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Biogenically produced magnesian calcite: inhomogeneities in chemical and physical properties; comparison with synthetic phases

WILLIAM D. BISCHOFF, FINLEY C. BISHOP, AND FRED T. MACKENZIE[1]

Department of Geological Sciences
Northwestern University, Evanston, Illinois 60201

Abstract

Magnesian calcites with compositions between 0 and 24 mole% $MgCO_3$ were synthesized at high temperatures and pressures in cold-seal and piston-cylinder apparatus. X-ray powder diffraction and atomic absorption analyses of these phases reveal a non-linear, but smooth, variation in volume and *c/a* with composition up to about 20 mole% $MgCO_3$. Negative excess volumes exist below 20 mole% $MgCO_3$, and positive excess volumes exist above 20 mole% $MgCO_3$.

Several samples of biogenic magnesian calcites in the same composition range exhibit chemical heterogeneities. Echinoid skeletal parts vary by up to 5 mole% $MgCO_3$. Algae has neighboring domains differing by up to 10 mole% $MgCO_3$. Difference in unit cell geometry with respect to synthetic phases were also observed. Cell volumes and *c/a* ratios for most biogenic specimens do not vary smoothly with composition and generally exceed those of synthetic phases. Minor element concentrations do not account for unit cell volume discrepancies. As a result, use of existing X-ray determinative curves based on synthetic phases can lead to errors of over 5 mole% $MgCO_3$ in the estimation of biogenic magnesian calcite compositions.

Introduction

Magnesian calcite skeletal particles and cements are ubiquitous in modern sediments. An understanding of reactions involving these materials in sedimentary and diagenetic environments is necessary for evaluation of processes involving maintenance of the saturation state of the world's oceans, potential for minor uptake of fossil fuel CO_2 by the carbonates in the ocean, and for explaining the lack of magnesian calcites in the ancient rock record.

Compositions of biogenic and inorganic magnesian calcites are often calculated by comparison of selected X-ray diffraction peaks with published determinative curves. There are at least five curves currently in the literature (Milliman *et al.*, 1971). Determinative curves based on synthetically prepared magnesian calcites (Goldsmith and Graf, 1958; Goldsmith *et al.*, 1961) are probably the most widely used, but few samples in the composition range relevant to biogenic magnesian calcites, 0–30 mole% $MgCO_3$, were synthesized. Also, widespread availability of unit cell refinement programs (Burnham, 1962) makes it desirable to establish volume and cell-edge curves rather than merely relying on the position of a single diffraction peak.

Efforts to determine a solubility curve for magnesian calcites as a function of $MgCO_3$ concentration have been made on biogenically produced materials (Chave *et al.*, 1962; Land, 1967; Plummer and Mackenzie, 1974). The discrepancies between and interpretation of the results of these sets of experiments have led to considerable discussion (Thorstenson and Plummer, 1977, 1978; Berner, 1978; Garrels and Wollast, 1978; Lafon, 1978; Pytkowicz and Cole, 1981; Schoonmaker, 1981). Compositional inhomogeneity in algae (Milliman *et al.*, 1971) and echinoids (Chave, 1954; Schroeder *et al.*, 1969; Weber, 1969) has been previously recognized. In addition, our study has revealed unit-cell irregularities in most biogenically produced magnesian calcites. Because these factors could be significant in the interpretation of the solubility experiments, we undertook a systematic comparison of the X-ray and compositional properties of many biogenic magnesian calcites with synthetic magnesian calcites having similar compositions.

Experimental procedures

Magnesian calcite was synthesized with closely-spaced compositions along the calcite–dolomite join in the range from 0 to 23.8 mole% $MgCO_3$. Syntheses were carried out in cold-seal pressure vessels and in a piston-cylinder apparatus using appropriate quantities of Fisher reagent grade $CaCO_3$ and basic $MgCO_3$. About 7 wt.% oxalic acid

[1] Present address: Department of Oceanography, University of Hawaii, Honolulu, Hawaii 96822.

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was added to each run, which, upon decomposition under the experimental conditions, provided sufficient CO_2 pressure to prevent decomposition of the synthetic run products. The mixtures for samples 7–11 (~300 mg) were sealed in welded Au capsules and placed in cold seal bombs at 2 kbar and 700°C for 72 hours. Samples 12 through 15 (~10 mg) were sealed in welded Pt capsules and run in a piston-cylinder apparatus at 10 or 15 kbar and 1000°C for eight hours. All runs were quenched.

