American Mineralogist, Volume 75, pages 1151–1158, 1990

Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals

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ABSTRACT

Structural parameters have been refined for two single crystals of biogenic magnesian calcite containing 6.4 and 12.9 mol% $MgCO_3$, respectively, and yielding weighted residuals of 0.027 and 0.035. Combined with existing data for pure calcite, the M^{2+}-O bond length and the volume of the M^{2+} (M^{2+} = Ca,Mg) coordination octahedron decrease linearly with Mg content. No evidence for cation ordering of the type found in dolomite was found. Equivalent isotropic temperature factors calculated for the M^{2+}, C, and O sites increase approximately linearly with Mg content and are significantly larger than in calcite, magnesite, and dolomite. The large vibrational ellipsoids, in part, reflect increased thermal vibrations. However, the change in shape of the vibrational ellipsoid of O atoms with increasing Mg content indicates substantial positional disorder, caused by local differences of M^{2+}-O bond lengths throughout the crystal. Octahedral distortion is the same as for pure calcite and is apparently insensitive to Mg content.

INTRODUCTION

Magnesian calcite containing up to 30 mol% $MgCO_3$ is an important constituent of modern marine carbonate sediments. A large proportion of these solid solution phases are of biogenic origin, although inorganic precipitates have been well documented (Mackenzie et al., 1983). Calcite in ancient sedimentary carbonate rocks, however, rarely contains more than just a few mol% $MgCO_3$ in solid solution, and the stabilization of magnesian calcite has been the focus of considerable interest in carbonate geochemistry. Numerous experimental studies have documented that highly magnesian calcite is metastable relative to nearly pure calcite + dolomite under sedimentary conditions (e.g., Graf and Goldsmith, 1955; Chave et al., 1962). Various workers (e.g., Goldsmith et al., 1961; Glover and Sippel, 1967) have synthesized magnesian calcite with Mg contents ranging up to, and even exceeding, the composition of dolomite, $Ca_{0.5}Mg_{0.5}CO_3$.

Magnesian calcite also occurs in metamorphic rocks and in carbonatites. The Mg content of calcite coexisting with dolomite has been used as a geothermometer with the polybaric solvus curves of Goldsmith and Heard (1961) and Goldsmith and Newton (1969). However, analyzed metamorphic calcite rarely contains more than 6–8 mol% $MgCO_3$, and many examples show evidence of reequilibration upon cooling (Essene, 1983).

A satisfactory understanding of the properties and behavior of this solid solution requires a knowledge of its structural variation with composition. However, detailed crystal-structure investigations of magnesian calcite have proved difficult owing to a lack of single crystals of suitable quality and size. Crystal sizes of natural inorganic precipitates and synthetic materials are nearly always less than 10 μm. Biogenic magnesian calcite exhibits a wide range of crystal sizes, including large single crystals in the form of various hard parts of echinoderms (e.g., spines, teeth, plates), which have been used in many studies. Nissen (1969) and Donnay and Pawson (1969) concluded that certain echinoid parts were indeed single crystals rather than highly oriented aggregates of microcrystals. Blake et al. (1984) confirmed this using TEM but showed that many such crystals exhibit considerable mosaic character. Compositions of echinoderm single crystals typically range between 4–15 mol% $MgCO_3$, and some compositional variation has been reported within single crystals (e.g., Chave, 1954; Weber, 1969).

The purpose of the present study is to examine more closely the structural variation of two magnesian calcite samples from echinoid fragments using single-crystal X-ray techniques. The results provide some insight to possible structural factors that may affect the stability of this complex solid solution.

PREVIOUS WORK

Most previous structural studies of magnesian calcite have sought to establish the relationship between unit-cell dimensions and Mg content (see Goldsmith et al., 1961; Bischoff et al., 1983; Mackenzie et al., 1983; and references therein). Bischoff et al. (1983) noted a discrepancy between the properties of biogenic and synthetic magnesian calcite. For equivalent Mg contents, biogenic materials have larger unit cells than synthetics. Bischoff et al. (1985) also examined the Raman spectra of synthetic and biogenic magnesian calcite. They noted generally systematic increases of Raman shifts and line widths with increasing Mg content for both internal and lattice modes of synthetic materials. Much greater variation was found for biogenic materials. Line widths of lattice modes

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for biogenic magnesian calcite were consistently larger than for synthetic materials. Bischoff et al. (1985) attributed this difference to positional disorder of the CO_3 group. However, it is not clear why biogenic solid solutions should exhibit greater positional disorder than synthetics if cation distributions are equally random.

