

## Reversed equilibrium solubility of a high-magnesium calcite

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**Abstract**—A new experimental technique has been developed to study reactions between magnesian calcite solid solutions and aqueous fluids. It results in congruent dissolution and precipitation of the mineral and yields a very accurate estimate of its solubility without relying on empirical extrapolations. Use of low fugacities of CO<sub>2</sub> (comparable to that of air) and varying the stirring rate provide a measure of control on reactions and permit accurate characterization of metastable states. Stirring of the solution and abrasion of the solids can be used to reach metastable supersaturation for extended periods of time. Through appropriate manipulation of experimental parameters, it is possible to reach equilibrium from both under- and super-saturation.

The reversed equilibrium solubility of a biogenic high-magnesium calcite has been experimentally determined at 25°C for the first time. A fragment of the sea urchin *Sphaerechinus granularis* containing 11.6 mol percent MgCO<sub>3</sub> was reacted with distilled water at equilibrium with a gas mixture of 377 ppm V CO<sub>2</sub> in N<sub>2</sub>. Congruent dissolution, precipitation and equilibrium data are presented for this material. Its free energy of formation is:  $-1,117.75 \text{ kJ mol}^{-1}$ .

### INTRODUCTION

MAGNESIAN CALCITES CONSTITUTE an isostructural solid-solution series between end-members calcite (CaCO<sub>3</sub>) and magnesite (MgCO<sub>3</sub>), and represent a major fraction of recent carbonate sediments and rocks. They occur mostly as biogenic skeletal grains, but are also commonly found as pore-lining cements precipitated from sea water. They can be classified in two main groups. The low-magnesium calcites, containing less than 4 to 6 percent MgCO<sub>3</sub>, are stable over periods of geologic time. High-magnesium calcites usually react with pore fluids over time spans of tens to hundreds of thousands of years to form low-magnesium calcites and possibly dolomite, and to release dissolved magnesium. This "stabilization process" plays an essential role in the early diagenesis of carbonate rocks (see, for instance BATHURST, 1976, chapters 8, 9 and 10).

The common occurrence in recent marine sediments of a variety of carbonate minerals with different structures and compositions is difficult to understand from a chemical equilibrium standpoint. The difficulty is compounded by selective reactions with pore fluids during early diagenesis. These problems have led numerous investigators to try and estimate the stability of magnesian calcite in order to answer questions such as: is sea water more supersaturated with respect to aragonite or magnesian calcite?; why are both aragonite and magnesian calcite cements precipitated during early marine diagenesis?; what is the composition of a magnesian calcite at equilibrium with sea water?; how can we explain the evolution of modern carbonate sediments toward the long-term stable assemblage calcite-dolomite-solution?

Three approaches have been used to estimate the stability of magnesian calcite: experimental precipitation from a solution of known Ca/Mg ratio to determine a partition coefficient, thermodynamic analysis of the magnesian calcite solvus, and equilibration with aqueous solution to derive a solubility. The first approach relies on a non-equilibrium process and interpreting the experimental distribution coefficients is difficult (compare WINLAND, 1969; KATZ, 1973; MUCCI and MORSE, 1983). The second approach requires long temperature extrapolations (LERMAN, 1965). Recent work has emphasized the third approach (PLUMMER and MACKENZIE, 1974; WALTER and MORSE, 1984; BISCHOFF *et al.*, 1987; BUSENBERG and PLUMMER, 1989).

Equilibrating a high-magnesium calcite with an aqueous solution is experimentally difficult because the desired equilibrium state is generally metastable with respect to the solubility of low-magnesium calcite. Early investigators such as CHAVE *et al.* (1962) and CHAVE and SCHMALZ (1966) assumed that the steady-state pH they observed could be interpreted in terms of relative stability or solubility. In contrast, upon dissolving high-magnesium calcites in water at fugacities of CO<sub>2</sub> between 0.32 and 100 kPa, PLUMMER and MACKENZIE (1974), WALTER and MORSE (1984) and BISCHOFF *et al.* (1987) all initially observed congruent dissolution, soon followed by a different reaction, precipitation of low-magnesium calcite. These observations led them to conclude that previously reported steady-state pH values were misleading and could not be translated into thermochemical properties. To interpret their data in terms of equilibrium, they had to *extrapolate the dissolution kinetics* to an estimated equilibrium

state. Using the subset of data corresponding to congruent dissolution, they applied an empirical linear extrapolation of solution pH against (reaction time)<sup>-1/2</sup>.

The latter procedure was originally introduced by GARRELS *et al.* (1960) as a technique which, if valid, would help determine the stability of carbonate minerals that had not yet been synthesized at room temperature and pressure. The key assumption, that the asymptotic variation of pH near its equilibrium value is well represented by a time<sup>-1/2</sup> function, lacks theoretical justification and is not self-consistent. If we use a similar extrapolation for other solution parameters such as the Ca or Mg concentrations, we obtain markedly different results for the estimated equilibrium state (LAFON, 1978). The pH extrapolation predicts an empirical order for calcite dissolution kinetics which is not compatible with that measured by PLUMMER and WIGLEY (1976). Although it leads to the correct value for the equilibrium of calcite with one atmosphere of CO<sub>2</sub> (GARRELS *et al.*, 1960; PLUMMER and MACKENZIE, 1974; BISCHOFF *et al.*, 1987), it also predicts a clearly erroneous stability for dolomite. In summary, extrapolation of solution pH against (reaction time)<sup>-1/2</sup> has no fundamental justification and should be considered unreliable.

Very recently, BUSENBERG and PLUMMER (1989) have used another experimental technique to inhibit the precipitation of unwanted low-magnesium phases. They added small concentrations of orthophosphate to initial dissolution runs of high-magnesium calcites and found that they could obtain reproducible congruent dissolution leading to well-defined steady-states and ion activity products. Orthophosphate irreversibly forms a strongly chemisorbed surface complex with Ca in calcite and similar minerals and it is not yet clear that the results of BUSENBERG and PLUMMER (1989) characterize the original magnesian calcites rather than the behavior of surfaces modified by their phosphate treatment.

For a magnesian calcite with a given composition, stability estimates based on pH extrapolations obtained by different investigators often conflict (compare results of PLUMMER and MACKENZIE, 1974; WALTER and MORSE, 1984; and BISCHOFF *et al.*, 1987). These discrepancies have been ascribed in part to differing sample treatments such as damage caused by grinding (WALTER and MORSE, 1984). Another source of uncertainty derives from the fact that biogenic materials have compositions and crystal structures which are subtly different from inorganic magnesian calcites of the same magnesium content (BISCHOFF *et al.*, 1983; BISCH-

OFF *et al.*, 1985; BUSENBERG and PLUMMER, 1989). Finally, the lack of consistency among extrapolations of differing chemical parameters against (reaction time)<sup>-1/2</sup> suggests that results from different investigators may not be directly comparable.

This report describes an experimental technique which allows an aqueous solution to reach equilibrium with magnesian calcite from both under and supersaturation, yielding a reversed solubility. This technique avoids the precipitation of low-magnesium phases and provides some measure of control on metastable supersaturation states by carefully controlling the following three experimental parameters.

1. Use of low CO<sub>2</sub> fugacity (comparable to that of air) leads to relatively small departures from equilibrium with low-magnesium calcite and with the high-magnesium calcite of interest.
2. A stirring effect, which inhibits precipitation from slightly supersaturated solutions, allows the persistence of metastably supersaturated states for extended periods.
3. Creation of high-energy dissolution sites by experimental abrasion of the solids allows attaining supersaturated states *via* congruent dissolution.

The technique has been successfully used to measure the reversed equilibrium solubilities of several magnesian calcites and is described in detail. The solubility and free energy of formation of a high-magnesium calcite containing 11.6 mol percent MgCO<sub>3</sub> are reported.

## EXPERIMENTAL METHODS

### Materials

The magnesian calcite studied here consisted of interambulacral plates of the recent sea urchin *Sphaerechinus granularis* from the Gulf of Corinth (Greece) kindly supplied by Dr. D. K. Richter, Geologisches Institut, Ruhr-Universität Bochum. This material had previously been found to yield very sharp X-ray powder diffraction peaks, suggesting a single phase of well-defined composition. Sizeable fragments were gently broken by hand and treated with 30% H<sub>2</sub>O<sub>2</sub> to remove reactive organic matter, then rinsed in distilled water and dried. No ultrasonication or annealing was necessary as the material had not been crushed or strained (contrast WALTER and MORSE, 1984 and BISCHOFF *et al.*, 1987). Inspection by S.E.M. confirmed that no impurities were present and that there was no significant difference between the initial material and what remained after the experiment. X-ray powder diffraction spectra with a fluorite internal standard, obtained before and after the experiment, showed no significant change due to the reactions (Table 1). A structure refinement yielded hexagonal cell parameter values of:  $a = 0.4947(2)$  nm and  $c = 1.6850(7)$  nm indicating a composition between 10 and 13 mol percent MgCO<sub>3</sub> if we use the data and the calibration curves of BISCHOFF *et al.* (1983) for synthetic magnesian calcite. A similar com-

Table 1. *d*-spacings of crystallographic planes in *Sphaerechinus granularis*. Filtered Cu K $\alpha$  radiation, fluorite internal standard

<i>hk.l</i>	<i>d</i> before reaction	<i>d</i> after reaction	Average
10.4	0.3006 nm	0.3004 nm	0.3005 nm
11.0	0.2473	0.2473	0.2473
11.3	0.2266	0.2267	0.22665
	0.2260	0.2262	0.2261
20.2	0.2071	n.a.	0.2071
10.8	0.1889	0.1890	0.1889
$a_0 = 0.4947(2)$ nm		$c_0 = 1.6850(7)$ nm	

Estimated composition:  $11.5 \pm 1.5$  percent MgCO<sub>3</sub>.

position with greater uncertainty is indicated for biogenic samples. The krypton B.E.T. surface area was determined to be  $0.11 \text{ m}^2 \text{ g}^{-1}$ .