In each synthesis, conditions were chosen to correspond to stable one-phase regions of the magnesian calcite phase diagram (Goldsmith and Heard, 1961; Goldsmith and Newton, 1969). To ensure homogenization, syntheses in the piston-cylinder apparatus were carried out at high temperature in the calcite II stability field (Goldsmith and Newton, 1969). Although recent evidence suggests that minor amounts of anion-disordering can be preserved under some quenching conditions (Gunderson and Wenk, 1981), resulting X-ray powder patterns indicate that an immediate, complete reaction to calcite I occurred during quenching, as also reported by other investigators (Jamieson, 1957).

Unit cell constants were determined by a least-squares regression analysis (Burnham, 1962) of data collected on a Norelco X-ray powder diffractometer. Diffraction patterns were taken at ¼°/min with metallic Si or synthetic spinel ($MgAl_2O_4$) as an internal standard. Up to ten reflections were used for refinements. In all synthesis with $MgCO_3$ less than 20 mole%, sharp, single-phase X-ray patterns were observed. For syntheses containing more than 20 mole% $MgCO_3$, some broadening, possibly corresponding to a few mole percent $MgCO_3$, was noticed.

Synthetic run products were analyzed for Mg and Ca by a Perkin Elmer 305 atomic absorption spectrophotometer. Samples were dissolved in concentrated HCl and diluted to appropriate concentrations. La and K were added to the solutions to prevent interferences. Up to four repetitions of each analysis were made. The results of unit cell refinements and atomic absorption analyses for synthetic samples are recorded in Table 1.

Several biogenically produced magnesian calcites in the same range of composition were selected for X-ray and atomic absorption analysis. Biogenic skeletons include the echinoid genera *Tripneustes, Diadema, Lytechinus,* and *Echinometra,* the foraminiferum *Homotrema,* the coralline algae *Amphiroa* and *Lithothamnium,* and a barnacle. All specimens were obtained in Bermuda, except for *Lithothamnium,* which was collected in Corsica. Organic material was removed by treatment with commercial Chlorox or H_2O_2. X-ray diffraction and atomic absorption analyses, and unit cell refinements were conducted exactly as described for synthetic samples. Results are recorded in Table 2.

Many of the biogenic samples were carefully analyzed by electron microprobe using wavelength-dispersive spectrometers, 0.5 μA beam current, 15 kV accelerating potential, and a 2 μm-diameter beam. Counting times were 10 seconds for Ca and Mg, 20 seconds for K, 30 seconds for Ba, Mn, S and Fe, and 60 seconds for Sr and Na. Some damage to specimens was noted during longer counting times.

Results and discussion

Synthetic materials

Figures 1 and 2 depict unit cell volumes and the *c/a* ratio as a function of $MgCO_3$ concentration as determined by AA analysis. Results of Goldsmith *et al.* (1961) in this composition range are also included. All of the synthetic materials fall close to a smooth curve drawn for *V,* and all but the 19.7 mole% and 21.8 mole% syntheses fall close to a smooth curve for *c/a.* As previously noted, it proved impossible to quench a completely homogeneous phase in this composition range. The aberrant *c/a* ratios are believed to be an artifact resulting from the inhomogeneities. Electron microscopy of these samples is underway to characterize their nature. Quadratic least-squares re-

Table 1. Analyses and cell dimensions: synthetic phases

Sample	Composition Mole % $MgCO_3$ $\sigma < 0.1$	V(Å^3)	a(Å)	c(Å)	c/a
NBS Calcite	0	367.78	4.989	17.062	3.4199
8B	1.8	366.02(9)	4.9820(6)	17.028(4)	3.418(1)
8A	1.9	366.1(1)	4.982(1)	17.031(4)	3.419(1)
9A	3.9	363.6(1)	4.9720(7)	16.984(4)	3.416(1)
9B	3.8	363.86(7)	4.9731(5)	16.988(3)	3.4160(9)
10A	5.7	361.60(7)	4.9641(4)	16.944(3)	3.4133(9)
10B	5.7	361.64(7)	4.9642(4)	16.945(3)	3.4134(9)
11	8.0	359.31(7)	4.9544(4)	16.903(2)	3.4117(7)
7A	13.0	354.3(1)	4.9336(7)	16.806(5)	3.406(1)
7C	13.0	354.87(7)	4.9369(5)	16.813(3)	3.4056(9)
7D	13.2	354.4(1)	4.9348(6)	16.805(4)	3.405(1)
12	17.6	350.2(2)	4.918(2)	16.724(8)	3.401(3)
14	19.7	349.3(2)	4.918(1)	16.680(7)	3.392(2)
13	21.8	348.4(2)	4.914(1)	16.658(6)	3.390(2)
15	23.8	346.81(9)	4.9044(7)	16.649(3)	3.395(1)

