

Influence of temperature on the stability of magnesian calcite

MIRIAM A. BERTRAM, FRED T. MACKENZIE

School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

FINLEY C. BISHOP

Department of Geological Sciences, Northwestern University, Evanston, Illinois 60201, U.S.A.

WILLIAM D. BISCHOFF

Department of Geology, Wichita State University, Wichita, Kansas 67208, U.S.A.

ABSTRACT

Free-drift dissolution experiments were conducted with synthetic calcite of between 1.9 and 15.1 mol% MgCO_3 over a range of temperatures (25–64 °C) and at P_{CO_2} of $10^{-2.5}$ atm. Inverse time plots of data from free-drift dissolution experiments were used to obtain parameter values (pH, Ca, Mg) at stoichiometric saturation.

Data show that the decrease in solubility of synthetic magnesian calcite with increasing temperature parallels that of calcite and aragonite between 25 and 45 °C. Some deviation from this parallelism is seen between 45 and 64 °C. These new stability data are discussed in terms of the diagenetic stabilization of polymineralic carbonate sediments and sea water saturation state. These data confirm that the recrystallization of magnesian calcite of 15 mol% MgCO_3 to dolomite and low magnesian calcite is thermodynamically favored at low temperatures. Also, low temperature favors the dissolution of a range of magnesian calcite compositions in sea water.

INTRODUCTION

The solubilities of pure calcite and aragonite are well established as functions of temperature (Plummer and Busenberg, 1982). However, the Mg content and presence of foreign ions in the crystal structure are factors known to affect the solubility of many CaCO_3 minerals. For example, SO_4^{2-} and Na^+ in solid solution with CaCO_3 (Busenberg and Plummer, 1985) and increasing concentrations of Mg^{2+} in solid solution in calcite cause an increase in disorder (Bischoff et al., 1985; Paquette and Reeder, 1990) and increase mineral solubility. Calcite with varying MgCO_3 content, magnesian calcite, plays important roles in many processes including biomineralization, carbonate diagenesis, and the regulation of atmospheric CO_2 and sea water saturation state.

Investigations into the solubility of magnesian calcite have yielded expressions and values for its stability at 1 atm pressure and 25 °C. Experimentally derived solubility data for magnesian calcite at 25 °C (e.g., Chave et al., 1962; Plummer and Mackenzie, 1974; Bischoff et al., 1987) can be compared with the activities of Ca, Mg, and carbonate ions in natural sea waters at various temperatures to obtain a crude estimate of sea water saturation state with respect to these solids. Carbonate saturation (Chave and Schmalz, 1966; Weyl, 1967) has also been used to obtain a qualitative measure of the saturation state of sea water.

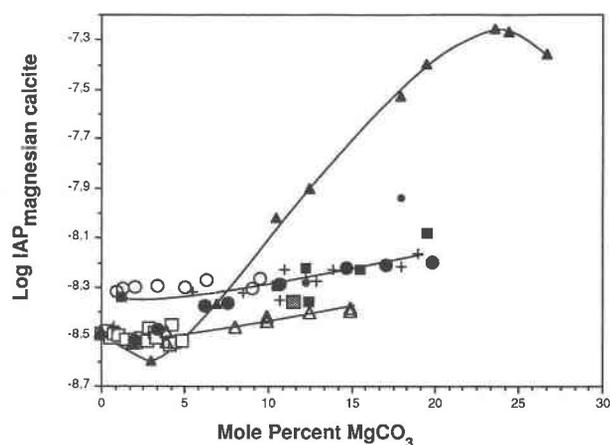
The effect of temperature on the solubilities of magnesian calcite is unknown. Consequently, the saturation state of sea water and other natural waters with respect

to these solids at temperatures other than 25 °C cannot be precisely determined at present. In addition, lack of knowledge of the relation between magnesian calcite solubility and temperature prevents accurate prediction of diagenetic pathways for the metastable assemblages of carbonate minerals deposited on the sea floor.

This paper reports the results of experimental solubility studies of magnesian calcite in distilled, deionized H_2O using the free-drift method. Extrapolation of $\log[\text{Ca}^{2+}]$, $\log[\text{Mg}^{2+}]$, and pH ($\log a\text{H}^+$) (where [] indicates concentration and a indicates activity) to infinite time are shown to yield comparable pH values at stoichiometric saturation. The data were obtained at temperatures from 27 to 64 °C for magnesian calcite of 1.9–15.1 mol% MgCO_3 at ten times atmospheric P_{CO_2} . The experimental results are applied in a discussion of solid transformations between magnesian calcite and dolomite + low magnesian calcite and the sea water saturation state.

PREVIOUS EXPERIMENTAL WORK

The thermodynamic stabilities of calcite, aragonite, and vaterite have been well characterized from free-drift dissolution experiments at P_{CO_2} of 1 atm and temperatures between 0 and 60 °C (Plummer and Busenberg, 1982). These minerals are single-component polymorphs of calcium carbonate (i.e., Ca^{2+} is the only cation associated with CO_3^{2-}). Calcite, aragonite, and vaterite exhibit an increase in K_{sp} (solubility product) with decreasing temperature, indicating higher solubility at reduced temperatures.