The initial aqueous solution was deionized distilled water saturated with an analyzed commercial gas mixture certified to contain 377 parts per million by volume of CO<sub>2</sub> (complement N<sub>2</sub>). The gas composition was checked by precision pH measurements in standard bicarbonate solutions equilibrated with the gas mixture, and was found to be correct within analytical uncertainty.

#### Experimental apparatus

Experiments were conducted in a jacketed 500 cm<sup>3</sup> Pyrex reaction vessel maintained at  $25.0 \pm 0.1^\circ\text{C}$  by a circulating Haake water bath and pump. Temperature was monitored with a precision mercury-in-glass thermometer. The vessel was tightly covered by a Plexiglass plate with holes for sampling, pH electrodes when necessary, thermometer and gas inlet and outlet. In preliminary experiments, it became apparent that stagnant solution in a standard glass frit bubbler could easily become supersaturated with calcite and lead to precipitation of an unwanted phase. To avoid this problem, gas was introduced by means of a Pasteur pipette where precipitation did not take place. Gas was presaturated with distilled water at reaction temperature before entering the reaction vessel to avoid excessive evaporation. To obtain accurate values of the CO<sub>2</sub> partial pressure, room pressure was measured with a precision mercury barometer before each sampling. The overpressure required to circulate the gas was measured with a water differential barometer and found equal to 391 Pa. The solution and solids were stirred with a magnetic stirring bar at a rate previously found sufficient to maintain equilibrium between gas and solution. This procedure resulted in minor abrasion of the solids through the course of the experiment.

#### Analytical techniques

A Radiometer research-grade combination pH electrode and pH meter were used for precision pH measurements at  $25.0^\circ\text{C}$ . Because the desired sample size was small (typically 2 to 5 cm<sup>3</sup>) and the anticipated concentrations low, calcium and magnesium analyses were obtained by atomic absorption spectrometry using an IL 151 spectrometer. Samples and standards were prepared to contain  $1.20 \text{ g l}^{-1}$  lanthanum to suppress ionization in the calcium anal-

yses. Standard calcium and magnesium chloride solutions were prepared gravimetrically by dissolving dry reagent grade calcium carbonate and magnesium metal, respectively, in dilute HCl. These standards were run after every three unknowns to correct for instrumental drift and assess analytical precision. All samples were run in duplicate or triplicate on separate dates. Precision and accuracy are estimated to be generally better than  $\pm 2$  percent, and always better than  $\pm 3$  percent.

After equilibrium had been reached from supersaturation, and at the conclusion of the experiment, 100 cm<sup>3</sup> aliquots of aqueous solution were analyzed for calcium and magnesium separately, using E.D.T.A. titrations at the appropriate pH. The indicators were Calcon for calcium and Eriochrome Black T for magnesium. Alkalinity was determined by a precision Gran titration. Results of these analyses agreed with the corresponding atomic absorption results within  $\pm 1$  percent.

#### Experimental procedure

Distilled deionized water was equilibrated at  $25.0 \pm 0.1^\circ\text{C}$  with the previously described CO<sub>2</sub>/N<sub>2</sub> gas mixture. The gas flow rate had previously been determined sufficient to maintain the system at equilibrium while carbonate dissolution took place. Once gas-liquid equilibrium was attained, as evidenced by negligible pH drift, several plate fragments of *Sphaerechinus granularis* (a total of 180 mg) were introduced. Dissolution was monitored by sampling and analyzing aliquots of the solution. Sampled volumes were replaced by equal volumes of distilled deionized water to prevent excessive decrease of the reacting solution volume. Therefore, the dissolution and precipitation data should not be used for a kinetic analysis, which was not the purpose of this study. Samples were analyzed shortly after being obtained and permitted preliminary identification and analysis of the reactions during the run. When it became clear, based on experience gained from similar runs, that the solution had become supersaturated with the magnesian calcite, stirring was stopped and precipitation was allowed to proceed until equilibrium was reached. Several aliquots were sampled over 8 days to establish an accurate estimate of solubility reached from supersaturation. Next, 200 cm<sup>3</sup> of solution were removed from the reaction vessel and replaced with an equal volume of distilled deionized water, ensuring that the system was now undersaturated with the magnesian calcite. Renewed dissolution was then monitored as above, but care was taken as equilibrium was approached to minimize stirring to the extent necessary to maintain gas-liquid equilibrium. This intermittent stirring then permitted the system to reach equilibrium from undersaturation, and several aliquots of solution were obtained to accurately define this condition.

### EXPERIMENTAL RESULTS AND INTERPRETATION

THORSTENSON and PLUMMER (1977) introduced the concept of "stoichiometric saturation" to describe reactions between aqueous solution and a solid-solution mineral when the latter's composition is held strictly constant. Under this constraint, the only mass transfers allowed are congruent dissolution and congruent precipitation. "Stoichiometric

saturation" defines one of the two possible equilibrium states between a solid-solution mineral and aqueous fluid (THORSTENSON and PLUMMER, 1977; LAFON, 1978) and, when demonstrated in practice, provides the only unambiguous experimental evidence for equilibrium between the phases.

The concept of "stoichiometric saturation" was originally formed to rationalize the interpretation of initial dissolution data sets, the "congruent dissolution stages" observed by PLUMMER and MACKENZIE (1974). It offered a theoretical framework for the use of empirical pH extrapolations and for the meaning of the free energy estimates derived from these extrapolations. The present work reports the first experimental verification of the validity of "stoichiometric saturation", covering all the congruent reactions between aqueous fluid and a biogenic magnesian calcite: dissolution, precipitation and equilibrium. To describe how experimental conditions vary with reaction time, it is convenient to show the variation of the relative super- or undersaturation with respect to the reacting material, expressed by the logarithm of the ratio of ion activity product to equilibrium constant (Fig. 1). In a first stage, we observe congruent dissolution of the magnesian calcite. Because this fragile material is abraded during the experiment, release of Ca and Mg to the fluid persists (presumably from high-energy damage sites) even at concentrations higher than those of the final equilibrium state, as shown by ion activity products greater than the equilibrium constant. In a second stage, we observe concomitant dissolution (at high-energy sites) and precipitation (at low energy sites), which can be manipulated to

reach equilibrium from supersaturation (Fig. 1a). Finally, renewed congruent dissolution following dilution permits reaching equilibrium again, this time from undersaturation (Fig. 1b). The three stages of this experiment are discussed below. Experimental analyses are reported in Appendix 1.

#### Congruent dissolution

The initial reaction of CO<sub>2</sub>-charged water with the magnesian calcite leads to release of calcium and magnesium to the aqueous solution in a constant mol ratio. Data for the first twenty solution samples (representing a reaction time of about 118 hours) are shown in Fig. 2 and accurately define the composition of the dissolving phase to be: 11.6 mol percent MgCO<sub>3</sub>. The dissolution line in Fig. 2 was obtained from a least squares fit of the calcium and magnesium concentrations forced to pass through the origin. The value of 11.6 percent is in good accord with the estimate of approximately 11.5 percent derived from the X-ray diffraction data, and with semi-quantitative E.D.S. analyses. For the aqueous sample with the highest Ca and Mg concentrations, more than 27 percent of the initial solid has been dissolved. Therefore, we are observing congruent dissolution of the bulk solid, one of the requirements of "stoichiometric saturation." Congruent dissolution has also been reported in other investigations (PLUMMER and MACKENZIE, 1974; WALTER and MORSE, 1984; BISCHOFF *et al.*, 1987) but has always been restricted to the initial stage of the reaction because precipitation of low-magnesium calcite soon caused the overall mass transfer

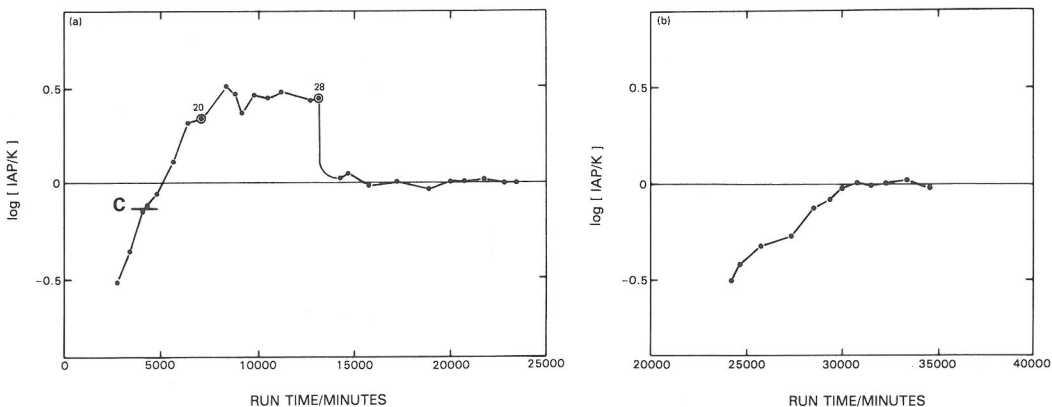


FIG. 1. Saturation state of the aqueous solution during the experiment. The saturation state is expressed by the logarithm of the ratio of ion activity product for magnesian calcite to the equilibrium product; positive values denote supersaturation, negative values undersaturation and zero represents equilibrium. (a) Congruent dissolution and precipitation followed by equilibrium; C denotes equilibrium with respect to pure calcite; samples No. 20 and No. 28 are identified (see discussion in text). (b) Redissolution following dilution with distilled water.