Table 2. Analyses and cell dimensions: biogenic phases

Specimen	Composition Mole % $MgCO_3$ $\sigma < 0.1$	V(Å^3)	a(Å)	c(Å)	c/a
Barnacle	1.2	367.4(1)	4.979(1)	17.111(6)	3.437(2)
Diadema antillarum (spine, specimen 1)	6.2	361.67(6)	4.9646(3)	16.944(3)	3.4130(8)
Lytechinus variegatus (spine, specimen 1)	6.5	361.6(1)	4.9635(6)	16.950(4)	3.415(1)
Diadema antillarum (spine tip, specimen 1)	9.1	358.6(1)	4.949(1)	16.904(6)	3.416(2)
Tripneustes esculentis (test)	10.5	357.4(1)	4.9460(8)	16.869(4)	3.411(1)
Lytechinus variegatus (test, specimen 2)	11.2	356.6(9)	4.9425(9)	16.854(6)	3.410(2)
Lytechinus variegatus (teeth, specimen 1)	11.3	357.4(1)	4.9461(6)	16.871(4)	3.411(1)
Diadema antillarum (test, specimen 1)	11.8	355.74(8)	4.9398(6)	16.834(4)	3.408(1)
Lytechinus variegatus (test, specimen 1)	12.0	356.2(1)	4.9421(8)	16.840(5)	3.408(2)
Diadema antillarum (test, specimen 2)	12.2	355.71(9)	4.9392(6)	16.837(3)	3.409(1)
Homotrema rubrim	12.4	355.99(6)	4.9397(4)	16.846(2)	3.4101(7)
Echinometra lucanter (teeth)	13.3	353.94(8)	4.9323(5)	16.800(4)	3.406(1)
Echinometra lucanter (test)	13.6	353.9(1)	4.9312(8)	16.803(5)	3.408(2)
Lithothamnium sp.	15.5	354.1(1)	4.9317(8)	16.809(4)	3.408(1)
Amphiroa sp.	19.5	349.3(1)	4.9139(8)	16.704(5)	3.399(2)

gressions through our smoothed data produce the following equations for unit cell constants as a function of composition:

$$V = 368.1 - 122X + 131X^2$$
$$a = 4.9906 - 0.50X + 0.56X^2$$
$$c = 17.069 - 2.27X + 2.1X^2$$
$$c/a = 3.420 - 0.118X + 0.05X^2$$

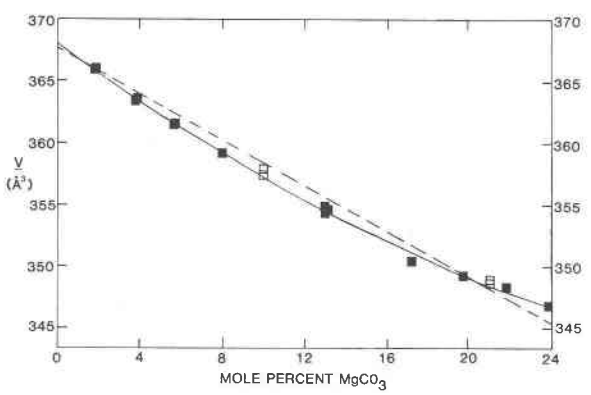

Fig. 1. Unit cell volume *vs.* composition for synthetic magnesian calcite. Closed squares—this study; open squares—Goldsmith *et al.*, 1961. Solid line is quadratic least-squares defined in text. Dashed line is straight line between calcite and disordered dolomite. Volumes were determined by refined X-ray powder diffraction methods, compositions by atomic absorption analysis.

where X is the mole fraction of $MgCO_3$ in the carbonate. These curves should not be used beyond the range of the present syntheses. Our results agree well with those of Goldsmith *et al.* (1961) in this composition range, and should be preferred over the results of Goldsmith and Graf (1958). It is encouraging to note the agreement in results despite the wide variation in synthesis conditions.