Several studies have demonstrated that aqueous solubilities of biogenic magnesian calcite are greater than synthetics having comparable Mg contents (e.g., Bischoff et al., 1983, 1987; Mucci and Morse, 1984; Walter and Morse, 1984; Busenberg and Plummer, 1989). Various explanations have been put forth to account for this difference, although few have been documented. Busenberg and Plummer (1985) found significant trace concentrations of Na^+ and SO_4^{2-} in solid solution in much marine magnesian calcite, with attendant effects on unit-cell dimensions and aqueous solubilities. Busenberg and Plummer (1989) have also drawn attention to the likelihood of higher defect densities in many biogenic samples.

Despite these obvious differences between biogenic and synthetic magnesian calcite, useful structural information can be obtained from carefully chosen and characterized biogenic samples. Althoff (1977) reported results of an X-ray structure refinement of a fragment of a single-crystal echinoid plate containing approximately 10 mol% $MgCO_3$. Although corrections were not made for absorption or extinction, her refined thermal parameters were quite large for all positions, possibly indicating positional disorder (cf. Reeder, 1983). Althoff also drew attention to the trigonal distortion of the octahedral site as a possible cause of metastability, and other workers subsequently considered octahedral distortion in relation to structural stability (e.g., Rosenberg and Foit, 1979; Effenberger et al., 1981; Reeder, 1983). More recently, however, Reeder and Dollase (1989) expressed doubts about the importance of octahedral distortion in rhombohedral carbonates.

SAMPLE DESCRIPTION AND COMPOSITIONS

The samples used in this study were obtained from Dr. W. D. Bischoff and are portions of samples previously examined by powder X-ray diffraction, atomic absorption, and Raman spectroscopy (Bischoff et al., 1983, 1985). Samples LS and LB are spine and tooth material, respectively, of a Recent echinoid, *Lytechinus variegatus,* collected in Bermuda. Compositions reported by Bischoff et al. (1983) for different portions of the same samples are 6.5 and 11.3 mol% $MgCO_3$ for LS and LB, respectively.

We determined the Mg contents of LS and LB independently by electron probe microanalysis (EPMA). Results for the crystal of LB used for refinement and for the region immediately adjacent to the crystal of LS are 12.9 and 6.4 mol% $MgCO_3$, respectively, which are in reasonable agreement with the values given by Bischoff et al. (1983).

During the latter stages of the refinements, and after other structural parameters had converged, Mg occupancies were refined as an additional check on composition. Refined compositions, constrained for full occupancy of the cation site, are 5.8(6) and 12.2(9) mol% $MgCO_3$, respectively, for LS and LB. These are in reasonable agreement with our accepted values of 6.4 and 12.9 mol%.

Busenberg and Plummer (1985) noted that Na^+ and SO_4^{2-} substitution in natural calcite is not uncommon, and it may affect cell dimensions. No attempt was made in this study to determine concentrations of these species. However, Busenberg and Plummer (1985) gave concentrations for similar echinoderm material as ~5000 ppm Na and 8600 ppm SO_4^{2-}. It is unlikely that such concentrations have any significant influence on the intensity data reported here.

Approximately equidimensional fragments were detached from the samples with a razor blade, examined optically, mounted on glass fibers, and placed on standard goniometer heads. The crystal of LS is approximately cylindrical in shape, with a diameter of 100 μm and a length of 120 μm. LB has the shape of a parallelepiped with dimensions 60 × 100 × 100 μm. Laue photographs of both crystals show sharp spots with no evidence of splitting.

DATA COLLECTION

Integrated intensity data were measured at 24 °C using an automated Picker four-circle diffractometer operating with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.7107 Å), at 50 kV and 20 mA. Intensities were collected in the ω-2θ scan mode, with a scan width of 2.0° + 0.7 $\tan\theta$ and a constant precision maintained with $\sigma_I/I = 0.01$, where σ_I is based on counting statistics. Intensities of 916 reflections were collected within the range $5° < 2\theta < 85°$ for LS, and of 912 reflections within the range $10° < 2\theta < 90°$ for LB. These totals include reflections allowed by $R\bar{3}$ symmetry but violating the rule $h\bar{h}0l$, $l = 2n$ for $R\bar{3}c$ symmetry. These intensities were statistically zero and were deleted prior to any data averaging and refinement.

The intensity of a reference reflection, $02\bar{2}4$, was measured once every 20 reflections throughout each data set. These intensities showed random variation not exceeding 3% for each data set.