- Busenberg and Plummer (1989); Natural (biogenic and inorganic precipitates) magnesian calcites.
- Busenberg and Plummer (1989); Synthetic magnesian calcites prepared in NaCl solutions.
- Busenberg and Plummer (1989); Synthetic magnesian calcites prepared from NaCl and K₂SO₄ solutions.
- + Busenberg and Plummer (1989); Biogenic magnesian calcites.
- △ Bischoff et al. (1987); Synthetic magnesian calcites.
- Bischoff et al. (1987); Biogenic magnesian calcites.
- ▲ Plummer and Mackenzie (1974); "uncleaned" biogenic magnesian calcites.
- Walter and Morse (1984); Biogenic magnesian calcites.
- Lafon (1990); 11.6 mol% Biogenic magnesian calcite

Fig. 1. Experimental determinations of magnesian calcite solubility at 25 °C, expressed as $\log IAP_{\text{magnesian calcite}}$, as a function of Mg content.

Multicomponent, metastable minerals do not necessarily attain thermodynamic equilibrium during dissolution experiments because a less soluble phase can precipitate prior to equilibrium with the initial solid phase. An estimate of the solubility product of a solution at equilibrium with a metastable phase ("metastable equilibrium") can be made with modified free-drift experiments. Extrapolation of pH measurements, taken at regular time intervals, to infinite time on an inverse time plot (see Plummer and Mackenzie, 1974; Walter and Morse, 1984; Bischoff et al., 1987, for discussion) or the attainment of "stoichiometric saturation" during dissolution and precipitation of the same phase (Plummer and Busenberg, 1987; Busenberg and Plummer, 1989; Lafon, 1990) have been the primary adaptations of the free-drift method.

Bischoff et al. (1987) conducted free-drift experiments on synthetic as well as biogenic magnesian calcite at 25 °C and P_{CO_2} of $10^{-2.5}$ atm. These results are plotted in Figure 1 along with the results of the dissolution of two varieties of biogenic magnesian calcite by Walter and Morse (1984) and of minimally cleaned biogenic samples by Plummer and Mackenzie (1974). Extrapolation of pH to infinite time was used to evaluate the solubility of each phase.

Busenberg and Plummer (1989) conducted a series of experiments on natural inorganic and biogenic phases and

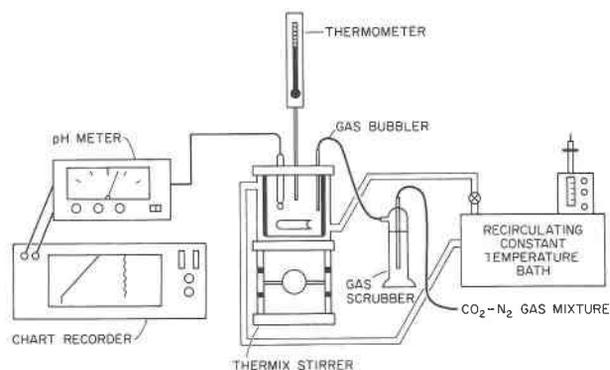


Fig. 2. Experimental apparatus used in the free-drift experiments.

on synthetic magnesian calcite. Incongruent precipitation was inhibited by the addition of phosphate. Saturation with respect to the dissolving phase was considered to occur when the solution maintained a constant ion activity product (IAP) over a period of days. These experiments distinguished two groups of carbonates with distinct solubilities, reflecting the extent of crystal structure defects in the different phases of identical MgCO₃ content. Physical and chemical defects originating from foreign ion substitution and rapid crystal growth during laboratory precipitation produced more soluble minerals, and well-crystallized precipitates produced the least soluble minerals. These analytical results agree reasonably well with those of Bischoff et al. (1987), Mucci and Morse (1984), and Walter and Morse (1984) for "impure" phases and with Bischoff et al. (1987) and Mucci and Morse (1984) for well-crystallized phases, as shown in Figure 1.

Free-drift experiments have recently been employed by Lafon (1990) to yield a solubility determination of biogenic magnesian calcite with 11.6 mol% Mg from under- and oversaturation without extrapolation or the use of chemical inhibitors. The data point is shown in Figure 1 and is somewhat lower than, but in reasonable agreement with, the trend of the experimental results for biogenic minerals. The agreement between various experimental approaches suggests that both the method of extrapolation of pH to infinite time and the attainment of a constant IAP in solution may be used to determine the relative solubilities of members of the MgCO₃-CaCO₃ solid solution series.

EXPERIMENTAL APPROACH

Apparatus and procedure

The experimental apparatus is schematically illustrated in Figure 2. A constant-temperature circulating pump was used to drive H₂O through a jacketed pyrex reaction vessel. The temperature was maintained at ± 0.2 °C of the desired temperature as verified by a thermometer submerged in the experimental solution. The reaction vessel was covered by a rubber stopper that held the pH electrode, gas dispersion pipette, thermometer, and a stop-

pered port for sample removal. A custom mixture of CO₂ in N₂ contained 3160 ± 284 ppm CO₂. This gas mixture was bubbled through distilled H₂O and then into the reaction vessel. The electrode was connected to a Corning pH meter and pH recorded continuously on a chart recorder. The electrode had a Nernst slope of 98% when calibrated with Fisher N.B.S. buffers of pH 4 and 7. An error of ±0.01 units is reported for the buffer readings at 25 °C and is the minimal error associated with the measurement of pH. Electrode drift was not significant for the average length of the experiments (10 h); however, experimental pH determinations for experiments greater than 15 h were connected for drift.

The gas phase was introduced to distilled, deionized H₂O, heated to the experimental temperature (between 25 and 64 °C), and allowed to equilibrate. When the solution pH remained stable for greater than 5 min, the solution was considered near equilibrium with the gas phase. The experiment was conducted only when a stable pH was within 0.02 units of the calculated equilibrium pH between the gas phase and distilled H₂O at the experimental temperature.