Our closely-spaced results with respect to magnesium content reveal that the volumes of disordered magnesian calcites exhibit negative deviations from ideality in the composition range 0 to about 20 mole% $MgCO_3$. At 20 mole%, the volume curve intersects that of the straight line joining the end-members and the excess volume

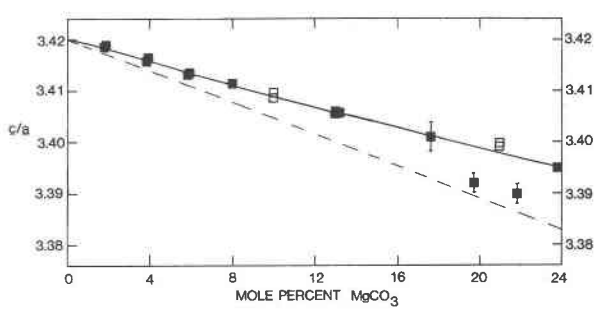

Fig. 2. Cell edge ratio *c/a vs.* composition for synthetic magnesian calcites. Symbols and procedures the same as for Fig. 1.

becomes positive. This may indicate that magnesian calcite volumes have a sigmoidal variation similar to the type discussed by Newton and Wood (1980), especially when the data of Goldsmith *et al.* (1961) for $MgCO_3$ concentrations exceeding 20 mole% $MgCO_3$ are also included. The magnesian calcite volumes, however, have negative excess volumes near the large end member, rather than near the small end member as discussed by Newton and Wood. Therefore, the site-filling mechanisms considered by them are inadequate to explain the magnesian calcite excess volumes. The absence of (10.1), (01.5), and (02.1) reflections in our X-ray patterns precludes the possibility of dolomite ordering. Short range ordering, however, not visible on X-ray patterns, may account for some of the negative excess volume.

Biogenic materials

Biogenic magnesian calcites commonly show deviations in unit cell parameters from those determined for synthetic samples of the same composition. Also, many biogenic samples are poorly crystallized or compositionally heterogeneous. Results of atomic absorption analyses of these materials are plotted versus unit cell constants in Figures 3 and 4. In general, the volumes of the biogenic phases are slightly larger than the volumes determined for synthetic phases of similar composition. Also, unit cell deviations are evident when the *c/a* ratio is examined. Most of the biogenic samples exhibit larger *c/a* ratios than the compositionally-equivalent synthetic magnesian calcites. In addition, considerable scatter among specimens is apparent. In particular, some biogenic phases (barnacle, *Diadema antillarum* (spine tip), *Lithothamnium* sp., and *Amphiroa* sp.) have *c/a* ratios significantly larger than the trend determined for synthetic phases. Once again X-ray scans were checked for reflections indicative of dolomite ordering, but none was found. Incorrect assessments of over 5 mole% $MgCO_3$ in the magnesium concentration of biogenic materials may be made from any set of curves of unit cell parameters or *d*-value *vs.* mole% $MgCO_3$.

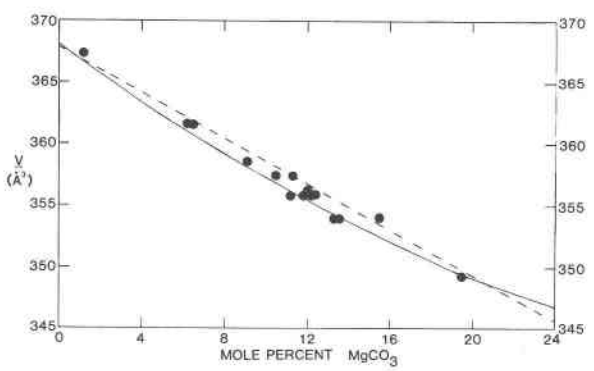

Fig. 3. Unit cell volume *vs.* composition for biogenic magnesian calcite. Curves are the same as in Fig. 1. Analytical procedures as for Fig. 1.

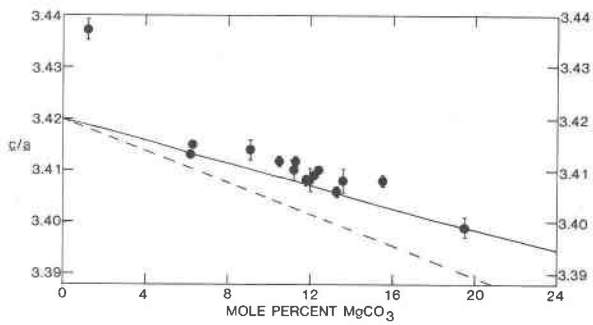

Fig. 4. Cell edge ratio *c/a vs.* composition for biogenic magnesian calcite. Symbols and procedures the same as for Fig. 3.