Unit-cell parameters were determined by least-squares refinement from the centered positions between 12 and 14 reflections from 32 to 44° 2θ.

REFINEMENT PROCEDURES

Intensities were corrected for Lorentz and polarization factors and for absorption using unpublished programs written by D. Swanson and L. W. Finger. A reflection was considered unobserved when $I_{obs} < 2\sigma_I$ and was eliminated from the refinement cycles.

The least-squares refinement program Prometheus (Zucker et al., 1983) was used in all structure refinements. The variable parameters included an overall scale factor, the x positional coordinate of O, four independent anisotropic temperature factors for O, and two independent anisotropic thermal parameters each for carbon and the M^{2+} (=Ca,Mg) site. Starting parameters for the refine-

Table 1. Data measurement and refinement information

Crystal	LS	LB
Obs. reflections	616	612
Indep. reflections	293	261
R*	0.023	0.037
R_w**	0.027	0.035

Note: Weights "w" are assigned proportionally to $1/\sigma^2$ where σ is based on counting statistics.

* R: residual = $\Sigma|F_o - F_c|/\Sigma F_o$.

** R_w: weighted residual = $[\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$.

Table 3. Refined positional parameters and anisotropic temperature factors for calcite and magnesian calcite crystals at 24 °C

Crystal*	CAL	LS	LB
mol% $MgCO_3$	0.0	6.4	12.9
M^{2+} site**			
β_{11}	0.0122(5)	0.0161(1)	0.0190(2)
β_{33}	0.00085(3)	0.00098(1)	0.00131(2)
C site†			
β_{11}	0.012(1)	0.0137(3)	0.0171(6)
β_{33}	0.0008(1)	0.00118(4)	0.00147(7)
O site‡			
x coordinate	0.2567(2)	0.2575(2)	0.2587(3)
β_{11}	0.1423(7)	0.0181(2)	0.0223(4)
β_{22}	0.0256(8)	0.0358(5)	0.044(1)
β_{33}	0.00159(5)	0.00210(3)	0.00259(5)
β_{23}	−0.0022(1)	−0.0024(1)	−0.0018(2)

* Labels correspond to those of crystals listed in Table 4.

** M^{2+} site positional coordinates (0,0,0).

† C site positional coordinates (0,0,¼).

‡ O site positional coordinates (x,0,¼).

ments were taken from a calcite structure refinement at 24 °C by Markgraf and Reeder (1985). Atomic scattering-factor curves for neutral atoms were taken from *International Tables for X-ray Crystallography,* Volume IV (Ibers and Hamilton, 1974). No correction was applied for anomalous dispersion. A parameter for isotropic extinction was refined using the correction of Becker and Coppens (1975) with Type I behavior. Refinements using Lorentzian and Gaussian mosaic spreads yielded comparable residuals and identical refined structural parameters within the precision of the refinements.

Structural and thermal parameters were refined using both absorption-corrected and uncorrected intensity data. Absorption-corrected data improved residuals for LB from 0.072 to 0.035. For each crystal, parameters refined from symmetry-averaged and nonaveraged intensity data were found to agree within the estimated standard deviations (esd). Selected data for intensity measurement and refinement are listed in Table 1. Observed and calculated structure factors are listed in Table 2.[1] Refined parameters and esd presented in Table 3 are those determined from absorption-corrected, symmetry-averaged intensity data. Final weighted residuals are 2.7% for LS and 3.5% for LB.

RESULTS

Unit-cell parameters

Hexagonal a and c cell parameters for the two magnesian calcite crystals are given in Table 4 and plotted as a function of Mg content in Figure 1, with other data reported by Bischoff et al. (1983) for various magnesian calcite specimens.

Polyhedral geometry

Positional coordinates for O (x,0,¼) are given in Table 3 and selected interatomic distances in Table 5. In the calcite structure, O atoms form a slightly trigonally distorted coordination octahedron around the M^{2+} site. The decrease of mean M^{2+}-O bond length with increasing substitution of Mg for Ca is nearly linear (Fig. 2) and compares well with values expected from linear interpolation between values in calcite and magnesite. Although octahedral volume decreases with increasing Mg substitution, there is essentially no change in distortion as shown