Solids

Calcite and magnesian calcite were synthesized by recrystallizing appropriate amounts of reagent grade calcite, MgCO₃, and oxalic acid (to prevent decomposition of products) in pressure bombs. The temperature and pressure of reaction, as well as the ratio of calcite to MgCO₃, determined the composition of the carbonate produced. The syntheses and cleaning procedures are discussed in detail by Bischoff (1985) and Bischoff et al. (1983). The samples were rinsed with acetone to remove any oxalic acid residue that may have remained after synthesis. The crystals were then rinsed with distilled H₂O and cleaned in an ultrasonic bath for approximately 15 min. Fine particles were removed by vacuum filtration through a 0.8 μm polycarbonate membrane filter. After the remaining solid was dried and annealed for 24 h at 60 °C, the samples were introduced into the reaction vessel.

Analysis of solutions

At regular intervals during the experiment, 2 mL aliquots of the suspension were extracted from the reaction vessel for Ca²⁺ and Mg²⁺ analysis. These samples were filtered through 0.8-μm polycarbonate filters then stored at dilutions of 1:1, 1:5, or 1:10 (depending upon the expected Ca and Mg concentrations). The samples were then refrigerated until analyzed by inductively coupled plasma atomic-emission spectrometry (ICP-AES) using a Leeman Labs Plasma Spec I. Analytical errors in the molarity of Ca²⁺ and Mg²⁺ concentrations are 1.5% and 0.2%, respectively.

Aqueous model

Equilibrium constants at the experimental temperature were calculated for (1) the carbonic acid system, calcite (*K_c*), CaHCO₃⁺, and CaCO₃⁰ using the equations of Plum-

mer and Busenberg (1982) and for (2) MgHCO₃⁺ and MgCO₃⁰ using the data of Riesen et al. (1977). Activity coefficients were calculated from the modified Davies (1963) equation. Carbonate species were calculated using the constants *K_H*, *K₁*, and *K₂* of Plummer and Busenberg (1982) at the experimental temperature, pH, and *P_{CO₂}*. For the dissolution of calcite, the concentration of Ca²⁺ ions were calculated from pH, *P_{CO₂}*, and the carbonate species concentrations from the ionic charge balance:

$$\begin{aligned} m\text{H}^+ + 2m\text{Ca}^{2+} + m\text{CaHCO}_3^+ \\ = m\text{OH}^- + 2m\text{CO}_3^{2-} + m\text{HCO}_3^- \end{aligned} \quad (1)$$

For magnesian calcite, the ionic charge in Equation 1 is balanced by the sum of Mg²⁺ + MgHCO₃⁺ and Ca²⁺ + CaHCO₃⁺ rather than simply Ca²⁺ and CaHCO₃⁺. These equations and procedures were used in a BASIC computer program modified after that used by Bischoff (1985) to calculate the IAP_{magnesian calcite} at the extrapolated pH.

Magnesian calcite at stoichiometric saturation with a solution can be presented by the chemical reaction:



where *x* represents the mole fraction of Mg in the solid phase. Congruent dissolution requires that the Mg²⁺:Ca²⁺ ratio of the solution equal that of the solid magnesian calcite phase over the course of an experiment. During congruent dissolution, the composition of the solid phase must also remain constant.

Thorstenson and Plummer (1977) describe stoichiometric saturation for stable and metastable phases when IAP = *K_{eq}*. The stoichiometric ion activity product used to determine the relative solubilities of the magnesian calcite is defined as

$$\text{IAP}_{\text{magnesian calcite}} = a_{\text{Ca}^{2+}}^{1-x} a_{\text{Mg}^{2+}}^x a_{\text{CO}_3^{2-}} \quad (3)$$

where *a_i* is the activity of the *i*th species in solution. Stoichiometric saturation has been shown to be well represented by the IAP_{magnesian calcite} of Equation 3. (See Bischoff et al. 1987; Walter and Morse, 1984; Busenberg and Plummer, 1989, for a discussion of expressions used to represent the stabilities of magnesian calcite.) If the magnesian calcite reacts as an invariant single component system during congruent dissolution, extrapolation of pH can be used to determine the IAP at stoichiometric saturation.

The extrapolated pH and known *P_{CO₂}* were used to calculate carbonate ion activity at stoichiometric saturation; the ratio of Ca²⁺:Mg²⁺ during congruent dissolution and charge balance at saturation were used to calculate Ca and Mg activity at saturation.

RESULTS

Preliminary experiments

Many physical parameters, including fine-grained materials, strained grain surfaces, and surface area/solution volume ratios, affect the extrapolation of pH to infinite time on inverse time plots (cf. Mackenzie et al., 1983).

TABLE 1. Initial conditions and results for the dissolution of recrystallized calcite

	Temperature (°C)	g/L ^a	-log IAP	IAP/ <i>K</i> _{eq} ^{**}
Untreated	40	0.167	9.14	0.28
	40	0.177	8.79	0.61
	40	0.173	8.98	0.40
Treated†	40	0.152	8.60	0.95
	53	0.074	8.73	0.91
	54	0.146	8.70	1.00‡

^a Solid-solution volume ratio.

^{**} Equilibrium constant calculated from data of Plummer and Busenberg (1982).

† Fine particles and oxalic acid were removed.