Broadened X-ray diffraction peaks were noted for the algae *Amphiroa* sp. and *Lithothamnium* sp. In general, degraded diffraction patterns can result from extremely fine crystal size, irregularly or poorly crystallized material, or inhomogeneities in chemical composition. Electron microprobe examination of these samples revealed domains up to 10 mole% higher in $MgCO_3$ than the surrounding material. These domains apparently contributed to the strongly asymmetric peaks in the *Lithothamnium* sp. X-ray pattern (*cf.*, Milliman *et al.*, 1971).

Previous microprobe studies of coralline algae and echinoids have shown that small domains of lower or higher magnesium concentration may exist within an otherwise homogeneous skeleton (Moberly, 1968, 1970; Schroeder *et al.*, 1969). Many algae have been shown to contain significant magnesium not apparent in the X-ray patterns, either as high-magnesium domains (Goldsmith *et al.*, 1955; Milliman *et al.*, 1971), or as a separate brucite phase (Schmalz, 1965; Weber and Kaufman, 1965). Aside from the two specimens indicated, no other biogenic specimen in this study exhibited high-Mg domains on the scale that could be detected by microprobe analysis. The existence of smaller domains cannot be excluded. O'Neill (1981) has suggested that Mg in the carbonate phase varies on the crystallite size scale (1300–3600Å) in the echinoid *Echinaster spinulosis,* although Blake and Peacor (1981) demonstrated homogeneity in the 200Å size range in the crinoid *Neocrinous blakei.* Moberly (1970) has suggested that brucite domains in coralline algae are submicron in size.

Inhomogeneities on a larger scale were noted during atomic absorption analyses of the biogenic skeletons. Spines of *Lytechinus variegatus* have 6.5 mole% $MgCO_3$, whereas teeth have 11.3 mole% $MgCO_3$. Comparable variations were found in *Diadema antillarum:* tests are 11.8 mole% $MgCO_3$, spines are 6.2 mole% $MgCO_3$, and spine tips are 9.1 mole% $MgCO_3$. Variations in magnesium content between tests and spines and within spines were noted for many sea urchins analyzed by Chave (1954) and Weber (1969). We also noted earlier minor variations in composition of tests between two specimens

of *Lytechinus variegatus* and *Diadema antillarum* (Table 2). From 12 X-ray diffraction patterns, Chave (1954) found compositional variations of 3.4 mole% $MgCO_3$ within the test of one specimen of *Lytechinus variegatus*.

Substitution of trace amounts of large ions into the biogenic skeletons could distort or increase the size of unit cells. K, Ba, Mn, Fe, Na, S and Sr were all analyzed by electron microprobe, but only Sr, Na, and S were found in quantities exceeding a few hundred ppm. An estimate of the excess volume from substituting Sr for Ca in the biogenic magnesian calcites was made by comparing strontianite and aragonite unit cell volumes. Only 5 to 50% of the volume discrepancy between the biogenic phases and the calculated volume from the results on the synthetic phases could be due to Sr substitution, and this small amount would decrease if the trace elements caused only local distortion of the crystal structure as found previously in silicates (Iiyama, 1974).

Na and S concentrations above 200 ppm were noticed, but the possibility of contamination cannot be excluded. If these elements are present within the crystal structure, they apparently have little effect on the excess volume because no correlation exists between Na + S + Sr and the observed volume deviations.

Conclusions

From the self-consistent, homogeneous set of synthetic magnesian calcites produced, it can be concluded that: (1) the determinative curve of Goldsmith *et al.* (1961) has been confirmed and filled-in for the composition range comparable to biogenic specimens; (2) biogenic magnesian calcites generally exhibit irregularities in unit cell parameters which apparently are not due to minor element substitution and which may affect other physical properties; and (3) errors of over 5 mole% $MgCO_3$ can be made in using any X-ray determinative curve on biogenic specimens. Studies of biogenic magnesian calcites must be undertaken with the aid of such instrumentation as X-ray diffraction, atomic absorption, and electron microprobe to determine the extent of chemical and physical inhomogeneities present in individual specimens.

Magnesian calcite in contact with seawater is mostly of biologic origin. In the studies of the solubility of biogenic magnesian calcite, little attempt has been made to evaluate the effects of chemical and structural inhomogeneities. A general study of the dissolution behavior of synthetic magnesian calcites is needed as a basis of comparison for the thermodynamic properties of biogenic magnesian calcite.

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