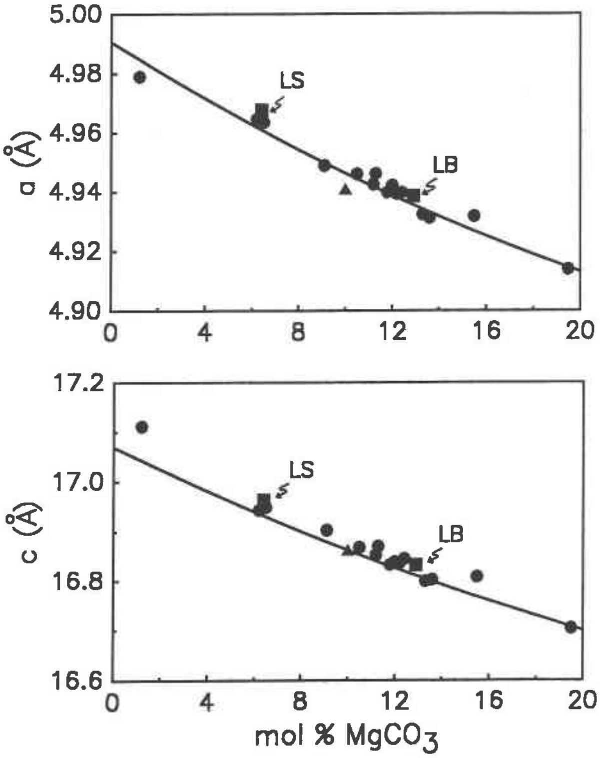

Fig. 1. Hexagonal a and c unit-cell parameters for several magnesian calcite samples. The squares correspond to crystals LS and LB from the present study. Circles are for various biogenic magnesian calcite samples reported by Bischoff et al. (1983). Triangles are from Althoff (1977). The curve is the second-order regression curve of Bischoff et al. (1983) for synthetic magnesian calcite samples.

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[1] A copy of Table 2 listing F_o and F_c values may be ordered as Document AM-90-436 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

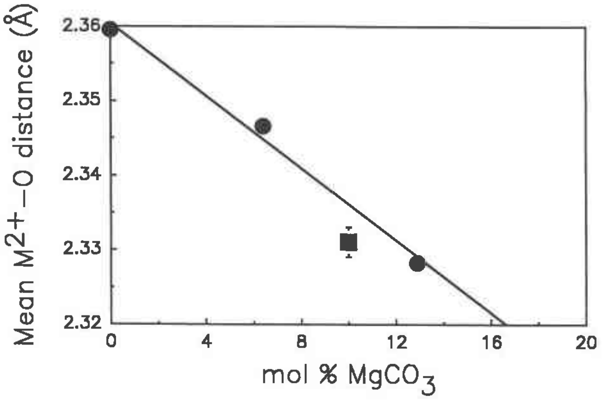

Fig. 2. M^{2+}-O interatomic distance as a function of composition for calcite (Markgraf and Reeder, 1985) and magnesian calcite crystals LS and LB. The square symbol represents the magnesian calcite of Althoff (1977). The line joins calcite and magnesite values from Markgraf and Reeder (1985). Estimated errors are less than symbol size unless otherwise shown.

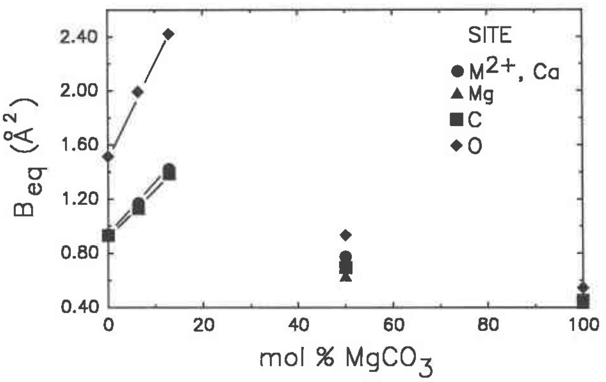

Fig. 3. Equivalent isotropic temperature factors as a function of composition on the $CaCO_3$-$MgCO_3$ join. Calcite and magnesite data at 24 °C from Markgraf and Reeder (1985), dolomite data at 24 °C from Reeder and Markgraf (1986). Estimated errors are less than symbol size.

by quadratic elongation parameters (Robinson et al., 1971) given in Table 5. O-M-O angles (Table 5) within the octahedra are also nearly the same as in pure calcite.

Thermal parameters

Refined anisotropic temperature factors and equivalent isotropic temperature factors are given in Tables 3 and 6. The equivalent isotropic temperature factors (B_{eq}) for all sites of the two magnesian calcite crystals are considerably larger than those of corresponding sites in pure calcite, dolomite, and magnesite, confirming the results of Althoff (1977). It should be noted that our comparison of thermal parameters is confined to results of previous refinements done in this laboratory, in which the same types of absorption and extinction corrections have been implemented as in the present study. All sites in the magnesian calcite crystals show an increase of B_{eq} with Mg content, but O shows a rate of increase that is twice as large as that of C and M^{2+} cations (Fig. 3).