‡ Particles dissolved rapidly to saturation, preventing extrapolation. The pH reported is that at the conclusion of the experiment (see text).

These parameters may yield variable dissolution rates during the linear, congruent leg of reaction. Fine-grained particles and strained grain surfaces were eliminated in sample preparation. The increase in reaction temperature was anticipated to affect the dissolution rate. Therefore, the surface area/solution volume ratio was adjusted to compensate for each temperature increase.

Table 1 presents the results of two sets of calcite dissolution experiments. Recrystallized calcite was reacted at 40 °C in the first set, but erratic extrapolated pH values and calculated solubilities were obtained from the three experiments. Fine particles and oxalic acid were removed from this recrystallized calcite, and several more experiments were conducted. At 40 °C and a solid/solution volume ratio of 0.15 g/L, the calculated solubility was within 5% of the value reported for calcite solubility by Plummer and Busenberg (1982). Using the same solid/solution volume ratio at 54 °C, no linear pH range was evident on the inverse time plot. The pH attained at the conclusion of the experiment was constant for several hours and yielded an ion activity product equal to the equilibrium constant at 54 °C. The solid/solution volume ratio was reduced by 50%, and extrapolation of pH to infinite time yielded an estimate of solubility within ±10% of *K*_{eq}.

Experiments using synthetic magnesian calcite were also conducted over a range of solid/solution volume ratios at different temperatures. Error in the extrapolated pH (*y* intercept) and the *R*² value obtained from the linear fit through the pH data on magnesian calcite are shown in Table 2. Experimental conditions were considered optimum for the dissolution of a magnesian calcite phase at a particular temperature when the *R*² value was greater than 0.99 and the error in the extrapolated pH was minimized. These pH data were then used to calculate magnesian calcite solubility, as previously described.

Figures 3a, 3b, and 3c display pH, log[Ca²⁺], and log[Mg²⁺], respectively, as a function of the inverse of the square root of time for the dissolution of a 15 mol% MgCO₃ calcite at 45 °C. The extrapolated region, linear best-fit line, *R*² value for that line, and the error in the *y* intercept are shown. The three extrapolated values may be used to calculate the charge balance at stoichiometric

TABLE 2. Results for the dissolution of synthetic magnesian calcite at different temperatures and solid/solution volume ratios

Mol% MgCO ₃ ^A	Temperature (°C)	g/L ^B	pH ^C	<i>R</i> ^{2D}
3.0	64	0.057	7.644(12)	0.985
	64	0.072	7.518(12)	0.989
	64	0.088	7.695(10)	0.979
	64	0.126	7.669(09)	0.978
	42	0.127	—	— ^E
	42	0.169	7.560(10)	0.998
8.0	42	0.223	7.699(14)	0.971
	42	—	7.640(20)	— ^F
	53	0.070	7.554(20)	0.859
	53	0.066	7.611(06)	0.998 ^G
	43	0.076	7.454(13)	0.994
	43	0.150	7.657(04)	0.995

^A Determined by atomic absorption analysis.

^B Solid-solution volume ratio.

^C The pH at infinite time unless otherwise specified.

^D Coefficient for the regression line fitted through pH and time^{-0.5}.

^E The pH during the experiment was never greater than 7.3; extrapolation is not valid for this experiment (see text).

^F The pH at the conclusion of the experiment; this value may represent the pH at stoichiometric saturation (see text).

^G Sample was treated twice to remove fine particles.

saturation; charge is balanced to ±10%. The number and accuracy (0.2%) of pH measurements favor the use of pH as the parameter to extrapolate. This figure is representative of the data obtained during each experiment, although the absolute values and slopes of different experiments may differ.

Congruent dissolution was evaluated from Ca and Mg concentrations. The Ca and Mg data from Figures 3a and 3b are plotted against each other in Figure 4 and show that congruent dissolution occurs during most, if not all, of the reaction. A linear regression is fitted to the data, and the slope of this line gives the composition of the dissolving phase. In this experiment, the value is 14.2 mol% MgCO₃ and is comparable to the 15.0 mol% MgCO₃ composition of the solid phase as determined by XRD. This dissolving composition is reported with other experimental conditions and results in Table 3.

Calcite and aragonite solubilities were shown to be logarithmic functions of temperature by Plummer and Busenberg (1982). The function is thermodynamically consistent with the dependence of heat capacity on temperature (Maier and Kelly, 1932):

$$\log \text{IAP} = A + B \times T (\text{K}) + C/T (\text{K}) + D \times \log T (\text{K}) \quad (4)$$

where A, B, C, and D are constants. Figure 5 illustrates the relationship between solubility and temperature for calcite and aragonite (after Plummer and Busenberg, 1982) and for the synthetic 1.9, 3.9, 8, and 15 mol% MgCO₃ magnesian calcite data of this study. Error bars are calculated from the error associated with the extrapolation of pH. The solubility of the magnesian calcite parallels that of calcite and aragonite at temperatures less than 42 °C. Between 25 and 42 °C, synthetic 15 mol% MgCO₃ calcite is stable relative to calcite but unstable with re-