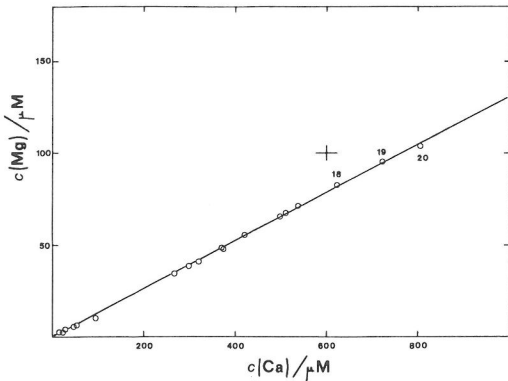


FIG. 2. Congruent dissolution of *Sphaerechinus granularis*. The dissolution line is a least squares fit to the concentration data forced to pass through the origin. Concentrations are micromolar at  $22.5 \pm 1^\circ\text{C}$ . The error bars illustrate a  $\pm 3$  percent error at typical concentrations near equilibrium.

to become incongruent. It is important to note that the calcium concentration in the present congruent dissolution process becomes significantly greater than that at equilibrium with pure calcite (condition denoted by point C on Fig. 1a) while there is no indication of the precipitation of this phase as long as the solution is sufficiently stirred. I interpret this observation as representing metastable supersaturation caused by Mg poisoning of low-magnesium calcite nuclei, and the absence of pre-existing low-energy growth sites for calcite such as could be provided by calcite seeds, together with precipitation inhibition due to a stirring effect. This interpretation is discussed below at greater length in a separate section.

#### Congruent dissolution and precipitation

After approximately 118 hours of reaction, the behavior of the solution chemistry changes (Fig. 1a and Fig. 3, samples No. 21 to 28). We now observe parallel increases and decreases of the calcium and magnesium concentrations which continue to obey the congruent reaction condition. It is particularly important to note that the calcium and magnesium concentrations cluster closely about the congruent dissolution line previously defined by the data in Fig. 2. This is evidence for concomitant and competing dissolution and precipitation of a composition identical to that of the bulk solid. While the variation of ion activity product vs. time for samples No. 21 to 28 could easily be interpreted as evidence for equilibrium, this would be a significant error as shown experimentally below. The solution is supersaturated with magnesian calcite, which permits

congruent precipitation because growth on the pre-existing mineral surface can take place at low supersaturation. However, continued dissolution is still possible as a result of mechanical abrasion of the sea urchin plates. Continuous production of fractures probably creates high energy dissolution sites which permit release of calcium and magnesium to the solution even though its bulk composition is supersaturated with respect to the bulk solid.

#### Congruent precipitation and equilibrium solubility from supersaturation

To test the hypothesis that the aqueous solution was supersaturated with the magnesian calcite, stirring was stopped, which had two distinct consequences: first, it stopped creation of high-energy dissolution sites through abrasion and allowed precipitation to predominate; and second, it permitted precipitation to reach equilibrium because stirring is known to inhibit carbonate precipitation in slightly supersaturated Ca-Mg solutions (L. A. HARDIE, personal communication). Control of this effect has been used successfully in the past to obtain homogeneous partition coefficients between chloride brines and carbonate solid solutions (FÜCHTBAUER and HARDIE, 1976, 1980).

After withdrawing aliquot No. 28, stirring was stopped and the solution was allowed to reach equilibrium over a period of about 7 days (samples No. 29 to 38). Previous tests of this procedure had shown that, once stirring has stopped, precipitation occurs

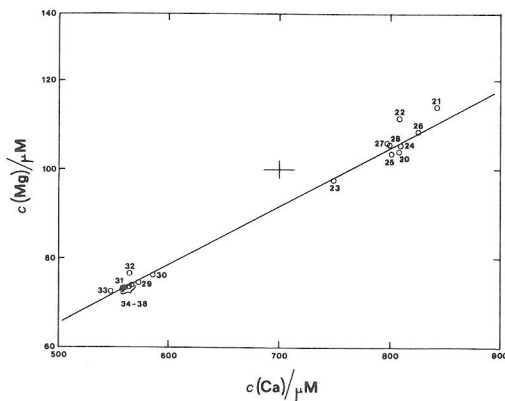


FIG. 3. Congruent dissolution and precipitation of  $\text{Mg}_{0.116}\text{Ca}_{0.884}\text{CO}_3$ . Note that the reaction line is taken from data in Fig. 1 and is completely independent of the data in this plot. Equilibrium from supersaturation is represented by samples No 34 through 38. Error bars represent  $\pm 3$  percent. The scale is slightly different from that in Fig. 2.

over a time scale of minutes and slows to a very low rate after about 15 minutes. The additional reaction time served to ensure that the system would be near equilibrium. Carbonate precipitation releases dissolved  $\text{CO}_2$  to the aqueous solution and upsets the previously established equilibrium between liquid and gas. In the absence of stirring, re-establishing this equilibrium requires an extended period of time because the transfer of  $\text{CO}_2$  across the gas-liquid boundary is slow and inefficient. To ensure that equilibrium was reached, several liquid samples were obtained over a period of 171 hours. The equilibrium solubility reached from supersaturation is reported in Table 2 and represents the average of samples No. 34 through 38, all of which are very close to equilibrium (Fig. 1a). Note that the ion activity product one could derive from samples No. 21 to 28 (which could be thought to represent near equilibrium steady-state) is about three times greater (0.5 log units) than that of the actual equilibrium state. Accuracy of the equilibrium concentrations is estimated to be better than  $\pm 1$  percent.

#### Redissolution and equilibrium from undersaturation

The preceding experimental procedure allowed attainment of equilibrium from supersaturation. To verify that this solubility was in fact correct, it was desirable to reverse the process and reach equilibrium from undersaturation. To this end, 200  $\text{cm}^3$  of aqueous solution were removed from the reaction vessel and replaced with an equal volume of distilled deionized water. This dilution immediately reduced the calcium and magnesium concentrations by two fifths and brought the system to a state of marked undersaturation with respect to the magnesian calcite. To avoid creating fresh fractures and abrasions, stirring was then limited to the strict minimum required to maintain equilibrium between gaseous and dissolved  $\text{CO}_2$ , which resulted in markedly slower dissolution than at the beginning of the experiment (compare Fig. 1a and Fig. 1b). The renewed dissolution of magnesian calcite was followed as before by sampling and analyzing the aqueous solution for calcium and magnesium over a period of 224 hours. These data are shown in Fig. 4, and their tight clustering about the dissolution line defined at the beginning of the experiment again demonstrates congruent dissolution of a composition identical to that of the bulk solid. The reaction slowed considerably as equilibrium was approached. After successive samples no longer showed a monotonic increase in calcium and magnesium

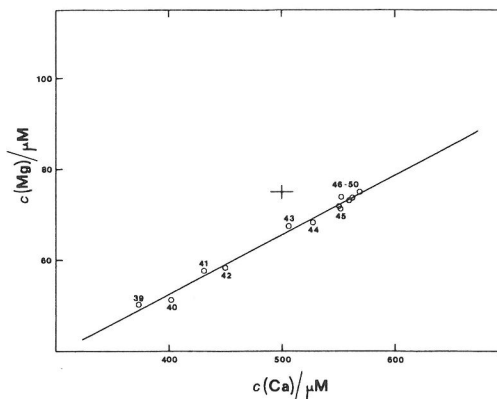


FIG. 4. Congruent redissolution of *Sphaerechinus granularis* and a precipitate of the same composition. Note that the reaction line is taken from data in Fig. 1 and is completely independent of the data in this plot. Equilibrium from undersaturation is represented by samples No. 46 through 50. Error bars represent  $\pm 3$  percent. The scale is slightly different from those in Figs. 2 and 3.

concentrations, the equilibrium solubility from undersaturation was determined using the average of samples No. 46 through 50 (Table 2). This value is within analytical error of the solubility obtained from supersaturation.

#### Discussion of the present experimental technique and comparison with previous work

In marked contrast to previously reported dissolution experiments, this work has succeeded in experimentally maintaining "stoichiometric saturation" throughout, without modifying the magnesian calcite. Even though the aqueous solution becomes supersaturated first with pure calcite, then with the reacting magnesian calcite, all mass transfers between solution and solids remain congruent during dissolution, precipitation, and at equilibrium. Variation of the composition of the aqueous

Table 2. Solubility of *Sphaerechinus granularis*, a magnesian calcite containing 11.6 mol percent magnesium carbonate, at equilibrium with 36.81 Pa of  $\text{CO}_2$

	[Ca]/ $\mu\text{M}$	[Mg]/ $\mu\text{M}$
From supersaturation, average of five samples	562	73.7
From undersaturation, average of five samples	559	73.5
Grand Average	560.5	73.6

Concentrations are micromolar at  $22.5 \pm 1^\circ\text{C}$ , the laboratory temperature, slightly lower than the experimental temperature of  $25.0^\circ\text{C}$ .

solution defines three distinct experimental regimes, all consistent with congruent reaction of the bulk solid. First, the high-magnesium calcite dissolves, eventually yielding calcium and magnesium concentrations in excess of the equilibrium solubility of low-magnesium calcite and of that of the reacting solid. Second, once the aqueous solution has reached a large enough supersaturation (of the order of 3 for CO<sub>2</sub> contents similar to that of air), congruent precipitation begins and competes with dissolution. Third, stopping the stirring action lifts the inhibition to magnesian calcite precipitation and stops the formation of high-energy dissolution sites, which allows precipitation of magnesian calcite to proceed until equilibrium is reached. Equilibrium solubility is verified by letting the solid react with diluted solution while restricting stirring to the absolute minimum. Through appropriate manipulation of stirring and of CO<sub>2</sub> fugacity, equilibrium solubilities can be obtained from both supersaturation and undersaturation. Both determinations agree within better than 1 percent, which is within analytical error.