The vibrational ellipsoids of atoms occupying the M^{2+} and C sites are constrained by symmetry to be ellipsoids of revolution ($R_1 = R_2$), with the unique axis coinciding with the threefold axis of the crystal. For both sites, the root-mean-square (rms) amplitudes of the three ellipsoid axes increase rapidly with Mg content (Table 6); however, the vibrational ellipsoid of M^{2+} cations remains nearly isotropic with increasing Mg content (Fig. 4, top), whereas the ellipsoid of C shows increasing anisotropy (Fig. 4, middle).

The vibrational ellipsoid of O is constrained to have one axis parallel to a twofold axis of the crystal. In calcite, this is the shortest principal axis ($\mathbf{R}_1$), which is parallel to the C-O bond. The intermediate axis ($\mathbf{R}_2$) is found to lie approximately in the plane of the M-O-M bond, and the longest axis ($\mathbf{R}_3$) lies approximately perpendicular to the plane of the M-O-M bond. The shape of the O ellipsoid is very anisotropic, both in pure calcite and in the magnesian calcite. As before, rms amplitudes increase with Mg content and do so at a greater rate than for M^{2+} and C atoms (Fig. 4, bottom). The O ellipsoid remains anisotropic with increasing Mg content, but its shape changes markedly, with rms amplitudes increasing more rapidly along $\mathbf{R}_2$ than along the other axes.

DISCUSSION

The most obvious structural variation upon increasing Mg content in calcite is the unit-cell contraction and the corresponding decrease in mean M^{2+}-O bond length and mean volume of the coordination octahedron of the M^{2+} site. As shown in Table 4, unit-cell contraction is highly anisotropic with the largest change along **c**. Such anisotropy is typical for rhombohedral carbonates and reflects

TABLE 4. Unit-cell parameters for magnesian calcite and other carbonates

Crystal	mol% $MgCO_3$	Reference	Axial parameters (Å) *a*	*c*	Unit-cell volume (Å³)	*c/a* Ratio
CAL	0.0	Markgraf and Reeder (1985)	4.988(1)	17.061(1)	367.6(1)	3.420
LS	6.4	This study	4.9673(3)	16.9631(7)	362.48(4)	3.4150(2)
AL	10.0	Althoff (1977)	4.941(2)	16.864(2)	356.60(22)	3.413
LB	12.9	This study	4.9382(4)	16.832(1)	355.48(7)	3.4085(3)
DOL	50.0	Reeder and Markgraf (1986)	4.8069(2)	16.0034(6)	320.24(2)	3.329
MAG	100.0	Markgraf and Reeder (1985)	4.635(2)	15.019(3)	279.3(2)	3.240