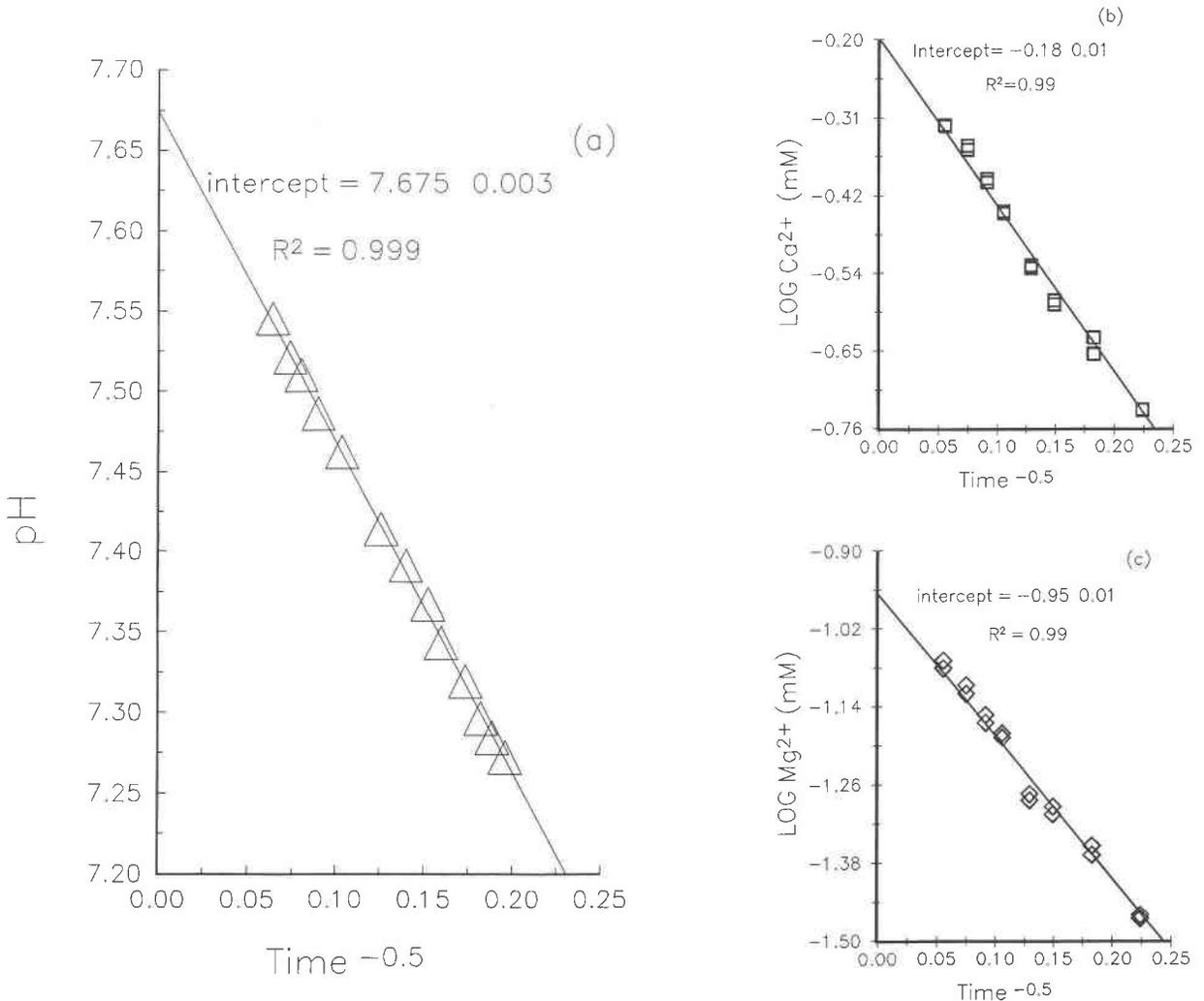


Fig. 3. Example of a reciprocal time plot used to extrapolate (a) pH, (b) $\log[\text{Ca}^{2+}]$, and (c) $\log[\text{Mg}^{2+}]$ for the dissolution of synthetic 15 mol% magnesian calcite at 45 °C.

spect to aragonite. A 1.9 mol% MgCO_3 calcite is stable with respect to both calcite and aragonite over the entire temperature range studied (25–64 °C). At temperatures greater than 42 °C, the data suggest that magnesian calcite of up to 15 mol% MgCO_3 is stable relative to calcite at 60 °C.

DISCUSSION

The results of our experimental determinations of magnesian calcite solubilities over a range of temperatures may be applied to the interpretation of a variety of carbonate mineral- H_2O reactions at low and moderate temperatures. As examples of applications, we discuss below mineral stabilities in a portion of the CaCO_3 - MgCO_3 system and in surface sea water.

Dolomite formation

The experimental results may be used to document diagenetic reactions observed in well-characterized car-

bonate sediments. Early diagenetic reactions are known to include the alteration of high magnesian calcite to dolomite and low magnesian calcite (e.g., Blake et al., 1982; Lohmann and Meyers, 1977). The concurrent preservation of some high magnesian calcite in zones of dolomite formation has also been documented petrographically (Aissaoui, 1988).

Transformation of a metastable algal magnesian calcite mineral to dolomite at metamorphic temperatures was established by Graf and Goldsmith (1955) in laboratory experiments. At temperatures of approximately 700 °C, magnesian calcite of 15 mol% MgCO_3 and dolomite should be the stable phases in a system containing high magnesian calcite and sufficient CO_2 .

