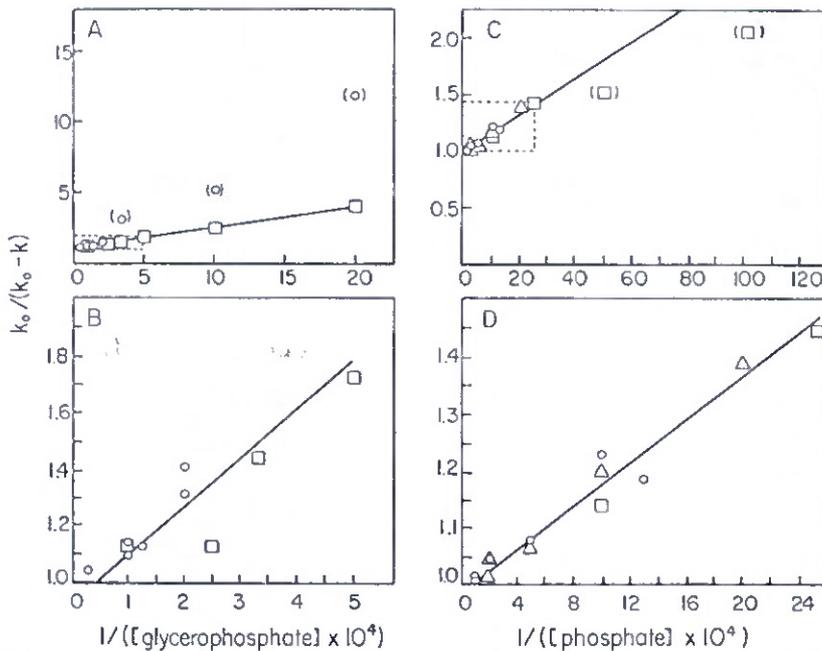


Fig. 7. Langmuir isotherm plot of $k_0/(k_0 - k)$ against the reciprocal of the additive concentration, where k_0 is the calcite growth rate constant in the absence of additive and k is the rate constant in the presence of additive. (A) Glycerophosphate as the additive ion; (o) $k_0 = 2.17 \pm 10\%$; (□) $k_0 = 1.34 \pm 14\%$. (B) Same as (A) with an expanded scale. (C) Phosphate as the additive ion; (o) $k_0 = 0.824$; (□) $k_0 = 1.205$; (△) $k_0 = 0.790$. (D) Same as (C) with an expanded scale.

apatite, phosphate plations, as concentr calcite cr

Acknowledgements

The assistance for the work was provided by the National Science Foundation, Grant No. EAR-77-10000. The authors are grateful to Dr. Wang for his helpful discussions.

References

- [1] T.F. ... (1940)
- [2] T.F. ... (1940)
- [3] R. Br ... Roy.
- [4] M. Mi ... 66 (19
- [5] M.M. ... (1976
- [6] M.M. ... (1973
- [7] M.M. ... 429.
- [8] G.H. ...

apatite, the thermodynamically stable calcium phosphate phase under these conditions. For these solutions, as well as all others examined, the phosphate concentration was essentially unchanged during the calcite crystallization reaction.

Acknowledgment

The author wishes to acknowledge financial assistance for part of this project through Health Research Inc., Albany, New York (Grant No. 35043.75). Support and encouragement of G.W. Fuhs during the course of this study is much appreciated. Mrs. K. Wang conducted laboratory work and Mr. T. Lyons performed computer programming.

References

- [1] T.F. Buehrer and R.F. Reitemeier, *J. Phys. Chem.* 44 (1940) 535.
- [2] T.F. Buehrer and R.F. Reitemeier, *J. Phys. Chem.* 44 (1940) 552.
- [3] R. Brooks, L.M. Clark and E.F. Thurston, *Phil. Trans. Roy. Soc. (London)* A243 (1950-51) 145.
- [4] M. Miura, H. Naono and S. Otani, *Kogyo Kagaku Zasshi* 66 (1963) 597.
- [5] M.M. Reddy and G.H. Nancollas, *J. Crystal Growth* 35 (1976) 33.
- [6] M.M. Reddy and G.H. Nancollas, *Desalination* 12 (1973) 61.
- [7] M.M. Reddy, *Verh. Intern. Verein. Limnol.* 19 (1975) 429.
- [8] G.H. Nancollas and M.M. Reddy, in: *Aqueous-Environmental Chemistry of Metals*, Ed. A.J. Rubin (Ann Arbor Science Publishers, Ann Arbor, Mich.) pp. 219-253.
- [9] G.H. Nancollas and N. Purdie, *Quart. Rev. (London)* 18 (1964) 1.
- [10] G.H. Nancollas, *J. Crystal Growth* 3/4 (1968) 355.
- [11] C.W. Davies, *Ion Association* (Butterworths, Washington, DC, 1962).
- [12] G.H. Nancollas, *Interactions in Electrolyte Solutions* (Elsevier, Amsterdam, 1966).
- [13] G. Schwarzenbach and G. Anderegg, *Helv. Chim. Acta* 40 (1957) 1229.
- [14] A. Chughtai, R.W. Marshall and G.H. Nancollas, *J. Phys. Chem.* 72 (1968) 208.
- [15] M.M. Reddy and G.H. Nancollas, *J. Colloid Interface Sci.* 36 (1971) 166.
- [16] G.H. Nancollas and M.M. Reddy, *J. Colloid Interface Sci.* 37 (1971) 824.
- [17] J. Murphy and J.P. Riley, *Anal. Chem. Acta* 27 (1962) 31.
- [18] G.H. Nancollas, *Croatica Chemica Acta* 45 (1973) 225.
- [19] R. Reich and M. Kahlweit, *Ber. Bunsenges. Physik. Chem.* 72 (1968) 66.
- [20] C.W. Davies and A.L. Jones, *Discussions Faraday Soc.* 5 (1949) 103.
- [21] A.L. Jones and H.G. Linge, *Z. Physik. Chem. NF* 95 (1975) 293.
- [22] T.S. Liu and G.H. Nancollas, *J. Colloid Interface Sci.* 44 (1973) 422.
- [23] H.S. Harned and R. Davis, *J. Am. Chem. Soc.* 65 (1943) 2030.
- [24] H.S. Harned and S.R. Scholes, *J. Am. Chem. Soc.* 63 (1941) 1706.
- [25] H.S. Harned and W.J. Hamer, *J. Am. Chem. Soc.* 55 (1933) 2194.
- [26] R.M. Garrels and M.E. Thompson, *Am. J. Sci.* 260 (1962) 57.
- [27] I. Greenwald, *J. Biol. Chem.* 141 (1941) 789.
- [28] D. Langmuir, *Geochim. Cosmochim. Acta* 32 (1968) 835.

(min)
 $-N_0^{-1}$ versus
 phosphate ion; (d)
 on concentra-

calcite growth
 rate as the ad-
 ditive ion;