While the results presented above apply to one experiment and one biogenic magnesian calcite, I have successfully conducted over ten similar long-term experiments with a variety of materials. These results will be published elsewhere. The experimental techniques described here can be used systematically and reproducibly to control the saturation state of solutions. They yield reversed equilibrium solubilities for high-magnesium calcites without requiring modification of the carbonate surfaces and without relying on empirical extrapolations of partial dissolution kinetics. In contrast, BUSENBERG and PLUMMER (1985, 1989) had to expose their materials to relatively high concentrations of orthophosphate (100  $\mu$ M) to suppress or retard the precipitation of unwanted phases, and this precluded precipitation of the magnesian calcites as well. Calcite surfaces exposed to such high concentrations of orthophosphate near equilibrium are covered by a complete monolayer of calcium phosphate and are not expected to behave identically to the original carbonate. I have discussed above the lack of foundation and the unreliability of empirical kinetic extrapolations against (time)<sup>-1/2</sup>, used in earlier works by PLUMMER and MACKENZIE (1974), WALTER and MORSE (1984) and BISCHOFF *et al.* (1987). In summary, I have obtained for the first time the composition of an aqueous solution unequivocally at equilibrium with a high-magnesium calcite.

Some concern might be raised by the simultaneous occurrence of precipitation and dissolution

(R. J. SPENCER, personal communication). While the solution analytical data clearly demonstrate that the precipitated, dissolved, and original carbonate all have the same composition, it is conceivable if highly unlikely that the reversed solubility may apply to the freshly precipitated material only and not to *Sphaerechinus granularis*. The solubility of this material could be different from that of the sea urchin because of differing degrees of structural disorder and defect densities, as has been suggested by BISCHOFF *et al.* (1987). To address this issue, Fig. 5 shows S.E.M. photographs of the experimental material as received and after the end of the experiment. Under close inspection, the reacted material (Figs. 5.2 and 5.4) appears to consist solely of partially dissolved sea urchin plates, indicating that the freshly precipitated magnesian calcite was entirely redissolved in the last stage of the experiment. Therefore, the equilibrium reached from undersaturation applied strictly to the original biogenic material, while the equilibrium reached from supersaturation applied to a mixture of the biogenic material and of fresh precipitate. This indicates that there is no significant free energy difference between the two, an important observation developed further in the section on free energies of formation.

The new experimental technique introduced here has considerable potential for the thermodynamic characterization of high-magnesium calcites, and perhaps, more generally, for the study of other metastable ionic solid solutions. Other investigators should reproduce its results and verify its applicability, using a variety of single phase magnesian calcites. The three key experimental variables which permit control of the experiments are discussed below.

First, the concentration of dissolved CO<sub>2</sub> (equivalently, the CO<sub>2</sub> fugacity) plays a crucial role. Low concentrations of dissolved CO<sub>2</sub> (similar to that at equilibrium with air) allow solutions to remain supersaturated for long periods of time in the presence of slight surface poisoning effects, provided that the supersaturation does not exceed a threshold value. In the writer's experience, metastable supersaturation with respect to calcite and magnesian calcite can be maintained indefinitely at 25°C with air-like fugacities of CO<sub>2</sub> so long as the supersaturation remains below 2, corresponding to:  $\log [IAP/K] \leq 0.3$ . This observation has not been reported by other workers, which suggests that CO<sub>2</sub> fugacities of 0.32 kPa and greater probably accelerate the precipitation of carbonate minerals. Most earlier dissolution experiments using magnesian calcites have been conducted at fugacities of CO<sub>2</sub> markedly higher than that of air, probably because this choice

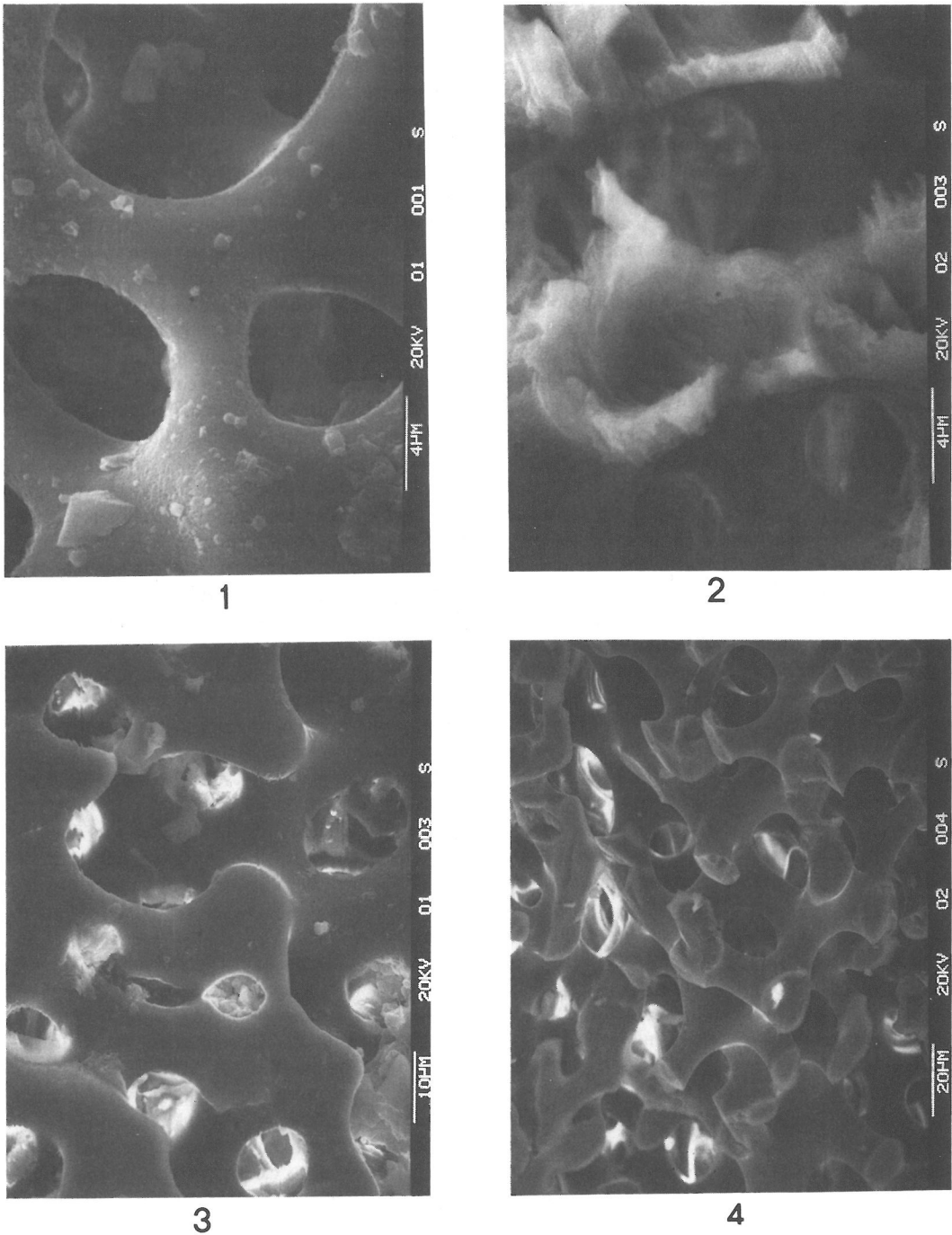


FIG. 5. Scanning electron microscope photographs of two plate fragments of *Sphaerechinus granularis*. 1. unreacted material, plan view at 5,000 $\times$  magnification; the small particles have the same composition as the bulk. 2. after reaction, plan view at 5,000 $\times$  magnification; note the extensive exfoliation and dissolution, attributed to combined mechanical damage and normal dissolution. 3. side view of unreacted material at 2,000 $\times$  magnification. 4. after reaction, side view at 1,000 $\times$  magnification. Note that the reacted samples show no evidence of retaining freshly precipitated magnesian calcite.



also significantly accelerates dissolution and shortens experimental runs. It is likely that the common precipitation of low magnesium calcite after a short congruent dissolution phase is in part directly related to the use of high  $\text{CO}_2$  fugacities.

Second, a proper match of substrate or seed composition to that of the potential precipitate is essential if one wants to obtain precipitation under the constraint of "stoichiometric saturation." I attempted to precipitate magnesian calcites congruently from bicarbonate solutions with a magnesium to calcium ratio of 0.10, using pure calcite as seeds. These attempts all failed, yielding only low magnesium calcite overgrowths in agreement with the observations of MUCCI and MORSE (1983). Growth of a different phase on pure calcite has to overcome an interfacial free energy barrier due to strains resulting from compositional and structural mismatch between two different lattices. Congruent precipitation seems to be greatly favored by the absence of this barrier and can presumably take place at lower supersaturation.