Graf and Goldsmith (1955) did not evaluate the system at temperatures below 500 °C because, at these low temperatures, transformation of metastable magnesian calcite to dolomite proceeded very slowly. The data from this study may be used to extend the results of Graf and

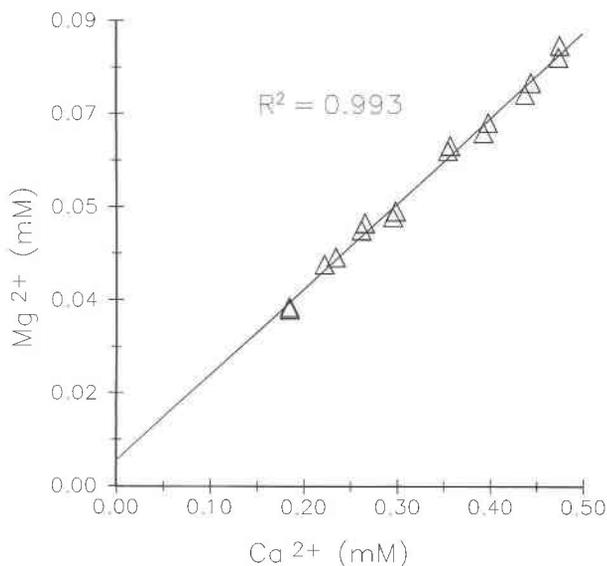


Fig. 4. Plot of $[Ca^{2+}]$ vs. $[Mg^{2+}]$ data for the dissolution of synthetic 15 mol% $MgCO_3$ magnesian calcite at 45 °C. Line drawn is a linear regression through the congruent dissolution data.

Goldsmith (1955) to lower temperatures, for which magnesian calcite is metastable, and to discuss the low-temperature diagenetic processes cited above. As an example, consider Equation 5, which represents the reaction of 15 mol% $MgCO_3$ magnesian calcite to dolomite and 1.9 mol% $MgCO_3$ magnesian calcite:

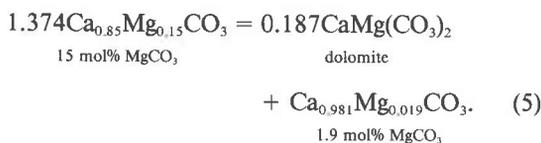


TABLE 3. Solubility data for the free-drift dissolution of magnesian calcite at a P_{CO_2} of $10^{-2.5}$ atm

T (°C)	Experiment no.	g/L*	mol% $MgCO_3$		pH‡	-log IAP§
			A**	B†		
27	7A-1	0.168	7.0	7.6	7.668(10)	8.48(03)
35	16A-1	0.199	15.0	14.4	7.693(10)	8.48(03)
42	8C-1	0.070	1.9	2.2	7.552(10)	8.75(03)
42	10A-1	0.069	5.7	6.3	7.621(10)	8.60(03)
42	11C-3	0.222	8.0	8.7	7.64(20)	8.58(06)
42	16A-2	0.072	15.0	14.3	7.681(09)	8.52(02)
43	8C-2	0.071	1.9	2.2	7.569(10)	8.70(03)
43	9C-1	0.068	3.9	4.1	7.598(07)	8.65(02)
43	12A-2	0.150	12.0	11.5	7.657(04)	8.59(01)
45	16A-4	0.120	15.0	14.2	7.671(05)	8.55(02)
53	3A-1	0.072	3.0	2.9	7.581(11)	8.68(03)
53	9C-2	0.070	3.9	3.2	7.589(10)	8.66(03)
53	11C-5	0.066	8.0	8.0	7.611(06)	8.66(02)
59	16A-6	0.090	15.0	14.2	7.588(20)	8.78(06)
60	7B-2	0.073	7.0	6.9	7.526(05)	8.90(02)
60	7B-4	0.069	7.0	N.A.	7.527(11)	8.89(03)
64	8C-8	0.072	1.9	2.6	7.487(03)	8.94(01)
64	3A-4	0.072	3.0	2.9	7.518(12)	8.87(03)

* Solid/solution volume ratio.

** Determined by atomic absorption or X-ray diffraction.

† Solid composition during congruent dissolution.

‡ Determined by extrapolation of pH to infinite time.

§ Solubility as defined by Equation 3 (see text).

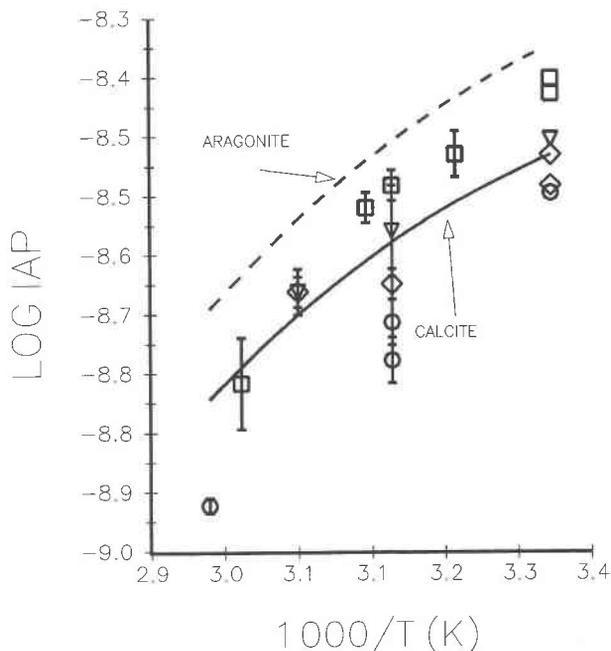


Fig. 5. Mineral solubility (log IAP) shown as a function of temperature for calcite, aragonite, synthetic 1.9 (circles), 3.9 (diamonds), 8.0 (triangles), and 15 (squares) mol% $MgCO_3$ magnesian calcite. Calcite and aragonite solubilities as a function of temperature are from Plummer and Busenberg (1982). Error bars are shown.