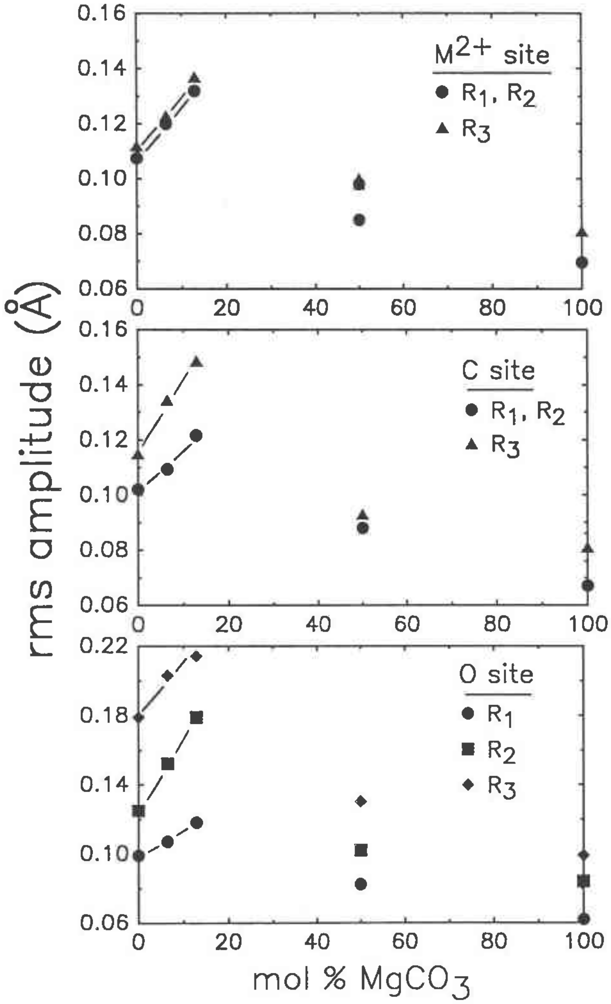

Fig. 4. The rms amplitudes of the principal axes of the vibrational ellipsoids for the M^{2+} (=Ca,Mg) site, the C site, and the O site as a function of composition on the $CaCO_3$-$MgCO_3$ join. Calcite and magnesite data at 24 °C from Markgraf and Reeder (1985). Dolomite data at 24 °C from Reeder and Markgraf (1986). Estimated errors are less than symbol size.

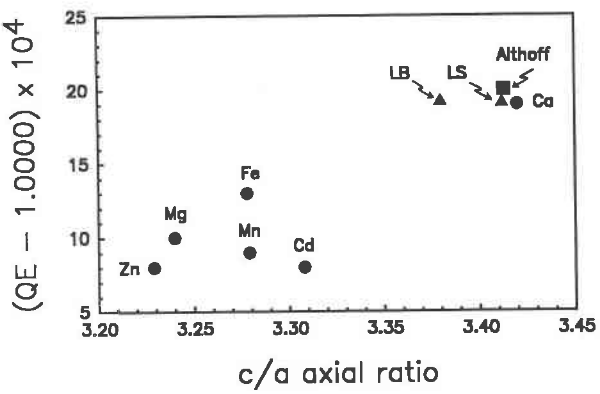

Fig. 5. Quadratic elongation as a function of the *c/a* axial ratio for calcite isotypes (data from Reeder, 1983, plotted as circles) and magnesian calcite crystals. Square: 10 mol% $MgCO_3$ from Althoff (1977). Triangles: LS and LB.

the linkage of strong C-O bonds in the basal plane (cf. Reeder, 1983). The decreases of mean M^{2+}-O bond length and mean octahedral volume with increasing Mg substitution are nearly linear and agree with changes expected from linear interpolation between values in calcite and magnesite. These observations are consistent with apparent normal behavior for substitutional solid solution.

Octahedral distortion

Previous workers have emphasized two structural aspects of magnesian calcite that may bear on their stability and behavior in nature—octahedral distortion and positional disorder. Althoff (1977) noted that the trigonal distortion of the cation octahedra, an elongation along **c**, is larger in her magnesian calcite (10 mol% $MgCO_3$) than in pure calcite and suggested this as a cause of instability. Other workers have also suggested that excessive octahedral distortion may limit the extent of solid solution in rhombohedral carbonates (e.g., Rosenberg and Foit, 1979; Reeder, 1983). Our present results, however, do not support such conclusions. Quadratic elongation values (Robinson et al., 1971) for our magnesian-calcite crystals (Table 5, Fig. 5) are the same as for pure calcite (1.0019)

TABLE 5. Geometry of coordination polyhedra for several carbonates

Crystal*	CAL	LS	AL	LB	DOL**	MAG
mol% $MgCO_3$	0.0	6.4	10.0	12.9	50.0	100.0
Octahedral volume (Å³)	17.43	17.176(5)	16.85	16.778(8)	17.95	12.36
QE†	1.0019	1.0019(2)	1.002	1.0019(2)	1.0016	1.0010
Mean M^{2+}-O bond length‡	2.3595(5)	2.3466(4)	2.331(1)	2.3282(7)	2.3816(5)	2.1018(4)
C-O bond length‡	1.281(1)	1.2790(8)	1.276(3)	1.277(1)	1.2858(4)	1.288(1)
Libration-corr.‡·§	1.290(1)	1.2920(4)	—	1.293(1)	1.2900(7)	1.289(1)
Selected bond angles‖ (°)						
O(1)-(M^{2+})-O(2)	87.44(1)	87.46(1)		87.45(2)	87.69(1)	88.17(1)
O(1)-(M^{2+})-O(6)	92.56(1)	92.54(1)		92.55(2)	92.31(1)	91.83(1)

* Labels correspond to those of crystals listed in Table 4.
** Only the Ca site data are shown for dolomite (DOL).
† Quadratic elongation as defined in Robinson et al. (1971).
‡ Bond-length units are in Å.
§ C-O bond length corrected for libration using the refined **L** rigid-body tensor coefficient.
‖ O atoms are labeled as in Reeder (1983).