Third, control of stirring can be exploited to maintain the solution in a metastable state. Stirring performs three different functions in these experiments.

1. Stirring is necessary to equilibrate gas and aqueous solution faster than  $\text{CO}_2$  is consumed or produced. This function is particularly important during the early part of the experiment, at low concentrations of bicarbonate, when relatively large amounts of  $\text{CO}_2$  must be efficiently transferred from the gas to the liquid. Equilibration becomes much easier as saturation with the solids is approached, and can be effected with intermittent or lower energy stirring.

2. Stirring is also responsible for the mechanical abrasion of the solids. This effect has been documented for carbonate minerals by a number of investigators (R. A. BERNER, personal communication; MORSE and BERNER, 1972). Fig. 5 demonstrates the effects of abrasion on *Sphaerechinus granularis* fragments. Figs. 5.1 and 5.2 are views of the flat surface of sea urchin plate fragments before and after reaction, respectively. The flat surface which has been repeatedly exposed to shocks from the stirring bar has been the site of extensive dissolution (Fig. 5.2). By contrast, Figs. 5.3 and 5.4 are side views of the same plate fragments. While some dissolution can be observed in Fig. 5.4, it does not display the extensive exfoliation and fissuring of Fig. 5.2. These observations support the hypothesis that mechanical damage due to stirring enhances dissolution at some locations of the sample.

The amount of agitation necessary to maintain gas-liquid equilibrium readily leads to steady formation of damaged sites on crystals and, if not recognized, can lead to incorrect interpretation of experimental data. Spuriously high steady-state concentrations such as the ones observed in samples No. 21 to 28 of this work could easily have been interpreted as evidence for equilibrium. Empirical extrapolation of dissolution kinetics obtained while stirring is highly uncertain because there is no independent way to quantify abrasion damage. Discrepancies between results obtained by extrapolating  $\text{pH vs. (time)}^{-1/2}$  may in part be attributable to these effects. On the other hand, a beneficial result of abrasion by stirring is that supersaturated states can be reached in a *dissolution* experiment, permitting reversal of reaction between solids and aqueous solutions.

3. Finally, stirring appears to inhibit homogeneous nucleation and growth in calcium-magnesium-bicarbonate-carbonate solutions. This phenomenon is what permits control of the experiment when solutions are supersaturated. FÜCHTBAUER and HARDIE (1976, 1980) exploited a similar effect to obtain reproducible homogeneous partition coefficients for magnesium between chloride solutions and magnesian calcites. Control of precipitation using stirring is crucial to obtaining reversed equilibrium solubilities of magnesian calcite and could perhaps also be used more generally in the study of other metastable ionic solid solutions. The experimental procedures described here are systematically reproducible with a variety of samples and can be widely used. However, it would be desirable to progress beyond a strictly empirical application of stirring control and to develop a more fundamental understanding of the interaction between fluid flow characteristics and precipitation kinetics. In the next section, I present a set of hypotheses which may serve as the sketch for a model of precipitation in calcium-magnesium-bicarbonate-carbonate solutions.

#### *Toward a model for the precipitation mechanisms*

A key observation is that precipitates from solutions containing calcium, magnesium, bicarbonate, carbonate and  $\text{CO}_2$  can vary greatly according as the solution is stirred or not. This suggests that there are chemically significant mechanical interactions between ions and solute molecules or aggregates, and with water molecules. One systematic set of hypotheses explaining presently known facts follows.

1. In supersaturated solutions, aggregates or

protonuclei for potential precipitates form from cations and anions in an electrically balanced configuration, most likely as aggregates of  $\text{CaCO}_3^0$  and  $\text{MgCO}_3^0$  ion-pairs. They are hydrated, with two or more  $\text{H}_2\text{O}$  per cation (solvent-bridged ion-pairs) and the  $\text{H}_2\text{O}$  molecules are fairly strongly bound to Mg, less so to Ca. I assume the formation of ion-pairs and aggregates is rapid so that they are in approximate equilibrium with the monomeric ions; consequently, the Mg/Ca mol ratio of aggregates is equal to that of the bulk solution multiplied by the ratio of the association constants (about 0.5 at  $25^\circ\text{C}$ ).

2. In many solutions of geochemical interest, such as seawater, the Mg/Ca ratio is high and the protonuclei also have a high Mg/Ca (for seawater, about 2.5). Potential precipitates with the same bulk composition are extremely unstable, much more so than commonly encountered natural solid-solutions. Precipitates that actually form will have a very much lower Mg/Ca ratio. This requires two important changes which act as kinetic barriers: loss of most of the magnesium so that the protonuclei reach a bulk composition which can be the precursor for a solid-solution, and loss of almost all the hydration water prior to growth of an anhydrous phase. Obvious modifications to the second requirement apply for precipitation of hydrous phases such as the hydrocalcites, hydromagnesite, nesquehonite, etc.

3. In the absence of strong mechanical interactions with their surroundings, free energy differences and statistical fluctuations will drive the compositions of aggregates toward much lower magnesium and  $\text{H}_2\text{O}$  contents, until the bulk composition of a nucleus is very similar to that of a potential precipitate (e.g. a magnesian calcite) and the nucleus can grow to form a macroscopic precipitate. However, this is probably a slow process (time scale on the order of milliseconds to seconds) as indicated by slow precipitation kinetics in unstirred solutions. For dolomite which requires the additional ordering of calcium and magnesium in separate planes, the time scale is of the order of days to months at higher than ambient temperatures.

4. In stirred solutions, hydrodynamic shear causes strong mechanical interactions between aggregates and water molecules. These encounters favor frequent splitting and erosion of protonuclei in addition to normal statistical fluctuations and their lifetime in stirred solutions is much shorter than in unstirred ones. While estimates of the lifetimes of aggregates are not available, I envisage that mechanical interactions in stirred solutions at low supersaturations make these lifetimes very short rel-

ative to the time necessary for cleaning the aggregates. As a result, aggregates split before they can reach a more stable composition and grow.

5. Crystal growth takes place on seeds and preexisting surfaces by adsorption of nuclei. If the seed has the same composition and structure as the potential precipitate, the activation energy is probably very small and the nucleus can consist of a small number of cations and anions. If, however, the potential precipitate has a different structure or composition, the interfacial mismatch and strain require a higher activation energy and a much larger nucleus. Inhibition of low-magnesium calcite growth in solutions containing significant magnesium ion concentrations is due to this effect.

This set of hypotheses appears to account for all the empirical observations which have served to develop the experimental technique used here. They have not yet been experimentally verified because the number and type of experiments required are beyond the scope of this research. Investigations would have to draw on modern techniques of physical chemistry and chemical physics. Some of the crucial parameters are the times required for magnesium loss and dehydration in aggregates. These times are likely to depend on the size and composition of an aggregate which are also highly time-dependent. Other crucial parameters are the size distribution of aggregates and their statistical evolution (composition and size) as function of time given a bulk supersaturation, temperature and concentration of  $\text{CO}_2$ . Experiments to quantify the properties of aggregates could measure the fluctuations and time dependence of variables such as the electrical conductivity, the viscosity and the ultrasound absorption of supersaturated stirred and unstirred solutions. In addition, the n.m.r. relaxation time of  $^{13}\text{C}$  in the rotating frame ( $T_{1\rho}$ ) could help directly to measure the number of C atoms in aggregates and relate it to their bulk concentration. Measurements of viscosity and conductivity as functions of shear would throw light on the relations between solution flow properties and precipitation mechanisms. Finally, it would be desirable to study precipitation kinetics in a rotating disc apparatus where flow properties are particularly well understood.

#### FREE ENERGY OF FORMATION OF MAGNESIAN CALCITE

The solubility obtained above can be used to calculate the standard free energy of formation for the test of *Sphaerechinus granularis*, a magnesian calcite containing 11.6 mol percent  $\text{MgCO}_3$ . This re-

quires converting the measured concentrations into activities. There are two generally accepted ways of deriving free energies from solubility data. The first relies on building a chemical model where we choose *a priori* simple expressions for the activity coefficients of individual species such as ions and molecules, and we represent ion-ion interactions by assuming the presence of well-defined complex species such as ion-pairs (see, for example, PLUMMER and BUSENBERG, 1982). The other approach uses empirical models for the mean activity coefficients of major dissolved components, usually based on a leading Debye-Hückel term followed by a virial expansion (*e.g.*, ROBINSON and STOKES, 1965; PITZER and SILVESTER, 1976). In the present case, the major solutes are calcium and magnesium bicarbonate, and there are also very minor concentrations of dissolved calcium and magnesium carbonate and CO<sub>2</sub>. While both approaches are self-consistent, they do not necessarily yield the same value for an activity product upon extrapolation to infinite dilution. For example, the activity product of calcium times carbonate for pure calcite *calculated from the same solubility data* is:  $3.31 \times 10^{-9}$  using the ion-pairing model (CHRIST *et al.*, 1974; PLUMMER and BUSENBERG, 1982), but  $3.98 \times 10^{-9}$  using the mean activity coefficient of Ca(HCO<sub>3</sub>)<sub>2</sub> (LAFON, 1975; HARVIE, 1982; HARVIE *et al.*, 1984). The extrapolation using mean activity coefficients rests on fewer, simpler and more direct assumptions, which recommends its choice in this work. In the following, the mean activity coefficients of Ca(HCO<sub>3</sub>)<sub>2</sub> and Mg(HCO<sub>3</sub>)<sub>2</sub> are given by the expression:

$$\log \gamma_{\pm} = -2 \times 0.5094 \sqrt{I} / (1 + 1.5\sqrt{I}) + 0.5536I \quad (1)$$

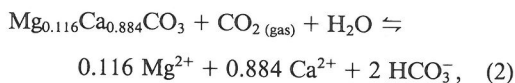
where  $I$  denotes the formal ionic strength of the solution on the molal scale. This expression fits the experimental solubilities of calcite in calcium bicarbonate solutions at 25°C up to an ionic strength of 0.03 molal with a standard deviation of residuals of 0.023 log units and affords a good estimate of the thermodynamic properties of dilute alkaline earth bicarbonate solutions (LAFON, 1975). For the standard state at 25°C and 100 kPa, it yields a solubility product for pure calcite of:

$$K_c = \gamma_{\pm}^2 [\text{Ca}][\text{HCO}_3^-]^2 / (f_{\text{CO}_2} a_{\text{H}_2\text{O}}) = 1.27 \times 10^{-6}, \quad \text{or} \quad \log K_c = -5.894,$$

corresponding to a standard free energy of formation of  $-1,129.27 \text{ kJ mol}^{-1}$ .