The stability of disordered dolomite is calculated from the hydrolysis constants of Bowers et al. (1984) and the CO_2 - H_2O equilibria of Plummer and Busenberg (1982). The stabilities of the 1.9 and 15 mol% magnesian calcite can be estimated from the log IAP data plotted in Figure 5 by calculation of their Gibbs free energies of formation at a defined temperature:

$$\Delta G_{RX} = -RT \ln k$$

$$(k = \text{IAP at equilibrium}) \quad (6)$$

$$\Delta G_{f, \text{magnesian calcite}} = (1 - x)\Delta G_{f, Ca^{2+}} + x\Delta G_{f, Mg^{2+}} + \Delta G_{f, CO_3^{2-}} - \Delta G_{RX} \quad (7)$$

where ΔG_{RX} is the Gibbs free energy of reaction, R is the molar gas constant, T is temperature (K), and $\Delta G_{f,i}$ is the Gibbs free energy of formation of the i th phase.

At 50 °C the calculated Gibbs free energy of reaction, ΔG_{RX} , is -1.63 kJ/mol, indicating that the reaction should proceed as written, forming dolomite plus calcite low in Mg, assuming no loss of CO_2 to the environment. This calculation confirms that given time at low temperatures, magnesian calcite may exsolve to dolomite plus calcite low in Mg, as predicted by the well-known phase relations (e.g., Graf and Goldsmith, 1955) and as observed petrographically (e.g., Lohmann and Meyers, 1977). At higher temperatures, the calcite at equilibrium should be more enriched in Mg. The exact equilibrium composi-

tions are not predictable because of lack of experimental data between about 65 and several hundred degrees Celsius. As further petrographic and chemical information on the diagenesis of magnesian calcite becomes available from field studies, the experimental solubility data given here may be used to confirm carbonate mineral paragenetic relationships at temperatures approaching 100 °C.

Sea water saturation state

The results of our experimental work may also be used to evaluate the equilibrium composition of magnesian calcite cement precipitated from sea water and the saturation state of a system with respect to 1.9–15 mol% MgCO₃ magnesian calcite. For example, given the constant Mg/Ca ratio of sea water and the fact that the concentration of activity of CO₃²⁻ can be used as an index of sea water saturation state (e.g., Broecker and Peng, 1982), in low-temperature surface polar waters, a range of magnesian calcite could dissolve in the absence of kinetic inhibition. Conversely, in warm equatorial surface waters most, if not all, biogenically produced calcite of <15 mol% MgCO₃ would persist until sinking to depth. The disappearance of high magnesian calcite during transport of sediment to depth in the open ocean has been documented in several studies (e.g., Friedman, 1965; Pilskahn et al., 1988; Droxler et al., 1988).

CONCLUSIONS

The present study shows that between 25 and 45 °C synthetic magnesian calcite of 1.9–15 mol% MgCO₃ decreases in solubility in a manner comparable to calcite. At higher temperatures, this similarity is less obvious, and there appears to be some convergence in the solubility values for calcite and Mg-enriched calcite. It is possible that as temperature increases during burial diagenesis magnesian calcite may dissolve before aragonite, producing secondary porosity in carbonate sediments (Moore, 1989). Mg-rich calcite may also attain stability relative to dolomite plus less Mg-enriched calcite if the position of the limb of the solvus is exceeded at higher temperatures during burial diagenesis, supporting observations of the coexistence of dolomite and magnesian calcite. Lastly, the dissolution of some magnesian calcite in surface sea water could become more pronounced with elevated atmospheric temperatures and anthropogenic CO₂ input, especially in regions where biogenic magnesian calcite is abundant.

ACKNOWLEDGMENTS

We thank Jane S. Tribble and Jozsef Urmos for their critical review of this manuscript and Lynn Walter for her review and encouragement to explore further the diagenetic implications of our work. This research was supported by NSF grants EAR 82-19513, EAR 82-13720 and EAR 89-15536. Contribution no. 2628, School of Ocean and Earth Science and Technology.