TABLE 6. Magnitudes* and orientations of the principal axes of vibrational ellipsoids for several carbonates

Crystal**	CAL	LS	LB	DOL	MAG
mol% $MgCO_3$	0.0	6.4	12.9	50.0	100.0
M^{2+} site†					
R_1	0.107(2)	0.1228(3) (0.123)‡	0.135(6) (0.133)	0.0906(5)	0.070(5)
R_3	0.112(2)	0.1198(7) (0.120)	0.137(1) (0.137)	0.0944(3)	0.081(2)
B_{eq}	0.94(3)	1.170(8) (1.17)	1.42(1) (1.42)	0.686(5)	0.43(2)
C site					
R_1	0.107(5)	0.113(1) (0.109)	0.126(2) (0.122)	0.0880(8)	0.075(5)
R_3	0.111(7)	0.131(2) (0.135)	0.145(3) (0.149)	0.093(1)	0.076(2)
B_{eq}	0.93(5)	1.13(2) (1.10)	1.39(3) (1.36)	0.638(7)	0.45(2)
O site					
R_1	0.099(4)	0.107(1) (0.110)	0.118(2) (0.123)	0.0821(9)	0.062(3)
R_2	0.125(3)	0.152(1) (0.150)	0.179(2) (0.178)	0.1019(8)	0.084(2)
R_3	0.179(2)	0.203(1) (0.202)	0.214(2) (0.213)	0.1300(7)	0.099(2)
B_{eq}	1.51(4)	1.99(2) (1.99)	2.42(3) (2.42)	0.896(7)	0.54(2)
α§		49	53		

* Units of rms amplitudes are in Å, and units of B_{eq} are in Å^2.

** Labels correspond to those of crystals listed in Table 4.

† Only the Ca site data are shown for dolomite (DOL).

‡ Values in parentheses are calculated from rigid-body parameters.

§ α is the angle (°) between $\mathbf{R}_3$ and the **c** axis. $\mathbf{R}_1$ is parallel to the **a** axis.

within the estimated errors. Quadratic elongation of Althoff's magnesian calcite (1.0020) must also be considered within the error (±0.0002) of these values. O-M-O angles within the coordination octahedra for the magnesian calcite crystals are essentially the same as for pure calcite (Table 5). Significantly, we find no increase in distortion with increasing Mg substitution within the compositional range studied.

Recently, Reeder and Dollase (1989) found that octahedral distortion is largely insensitive to Fe substitution in the dolomite-ankerite solid solution, and they pointed out that absolute magnitudes of trigonal distortions in rhombohedral carbonates are very small. Their study, as well as our present work, casts doubt on any relationship between stability and octahedral distortion.

Thermal parameters and positional disorder

We have already pointed out that thermal parameters in both magnesian calcite crystals are significantly larger than corresponding values in either pure calcite, dolomite, or magnesite. Figures 3 and 4 also reveal that values of B_{eq} and rms amplitudes in pure calcite are themselves noticeably larger than corresponding values in either dolomite or magnesite. This is especially obvious for B_{eq} values of the O sites (Fig. 3), and it apparently reflects the large size of Ca for sixfold coordination (cf. Reeder, 1983).

Increasing thermal parameters with increasing Mg substitution in calcite are not unexpected. Burnham (1964, 1973) demonstrated that solid solutions and disordered phases involving site substitution can be expected to exhibit positional disorder. The extent of the effect is related to the difference in M^{2+}-O bond lengths for the substituting cations. The Ca-O bond distance in calcite is 2.36 Å, and the Mg-O bond distance in magnesite is 2.10 Å, yielding a difference of 0.26 Å, which is greater than 10%. Depending on the combination of cations coordinating with it, an O atom will take slightly different positions, thereby giving rise to positional disorder when averaged over many unit cells. Since the CO_3 groups behave essentially as rigid bodies, individual O atoms are not displaced or disordered independently, but rather the CO_3 groups are. The positional disorder is not restricted to the anions, and cations show similar effects (also see Ohashi et al., 1975).

Temperature factors do not discriminate between the causes of the effective smearing of electron density, and therefore positional disorder appears as increased thermal motion. However, positional disorder effects can be identified if the greatest increase of rms amplitudes (upon substitution) occurs in a direction corresponding to one or more M^{2+}-O bond directions. Burnham (1964) identified positional disorder effects in mullite in this manner.