The average solubility of Mg<sub>0.116</sub>Ca<sub>0.884</sub>CO<sub>3</sub> at

equilibrium with 36.81 Pa of CO<sub>2</sub> is 560.5 μM calcium and 73.6 μM magnesium (Table 2), corresponding to 561.8 and 73.8 μm on the molal scale, respectively. To obtain an activity product, we can write the reaction as:



with the equilibrium constant:

$$K_{mc} = \gamma_{\pm}^2 [\text{HCO}_3^-]^2 [\text{Mg}]^{0.116} [\text{Ca}]^{0.884} / (f_{\text{CO}_2} a_{\text{H}_2\text{O}}), \quad (3)$$

where brackets denote molal concentrations,  $f$  the fugacity and  $a$  the activity of the subscripted species. To obtain the concentrations of the bicarbonate components, the solubilities reported above must be corrected for the presence of trace amounts of carbonate ion and of the CaCO<sub>3</sub><sup>0</sup> and MgCO<sub>3</sub><sup>0</sup> ion-pairs. Calculations are based on thermochemical properties for CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> reported by WAGMAN *et al.* (1982) and on the association constants determined by SIEBERT and HOSTETLER (1977) for MgCO<sub>3</sub><sup>0</sup> and by PLUMMER and BUSENBERG (1982) for CaCO<sub>3</sub><sup>0</sup>. At the equilibrium pH of 8.35, the concentration of carbonate is 15 μm, that of CaCO<sub>3</sub><sup>0</sup> 8.9 μm and that of MgCO<sub>3</sub><sup>0</sup> 0.56 μm. The equilibrium bicarbonate concentrations are 540 μm for Ca(HCO<sub>3</sub>)<sub>2</sub> and 71.4 μm for Mg(HCO<sub>3</sub>)<sub>2</sub>. Substituting these values into Equation (3), we obtain:

$$K_{mc} = 0.7564 \times 0.001223^2 \times 0.000540^{0.884} \times 0.0000714^{0.116} / 0.0003681 = 1.31 \times 10^{-6},$$

and  $\log K_{mc} = -5.881$  for the standard state at 25°C and 100 kPa.

The corresponding value for the standard free energy of formation of Mg<sub>0.116</sub>Ca<sub>0.884</sub>CO<sub>3</sub> is  $\Delta G_f^0 = -1,117.75 \text{ kJ mol}^{-1}$ . An error analysis presented in Appendix 2 estimates the uncertainty on this value at:  $\pm 0.10 \text{ kJ mol}^{-1}$ , relative to the free energy of formation of pure calcite reported above ( $-1,129.27 \text{ kJ mol}^{-1}$ ).

#### Comparison with other free energy estimates

The free energies of formation of magnesian calcites are significantly different from that of pure calcite. Most investigators have assumed that this effect is primarily controlled by the magnesium content and that other compositional or structural factors are secondary, if at all significant. Recently, however, BISCHOFF *et al.* (1987) and BUSENBERG and PLUMMER (1985, 1989) have drawn attention to the potential roles of structural disorder and of

trace concentrations of sulfate and sodium. BUSENBERG and PLUMMER (1985) found that trace concentrations of Na and  $\text{SO}_4$  greatly decrease the stability of synthetic calcites. They correlated the levels of impurity concentrations in experimental precipitates with their growth rate from salt solutions containing sodium and sulfate. BISCHOFF *et al.* (1987) reported that magnesian calcites synthesized from  $\text{CaCO}_3$  and  $\text{MgCO}_3$  are more stable than biogenic materials with the same magnesium concentration. They attributed this difference to the greater structural, physical and chemical heterogeneity of biogenic samples but declined to assign the free energy differences ( $0.20$  to  $0.85 \text{ kJ mol}^{-1}$ ) to particular characteristics. BUSENBERG and PLUMMER (1989) now make a major distinction between "Group II" magnesian calcites which have significant defect densities due to trace concentrations of Na,  $\text{SO}_4$  and vacancies and the simpler "Group I" magnesian calcites. They report two markedly different curves for the variation of apparent ion activity product versus magnesium mol fraction, with "Group II" magnesian calcites much more soluble than "Group I" materials.

Explicit consideration of components other than  $\text{CaCO}_3$  and  $\text{MgCO}_3$  raises new and important issues in the interpretation of experimental dissolution data and the relations between ion activity products and the stability of magnesian calcite. While a complete discussion of the thermodynamic consequences is beyond the scope of this paper, the following points are worth noting.

We can choose to consider the congruent dissolution properties of the whole solid, including sodium and sulfate in the ion activity product and using the concept of "stoichiometric saturation" to derive free energies of formation, if we assume that steady-state properties represent near-equilibrium. However, this approach has two major drawbacks. First, dissolution experiments have not led to reversible transfer of sodium and sulfate between solids and liquid because Na and  $\text{SO}_4$  are strongly partitioned into the aqueous solution (BUSENBERG and PLUMMER, 1985 and references therein). All experimental precipitates in dissolution experiments to-date have had insignificant concentrations of sodium and sulfate. Interpretation of steady-states reported by PLUMMER and BUSENBERG (1989) as representing "stoichiometric saturation" appears unwarranted so long as such an asymmetry between dissolution and precipitation exists. Second, the free energies of formation of a complex solid-solution series with at least four end-members cannot easily be used to extract mixing properties for the  $\text{CaCO}_3$  and  $\text{MgCO}_3$  components, or to evaluate the roles

of the sodium and sulfate-bearing components relatively to that of  $\text{MgCO}_3$ . To obtain free energies for the components, we have to know the dependence of the total free energy of formation on component concentrations accurately enough that partial derivatives can be calculated at the composition of interest (DARKEN and GURRY, 1953). This requires that, for each mol fraction of  $\text{MgCO}_3$ , we need the variation of free energy with respect to sodium and sulfate mol fractions, separately. Such data are not available and are not likely to be collected for a considerable time. In summary, if it were necessary to incorporate sodium and sulfate in ion activity products and in free energies of formation, we would still be far from understanding the chemical properties of magnesian calcites.

We can, instead, focus our attention on the ion activity product and the free energy of formation of the idealized magnesian calcite formula with the two components  $\text{CaCO}_3$  and  $\text{MgCO}_3$  only. This is the approach followed by BUSENBERG and PLUMMER (1989) in their discussion of mixing properties and by all previous investigators. The reversed equilibrium demonstrated in the present work provides strong support for using the two-component magnesian calcite formula. The precipitated material must have contained negligible amounts of sodium and sulfate because the concentrations of these impurities in the liquid were very low. Taking as representative the sea urchin analyses reported by BUSENBERG and PLUMMER (1989), I estimate that the solution from which the precipitate formed contained at most about  $22 \mu\text{M}$  sodium and  $9 \mu\text{M}$  sulfate. Such very low concentrations of impurities could not have produced a solid carbonate with significant defects. Because solubilities reached from undersaturation and supersaturation are identical, this work experimentally demonstrates that trace amounts of sodium and sulfate in *Sphaerechinus granularis* did not have a significant effect on its solubility.