REFERENCES CITED

- Aissaoui, D.M. (1988) Magnesian calcite cements and their diagenesis: Dissolution and dolomitization, Mururoa Atoll. *Sedimentology*, 35, 821–841.
- Bischoff, W.D. (1985) Magnesian calcites: Physical and chemical properties and relative stabilities in aqueous solution of synthetic and biogenic phases. Ph.D. dissertation, Northwestern University, Evanston, Illinois.
- Bischoff, W.D., Bishop, F.C., and Mackenzie, F.T. (1983) Biogenically produced magnesian calcites: Inhomogeneities in chemical and physical properties; comparison with synthetic phases. *American Mineralogist*, 68, 1183–1188.
- Bischoff, W.D., Sharma, S.K., and Mackenzie, F.T. (1985) Carbonate ion disorder in synthetic and biogenic magnesian calcites: A Raman spectral study. *American Mineralogist*, 70, 581–589.
- Bischoff, W.D., Mackenzie, F.T., and Bishop, F.C. (1987) Stabilities of synthetic magnesian calcites in aqueous solution: Comparison with biogenic materials. *Geochimica et Cosmochimica Acta*, 51, 1413–1423.
- Blake, D.F., Peacor, D.R., and Wilkinson, B.H. (1982) The sequence and mechanism of low-temperature dolomite formation: Calcian dolomites in a Pennsylvanian echinoderm. *Journal of Sedimentary Petrology*, 52, 59–70.
- Bowers, T.S., Jackson, K.J., and Helgeson, H.S. (1984) Equilibrium activity diagrams for coexisting minerals and aqueous solutions at pressures and temperatures to 5 kb and 600 °C, 397 p. Springer-Verlag, New York.
- Broecker, W.S., and Peng, T.-H. (1982) *Tracers in the sea*, 690 p. Eldigio Press, Palisades, New York.
- Busenberg, E., and Plummer, L.N. (1985) Kinetic and thermodynamic factors controlling the distribution of SO₄²⁻ and Na⁺ in calcites and selected aragonites. *Geochimica et Cosmochimica Acta*, 49, 713–725.
- (1989) Thermodynamics of magnesian calcite solid-solutions at 25 °C and 1 atm total pressure. *Geochimica et Cosmochimica Acta*, 53, 1189–1208.
- Chave, K.E., and Schmalz, R.F. (1966) Carbonate-seawater interaction. *Geochimica et Cosmochimica Acta*, 30, 1037–1048.
- Chave, K.E., Deffeyes, K., Weyl, P., Garrels, R.M., and Thompson, M.E. (1962) Observations on the solubility of skeletal carbonates in aqueous solutions. *Science*, 137, 33–34.
- Davies, C.W. (1963) *Ion association*, 190 p. Butterworth, Washington, DC.
- Droxler, A.W., Morse, J.W., and Kornicker, W.A. (1988) Controls on carbonate mineral accumulation in Bahamian basins and adjacent Atlantic Ocean sediments. *Journal of Sedimentary Petrology*, 58, 120–130.
- Friedman, G.M. (1965) Occurrence and stability relationships of aragonite, high-magnesian calcite, and low-magnesian calcite under deep-sea conditions. *Geological Society of America Bulletin*, 76, 1191–1196.
- Graf, D.L., and Goldsmith, J.R. (1955) Dolomite-magnesian calcite relations at elevated temperatures and CO₂ pressures. *Geochimica et Cosmochimica Acta*, 7, 109–128.
- Lafon, G.M. (1990) Reversed equilibrium solubility of a high-magnesian calcite. *Geochemical Society Special Publication* 2, 23–40.
- Lohmann, K.C., and Meyers, W.J. (1977) Microdolomite inclusions in cloudy prismatic calcites: A proposed criterion for former high-magnesian calcites. *Journal of Sedimentary Petrology*, 47, 1078–1088.
- Mackenzie, F.T., Bischoff, W.D., Loijens, F.C., Schoonmaker, M., and Wollast, R. (1983) Magnesian calcite: low temperature occurrence, solubility, and solid solution behavior in carbonates; mineralogy and chemistry. In *Mineralogical Society of America Reviews in Mineralogy*, 11, 97–144.
- Maier, C.G., and Kelly, K.K. (1932) An equation for the representation of high temperature heat content data. *Journal of the American Chemical Society*, 54, 3243–3246.
- Moore, C. (1989) *Carbonate diagenesis and porosity*, 338 p. Elsevier, New York.
- Mucci, A., and Morse, J.W. (1984) The solubility of calcite in seawater solutions of various magnesium concentration, I₁ = 0.6 at 25 °C and one atmosphere total pressure. *Geochimica et Cosmochimica Acta*, 48, 815–822.
- Paquette, F., and Reeder, R.J. (1990) Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals. *American Mineralogist*, 75, 1151–1158.
- Pilskahn, C.H., Neumann, A.C., and Banc, J.M. (1988) The flux and deposition of periplatform carbonates in Northwest Providence Channel,

- Bahamas. Proceedings of the Symposium on the Geology of the Bahamas, Fort Lauderdale, Florida, 3, 123–138.
- Plummer, L.N., and Busenberg, E. (1982) The solubilities of calcite, aragonite and vaterite in CO_2 - H_2O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system CaCO_3 - CO_2 - H_2O . *Geochimica et Cosmochimica Acta*, 46, 1011–1040.
- (1987) Thermodynamics of aragonite-strontianite solid solutions: Results from stoichiometric solubility at 25 and 76 °C. *Geochimica et Cosmochimica Acta*, 51, 1393–1411.
- Plummer, L.N., and Mackenzie, F.T. (1974) Predicting mineral solubility from rate data: Application to the dissolution of magnesian calcites. *American Journal of Science*, 274, 61–83.
- Riesen, W., Gamsjager, H., and Schindler, P.W. (1977) Complex formation in the ternary system $\text{Mg(II)}\text{-CO}_2\text{-H}_2\text{O}$. *Geochimica et Cosmochimica Acta*, 41, 1193–1200.
- Thorstenson, D.C., and Plummer, L.N. (1977) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase-example: The magnesian calcites. *American Journal of Science*, 277, 1203–1223.
- Walter, L.M., and Morse, J.W. (1984) Magnesian calcite solubilities: A reevaluation. *Geochimica et Cosmochimica Acta*, 48, 1059–1069.
- Weyl, P.K. (1967) The solution behavior of carbonate minerals in sea water. Proceedings of the International Conference on Tropical Oceanography, Miami, Florida, 178–228.

MANUSCRIPT RECEIVED MARCH 12, 1990

MANUSCRIPT ACCEPTED JULY 13, 1991