Owing to the symmetries of the C and M^{2+} sites in calcite, their vibrational ellipsoids would not be expected to reveal positional disorder as clearly as the O ellipsoid. Data for the O site (Fig. 4) show that the most rapidly increasing principal axis of the vibrational ellipsoid for the O site is R_2, the intermediate axis, which lies in the M-O-M plane. Smaller increases are found for R_1 and R_3, which are oriented along the C-O bond direction and normal to the M-O-M plane, respectively. These findings are precisely what would be predicted for positional disorder.

Similar positional disorder effects were found by Reeder and Wenk (1983) in structure refinements of substitutionally disordered dolomite. O vibrational ellipsoids showed the greatest increase along $\mathbf{R}_2$ with increasing disorder. Since $\mathbf{R}_2$ lies approximately in the M-O-M plane, it should be more sensitive to variations in M^{2+}-O bond distances. In contrast, refinements of ordered dolomite with increasing temperature (24–600 °C) show a very different effect (Reeder and Markgraf, 1986). Greatest increases in the vibrational ellipsoid for the O atom are along $\mathbf{R}_3$, which has an orientation normal to the M-O-M plane and is the direction least constrained by bonding.

The Raman spectroscopic study of magnesian calcite by Bischoff et al. (1985) demonstrated increasing line width for lattice modes with increasing Mg content. They concluded that positional disorder was the probable cause for this increase. Our present findings support their conclusions, but they also serve to emphasize that positional disorder is not wholly limited to the CO_3 group but also affects the cation positions. The large thermal parameters for the magnesian calcite crystals almost certainly reflect increased thermal vibrations in addition to positional disorder. These factors combined should be reflected in the thermodynamic properties of the crystals and may be a significant structural factor contributing to their relative instability.

TLS analysis

T, L, and S rigid-body tensor coefficients were also refined for the magnesian calcite structures, as implemented by Reeder and Markgraf (1986). The thermal parameters determined by anisotropic and rigid-body refinements are nearly identical (Table 6), as are the residuals. This could be considered permissive evidence that the CO_3 groups retain a rigid-body configuration while positionally disordered.

Cation ordering

Evidence for cation ordering of the type found in dolomite was sought by refining the structure with two distinct cation sites in the dolomite space group, $R\bar{3}$. However, refined site occupancies were identical with those for the single-site model in $R\bar{3}c$. In addition, no indication of deviation from a plane for the geometry of the CO_3 group was found with the $R\bar{3}$ model.

The magnesian calcite specimens were examined by transmission electron microscopy, and these results will be reported separately. However, we note that selected-area electron diffraction patterns of both LS and LB magnesian calcite samples exhibit extremely weak extra reflections that violate $R\bar{3}c$ (and $R\bar{3}$) symmetry. These have been called *c*-type reflections by previous workers (cf. Reeder and Wenk, 1979; Reeder, 1981), and they occur midway between $\{10\bar{1}4\}$, $\{11\bar{2}0\}$, and $\{01\bar{1}8\}$ fundamental calcite reflections. In previous studies, *c*-type reflections have been attributed to various cation-ordering schemes within locally restricted domains (e.g., Van Tendeloo et al., 1985). The present results, therefore, strictly pertain to the average structure, pending further interpretation of the *c* structure. Moreover, our findings do not preclude locally restricted ordering and lower symmetry. However, the low residuals and goodness-of-fit parameters are entirely consistent with the calcite structure.

SUMMARY

The nearly linear relationship between Mg content and M^{2+}-O bond lengths and Mg content and octahedral volume relative to the end-members calcite and magnesite are consistent with normal behavior for substitutional solid solution over the compositional range investigated. There is no evidence for dolomite-like ordering of Mg and Ca in the samples investigated.

Changes in amplitude and shape of the O vibrational ellipsoids indicate increasing positional disorder with Mg content. Significant positional disorder should be expected, given the difference in Ca-O and Mg-O bond lengths. Octahedral distortion appears to be largely insensitive to increasing Mg content, and proposed relationships between octahedral distortion and stability are not supported.

Unfortunately it is not possible to compare our results for biogenic single crystals with synthetics. However, it is clear that these biogenic materials, despite their greater solubilities, show uniform and predictable structural variation.

ACKNOWLEDGMENTS

Samples were kindly provided by W.D. Bischoff, who also provided helpful comments on the manuscript. X-ray intensity data were collected with assistance from K. Baldwin, who also provided assistance with the computing facilities. P. Bartholomew and D. Moecher assisted with electron probe microanalysis. This research was supported by NSF grant EAR-8803423. J.P. also acknowledges the support of a Centennial Science & Engineering Scholarship from NSERC.

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Manuscript received December 11, 1989
Manuscript accepted July 11, 1990