If we use the two-component approach to interpret experimental reaction data for magnesian calcites, we are also implicitly stating that the effects of impurities and defects can be separated from the mixing properties of the calcium and magnesium carbonate components. Instead of envisaging a complex multicomponent solid-solution, we represent magnesian calcites as groups of pseudo-binary solutions and let the properties of the end-members account for other components such as sodium, sulfate, vacancies and defects. This approach was taken by BUSENBERG and PLUMMER (1989) who fitted their ion activity products to the  $\text{CaCO}_3$ - $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$  idealized solid-solution. They used

Table 3. Free energies of formation (in kJ mol<sup>-1</sup>) for magnesian calcites with compositions near Ca<sub>0.884</sub>Mg<sub>0.116</sub>CO<sub>3</sub>

Source	Material	MgCO <sub>3</sub> mol fraction	$\Delta G_f^0$	$G_{mc}$	
This work	<i>Sphaerechinus granularis</i>	0.116	-1117.75	-1129.34	
PLUMMER and MACKENZIE (1974)	?	0.069	-1121.98	-1128.88	
	?	0.104	-1119.06	-1129.46	
	?	0.127	-1113.49	-1126.19	
		0.12	-1116.9	-1128.9	
WALTER and MORSE	<i>Clypeaster</i> <i>Tripneustes</i>	0.12	-1116.9	-1128.9	
BISCHOFF <i>et al.</i> (1987)	Synthetic samples	0.08	-1121.8	-1129.8	
		0.10	-1119.6	-1129.6	
		0.101	-1119.6	-1129.7	
		0.125	-1117.0	-1129.5	
		<i>Diadema</i> (spine)	0.07	-1122.3	-1129.3
		<i>Tripneustes</i>	0.109	-1118.0	-1128.9
		<i>Homotrema</i>	0.124	-1116.9	-1129.3
		<i>Diadema</i> (plate)	0.124	-1116.1	-1128.5
		<i>Diadema</i> (plate)	0.128	-1115.7	-1128.5
	BUSENBERG and PLUMMER (1989)	Synthetic samples	0.0753	-1121.7	-1129.2
			0.1068	-1118.2	-1128.8
			0.1467	-1113.8	-1128.5
			0.0900	-1119.9	-1128.9
			0.123	-1116.5	-1128.8
Biogenic samples		0.108	-1118.0	-1128.8	
		0.112	-1116.3	-1127.5	
		0.109	-1117.6	-1128.5	
		0.129	-1115.9	-1128.8	
		0.127	-1118.5	-1131.2	
	0.139	-1114.6	-1128.5		

## Notes:

1. The dissolving phases of PLUMMER and MACKENZIE (1974) had compositions markedly different from the bulk solids and probably do not represent well-defined minerals, but rather mixtures.
2.  $G_{mc} = \Delta G_f^0 - 100x$ , where  $x$  denotes the mol fraction of MgCO<sub>3</sub>.

for the Mg-free end member either pure calcite ("Group I" materials) or a defect-rich, sodium and sulfate bearing calcite ("Group II" materials). In the following discussion of free energies of formation, I follow the binary solid-solution model and assume that the magnesium carbonate concentration is the principal controlling factor.

The standard free energy of formation of magnesian calcite has a steep upward trend with increasing magnesium carbonate mol fraction, which can mask small variations over a limited composition range. While this effect would be best compensated by using free energies of mixing, present uncertainties in the standard free energy of formation of magnesite make this approach inadvisable. A similar result can be obtained if we use an empirical correction to flatten the compositional trend. I use the quantity:  $G_{mc} = \Delta G_f^0 - 100x$  (kJ mol<sup>-1</sup>), where  $x$  denotes the mol fraction of magnesium carbonate in the formula Ca<sub>1-x</sub>Mg<sub>x</sub>CO<sub>3</sub>, to compare estimates from other investigators to the free energy measured in this study. The mol fractions considered here range from 0.06 to 0.15, bracketing the composition of *Sphaerechinus granularis*.

The original free energy estimates of PLUMMER and MACKENZIE (1974), WALTER and MORSE (1984), BISCHOFF *et al.* (1987) and values computed from the ion activity products of BUSENBERG and PLUMMER (1989) are listed in Table 3. The values reported by PLUMMER and MACKENZIE (1974) are probably in error because the compositions interpreted as dissolving congruently were markedly different from the bulk compositions and it is likely that several distinct phases were dissolving simultaneously (LAFON, 1978), which would have made the pH extrapolations invalid. Data from the other references are plotted in Fig. 6. The results for the synthetic samples of BISCHOFF *et al.* (1987) define a consistent trend of lower free energies. The estimates of WALTER and MORSE (1984), BISCHOFF *et al.* (1987) and BUSENBERG and PLUMMER (1989) for impure and/or biogenic samples are much more widely scattered and are, on average, about 0.6 to 0.8 kJ mol<sup>-1</sup> less negative. These two trends correspond to the "Group I" and "Group II" classification of BUSENBERG and PLUMMER (1989). The result of this study is intermediate between the two general trends, and somewhat closer to the estimates

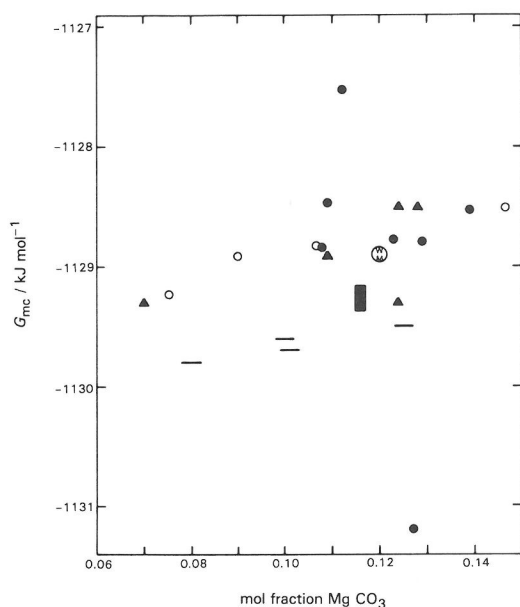


FIG. 6. Free energy of magnesian calcites with compositions near 11.6 mol percent  $\text{MgCO}_3$  plotted against the mol fraction of magnesium carbonate. The quantity;  $G_{mc} = \Delta G_f^0 - 100x$  is used to suppress the upward trend of the free energy of formation with increasing mol concentration of  $\text{MgCO}_3$  (see text). The filled box illustrates results from this work. Other sources are: (M) estimate from WALTER and MORSE (1984); (—) estimates for synthetic samples (BISCHOFF *et al.*, 1987), and ( $\blacktriangle$ ) (filled triangles) estimates for biogenic samples (BISCHOFF *et al.*, 1987); (O) (open circles) synthetic samples from BUSENBERG and PLUMMER (1989), and ( $\bullet$ ) (filled circles) biogenic samples from BUSENBERG and PLUMMER (1989).

of BISCHOFF *et al.* (1987) for their synthetic, more perfect samples.

The clustering of estimated free energies of magnesian calcites along two trends has been interpreted by BUSENBERG and PLUMMER (1989) as characterizing two distinct families of materials. Their "Group I" consists of the simpler magnesian calcites which approach the ideal binary  $\text{CaCO}_3$ - $\text{MgCO}_3$  solid-solution with pure calcite as the Mg-free end-member. "Group II" comprises the more complex, more impure materials, with significant concentrations of sodium and sulfate, structural defects and disorder. The Mg-free end-member of these samples would be an impure, defect-laden calcite with a much less negative free energy of formation. A similar but less far-reaching proposal was advanced by BISCHOFF *et al.* (1987) to explain the systematic difference between their estimates for synthetic and biogenic samples. Given the large uncertainties of kinetic extrapolations and the poor understanding of the effects of phosphate poisoning,

together with the considerable scatter in Fig. 6, a key question remains unanswered. Does the small but systematic difference between the average free energy trends of "Group I" and "Group II" reflect a genuine difference between the true free energies of formation of these materials? Or does it, instead, reflect how structural and compositional variations modify dissolution kinetics, leading to systematically different extrapolated values but not to reliable differences between the equilibrium free energies?

Distinguishing between these alternatives is crucial for reliable equilibrium modeling of magnesian calcites in nature. While the proposed free energy difference between "Group I" and "Group II" materials is numerically small (a fraction of one  $\text{kJ mol}^{-1}$ ), it leads to large differences between the calculated activities of the  $\text{MgCO}_3$  component in the solids because these activities are related to the derivative of total free energy with respect to the  $\text{MgCO}_3$  mol fraction (THORSTENSON and PLUMMER, 1977; BUSENBERG and PLUMMER, 1989). They control important geological parameters such as the equilibrium magnesium-to-calcium ratio of fluids and the relative stabilities of different carbonate mineral phases. As was well shown by BUSENBERG and PLUMMER (1989), their "Group I" and "Group II" magnesian calcites must have markedly different stability ranges and phase relationships. If, however, the two apparent trends of free energies in Fig. 6 correspond to the effects of impurities on dissolution kinetics but not to stability differences, little can be stated at this time regarding equilibrium phase relations because the solubility reported in this work is the only one that unambiguously pertains to a documented equilibrium condition. In this case, previously reported free energy estimates for magnesian calcites would be of little value, serving at best to illustrate the effects of composition, structure and defects on dissolution kinetics.

Because the free energy differences between "Group I" and "Group II" materials are very small, we must have great confidence in extrapolations of dissolution kinetics or in the close approach of steady states to true equilibrium states before we can trust that estimates will resolve two truly distinct populations of magnesian calcites. To the contrary, a strong case can be made that the small differences between the estimated stabilities of "Group I" and "Group II" materials cannot be reliably derived from kinetic extrapolations and from reactions inhibited by phosphate. The free energy estimates obtained from these experiments are extremely sensitive to minor sample variations and differences in sample treatment. WALTER and MORSE (1984) ex-

perimentally demonstrated that cleaning and a mild temperature treatment of their biogenic materials led to marked changes in the extrapolated equilibrium pH. Estimated free energies of "Group II" materials obtained from both pH extrapolations of dissolution kinetics and steady-states with phosphate poisoning are widely scattered at a given mol fraction of  $\text{MgCO}_3$  (see Fig. 6). Both experimental techniques yield data that show poor consistency within a given study and between different investigators. Several inconsistencies remain to be resolved and the following list is not exhaustive.

1. "Group II" does not correspond to a well-defined population of materials because of wide variability in sodium, sulfate and defect concentrations. Although the mol fractions of Na and  $\text{SO}_4$  in "Group II" magnesian calcites are small, their ranges from less than 0.5 percent to nearly 3 percent are large relative to their mean values and clearly show that they cannot be taken as constant. This observation is hardly compatible with defining a pseudo-binary solid-solution and its end-member. We would have to believe that the presence of sodium and sulfate in this concentration range is enough to fix a free energy of formation for the Mg-free end member which does not depend significantly on the concentrations of impurities. In contrast, BUSENBERG and PLUMMER (1985) have reported that increasing the mol fractions of Na or  $\text{SO}_4$  in calcite from 0.5 to 3 percent increases the apparent ion activity product by about 0.1 log unit, which is comparable to the difference between "Group I" and "Group II" materials.

2. Some of the data presented by BUSENBERG and PLUMMER (1989) in support of their interpretation can also support alternative models. For example, steady-state ion activity products for synthetic sodium-containing magnesian calcites (their Table 3) help define the stabilities of "Group II" materials. The same data converted to free energies of formation extrapolate naturally to pure calcite as the Mg-free end member. This observation once again suggests that the distinction between "Group I" and "Group II" may be more apparent than real.

3. Many of the materials used in kinetic extrapolations or phosphate-poisoned dissolution were in fact composites, not single phases. BUSENBERG and PLUMMER (1989) grew their synthetic samples from calcite seeds which constituted a non-negligible fraction of the final products. BISCHOFF *et al.* (1987) report that their synthetic, more perfect samples had bulk compositions slightly different from the dissolving ones. Most biogenic materials, unless carefully selected, have variable compositions on a

microscopic scale (MOBERLY, 1968) and consist of a mixture of different minerals or mineral domains. We do not expect that the dissolution behavior of a composite sample can be meaningfully extrapolated to an accurate equilibrium state.

Structural disorder, impurities and compositional heterogeneities are well documented in biogenic magnesian calcites and in samples rapidly precipitated from seawater. These lattice imperfections probably modify dissolution kinetics much more markedly than equilibrium solubilities. At the present time, almost all free energy estimates for magnesian calcites are based on empirical extrapolations of dissolution kinetics or steady states obtained in strongly inhibited conditions. The clustering of these estimates and differences between groups of materials are likely to reflect kinetic variability rather than thermochemistry. Existing data are clearly not accurate enough to decide whether classification of magnesian calcites in "Group I" and "Group II" corresponds to significantly different solubilities and phase relations. We must obtain more reversed equilibrium solubilities or data of comparable quality before we can fruitfully model the mixing thermodynamics and the phase relations of magnesian calcites.

## CONCLUSIONS

THORSTENSON and PLUMMER (1977) introduced the concept of "stoichiometric saturation" to describe the reactions between a solid solution and aqueous fluid under the added constraint that the composition of the solid must remain constant. Mass transfers between solid and fluid then reflect only congruent dissolution and precipitation. This work reports on a new experimental technique which allows magnesian calcite solid solutions to react with aqueous solution under the constraint of "stoichiometric saturation". Application of this technique to a biogenic magnesian calcite containing 11.6 mol percent  $\text{MgCO}_3$  yielded a reversed equilibrium solubility which was used to derive an accurate free energy of formation. The free energy of formation for this composition is:  $-1,117.75 \text{ kJ mol}^{-1}$ .

The technique used in this work exploits the long-term persistence of solution compositions which are metastable relative to the lower-energy equilibrium states. It requires using relatively low fugacities of  $\text{CO}_2$ , comparable to that of air, and low supersaturations. In addition, it relies heavily on the fact that a stirred solution slightly supersaturated with respect to magnesian calcite will not precipitate this solid over a laboratory time scale. It also exploits the continuous creation of high energy dissolution

sites by abrasion caused by mechanical stirring. Finally, it relies on the fact that precipitation on a seed with the same composition has less of a kinetic barrier than precipitation on a different substrate such as low-magnesium calcite. These observations give the experimenter a fair degree of control over dissolution and precipitation of magnesian calcites and suggest a new conceptual model to interpret precipitation observations in supersaturated calcium-magnesium-bicarbonate-carbonate solutions.

Many of the previously reported stabilities for magnesian calcites are based on empirical extrapolations of pH against reaction time during the initial dissolution stage. This procedure approximates the true reaction kinetics over a small time span only and appears to be very sensitive to the presence of minor defects in the dissolving solids. Other stability estimates recently reported by BUSENBERG and PLUMMER (1989) correspond to apparent dissolution steady-states in the presence of orthophosphate inhibition. Large discrepancies between the estimated stabilities of biogenic samples with comparable compositions probably reflect differences between dissolution kinetics rather than true differences between their free energies of formation. While estimates of free energies based on kinetic extrapolations may provide good first approximations, they are not accurate enough to permit calculation of the activities of the  $\text{CaCO}_3$  and  $\text{MgCO}_3$  components, to obtain reliable phase relationships, or to distinguish between the stabilities of different materials such as the "Group I" and "Group II" proposed by BUSENBERG and PLUMMER (1989).

The free energy reported here for  $\text{Ca}_{0.884}\text{Mg}_{0.116}\text{CO}_3$  is the first that corresponds to a documented, reversed equilibrium state. Additional data of comparable quality are required before thermodynamic modeling of the pseudo-binary magnesian calcite solid solution can yield useful analogs to natural carbonate assemblages. Additional experiments have been conducted on single-phase biogenic magnesian calcites with a range of compositions. Free energies of formation have been derived from these equilibrium solubilities and will be reported elsewhere. These new data improve our understanding of the saturation-states of sea water with respect to aragonite, magnesian calcite and low-magnesium calcite.

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#### APPENDIX 1 SOLUTION ANALYTICAL DATA

Concentrations are micromolar at 22.5 ± 1°C (the laboratory temperature). The CO<sub>2</sub> fugacity in Pa is given by:  
 $f = 377 (P + 0.391 - 3.126)/1000$ .

Sample No.	Run time minutes	[Ca]/μM	[Mg]/μM	Pressure kPa	Sample No.	Run time minutes	[Ca]/μM	[Mg]/μM	Pressure kPa
1	15	13.7	2.3		26	11,208	825.	108.5	100.10
2	30	21.8	2.6		27	12,703	797.	106.	101.76
3	60	28.2	4.2		28	13,136	799.	105.7	101.23
4	121	44.9	5.44		29	14,277	573.	74.5	99.69
5	180	51.7	6.15		30	14,737	586.	76.3	100.55
6	354	95.4	10.0		31	15,731	559.	73.4	101.24
7	546	140.	14.6		32	17,232	565.	76.7	102.00
8	1,110	244.	28.7		33	18,865	548.	72.6	101.41
9	1,315	266.	34.6		34	19,985	567.	74.0	101.20
10	1,642	298.	38.7		35	20,692	565.5	73.55	101.05
11	1,904	319.	41.1		36	21,751	568.5	74.25	99.93
12	2,591	373.	48.0		37	22,800	558.5	73.0	100.25
13	2,747	370.	48.6	99.20	38	23,397	561.	73.2	
14	3,388	420.	55.7	99.64	39	24,189	373.5	50.2	101.00
15	4,010	498.5	65.7	100.18	40	24,635	402.	51.35	100.80
16	4,277	510.5	67.7	100.04	41	25,750	431.	57.6	100.65
17	4,780	537.	71.35	100.10	42	27,311	450.	58.3	99.65
18	5,590	624.	82.9	99.87	43	28,521	506.	67.5	100.15
19	6,345	724.	95.2	100.00	44	29,356	527.5	68.3	100.67
20	7,054	807.	104.	100.42	45	30,006	552.	71.2	100.55
21	8,324	841.5	114.	99.97	46	30,788	562.5	73.6	100.03
22	8,805	808.	111.5	98.30	47	31,491	552.5	73.95	99.73
23	9,135	749.	97.6	98.25	48	32,240	559.5	73.15	99.71
24	9,750	809.	105.5	98.30	49	33,352	569.	75.0	100.82
25	10,474	801.	103.5	98.86	50	34,520	550.5	71.8	100.60

## APPENDIX 2 ERROR ANALYSIS

The accuracy of the equilibrium concentrations of calcium and magnesium is estimated at better than  $\pm 1$  percent, given the reproducibility of the experiment. The accuracy of the  $\text{CO}_2$  fugacity is more difficult to evaluate because the pressure reading itself does not introduce significant error and most of the uncertainty is due to potential disequilibrium between gas and liquid. After reaching equilibrium from supersaturation, an accurate alkalinity determination on the aqueous solution yielded a computed value of the  $\text{CO}_2$  fugacity of: 36.44 Pa vs. the measured 36.82, indicating no measurable disequilibrium for that sample within the analytical uncertainty. It is reasonable to conclude that the uncertainty of the  $\text{CO}_2$  fugacity is given by the variation of total pressure, that is:  $\pm 0.6$  percent.

Other sources of uncertainty are the composition of the solid, which is estimated accurate to better than  $\pm 0.1$  mol

percent  $\text{MgCO}_3$ , and the expression for the mean activity coefficient of calcium and magnesium bicarbonate. Estimates of uncertainty for the mean activity coefficient cannot be separated from that for the solubility product of calcite (and also its free energy of formation). When the free energy of mixing is computed, this part of the uncertainty cancels out. It is unlikely that the uncertainty of the mean activity coefficient itself exceeds 2 percent.

Combining the relative uncertainties, we obtain for the equilibrium constant:

$$\Delta K_{mc}/K_{mc} = 3 \times 0.02 + 3 \times 0.01 + 0.006 = 0.096.$$

The corresponding uncertainty for the logarithm of the solubility product is:  $\pm 0.039$  and that for the free energy of formation is:  $\pm 0.10 \text{ kJ mol}^{-1}$ , relative to a free energy of formation of pure calcite of:  $-1,129.27 \text{ kJ mol}^{-1}$ .