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Structural refinements of dolomite and a magnesian calcite and implications for dolomite formation in the marine environment

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Abstract

The structures of dolomite and a calcite containing 10 mole percent $MgCO_3$ were anisotropically refined, using single-crystal X-ray techniques. Cell constants and bond lengths were determined as: a = 4.8033(9), c = 15.984(4) A, V = 319.3(1) A^3, Ca–O = 2.378(1), Mg–O = 2.081(1), C–O = 1.2835(15) A for dolomite; and a = 4.941(2), c = 16.864(2) A, V = 356.60(22) A^3, M–O = 2.331(1), C–O = 1.276(3) A for magnesian calcite. Interatomic bond lengths and angles in the dolomite structure are more ideal than those in the calcite, magnesite, and magnesian calcite structures. Therefore the octahedra are less distorted and provide better cation shielding for both Ca and Mg in dolomite than in the other carbonate structures. Substitution of Mg in the calcite structure distorts the octahedra, diminishing cation shielding. This results in exaggerated thermal motion of ions and bond weakening.

In the marine environment, hydration of Mg and the problem of cation ordering combine to prevent dolomite precipitation. Metastable magnesian calcite forms instead. Once magnesian calcite is formed, pressure increases (less than 1 kbar) in the marine environment may cause sufficient additional disequilibrium to produce dolomite. Increased pressure favors dolomitization of magnesian calcite because dolomite is denser, occupies less volume, and closely approaches an ideal atomic arrangement. Dolomite can form from magnesian calcite by ordering of the Mg already in the structure, and by cation exchange of Mg from sea water for Ca in the structure. Weakened bonding in magnesian calcite facilitates these processes. With increasing pressure, 10 mole percent $MgCO_3$ in calcite is sufficient to favor the formation of dolomite rather than low-magnesium calcite.

Introduction

Despite the abundance and economic importance of dolomite, its origin is not well understood. Although many chemical aspects have been considered in an effort to understand the origin of dolomite, its crystal chemistry has not been fully explored. Furthermore, mineral stability is defined with respect to pressure, temperature, and chemical environment. The effects of chemical environment and temperature have been examined, but the effects of pressures attainable in the marine environment have largely been neglected.

An experimental approach to the evaluation of pressure on dolomitization would seem fruitless for many reasons. Simulation of marine environments could only involve pressures of less than 1 kbar, and reactions at low temperature and pressure are sluggish at best. Furthermore, other attempts to synthesize dolomite have been unsuccessful at temperatures below 100°C. It therefore remains to take a theoretical approach by examining and comparing the crystal structures of the common carbonate minerals and evaluating their relative stabilities in relation to pressure. To that end the dolomite structure and a magnesian calcite structure have been refined and are compared with calcite and magnesite.

Structural refinement of dolomite

Steinfink and Sans (1959) performed the most recent refinement of the dolomite structure. They reported hexagonal cell constants of a = 4.815, c = 16.119 A, and determined that dolomite belongs in space group $R\bar{3}$. They assigned Ca to site 3(a), Mg to site 3(b), C to site 6(c) and O to site 18(f). Atom positions were given as in Table 1. Bond lengths of Ca–O = 2.390(4), Mg–O 2.095(4), and C–O = 1.283(4) A were also reported. (Standard deviations

Table 1. Positional parameters of atoms in the calcium–magnesium carbonates

		Dolomite	Dolomite*	Calcite**	Mg-calcite	Magnesite***
	x	0	0	0	0	
	y	0	0	0	0	
Ca	z	0	0	0	0	
	β_{11}	0.0055(5)			0.0249(4)	
	β_{33}	0.00038(7)			0.00153(4)	
	x	0	0		0	0
	y	0	0		0	0
Mg	z	$\frac{1}{2}$	$\frac{1}{2}$		0	0
	β_{11}	0.0041(9)			0.002(3)	0.0063(4)
	β_{33}	0.0004(1)			0.0002(3)	0.00060(3)
	x	0	0	0	0	0
	y	0	0	0	0	0
C	z	-0.2423(2)	0.2435(3)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	β_{11}	0.0050(15)			0.0178(17)	0.0072(8)
	β_{33}	0.0001(1)			0.0013(1)	0.00052(6)
	x	0.2829(3)	0.2474(6)[a]	0.25706(33)	0.2583(6)	0.2767(2)
	y	0.0350(4)	-0.0347(6)	0	0	0
	z	-0.24397(9)	0.2440(1)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	β_{11}	0.0041(19)		0.00524(59)	0.027(1)	0.0059(3)
O	β_{22}	0.0100(15)		0.01775(90)	0.049(2)	0.0091(4)
	β_{33}	0.0008(1)		0.00104(5)	0.0028(1)	0.0083(3)
	β_{12}	0.0041(15)				
	β_{13}	-0.0003(1)				
	β_{23}	-0.0009(1)		-0.00218(19)	-0.0026(4)	-0.00027(9)

* Steinfink and Sans (1959)
a Graf (1969)
** Chessin et al (1965)
*** Oh et al (1973)
(Estimated standard deviations are given in parentheses and refer to the least significant figures.)

in the least significant figures, in the text and tables, are given in parentheses.) However, bond lengths calculated using Steinfink and Sans' cell parameters and atom positions disagree with those they reported. Graf (1969) discovered that their *x* coordinate of oxygen had been misprinted as 0.2374 instead of 0.2474. Unfortunately, the misprinted oxygen *x* coordinate from the Steinfink and Sans paper continues in use. Since Steinfink and Sans' refinement was only two-dimensional, based on single-crystal film data, and their cell dimensions are larger than those determined by Howie and Broadhurst (1958) and Graf (1961), a new refinement was justified.

A cleavage rhomb 0.18 × 0.20 × 0.25 mm of dolomite from Binnenthal, Switzerland, was mounted for data collection, using a Syntex $P2_1$ four-circle computer-controlled automatic diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation. Table 2 gives the chemical analysis of this dolomite specimen.

In this work, a right-handed hexagonal unit-cell orientation was chosen so that the highest-intensity reflection could be indexed as *hkl* = 104, thus having the same orientation as in the calcite (Chessin *et al.*, 1965) and magnesite (Oh *et al.*, 1973) structures. This orientation also produced *hkl* indexing consistent with published dolomite powder patterns.

Thirteen medium-angle reflections were then accurately centered and refined by least-squares techniques. The unit-cell dimensions obtained by this procedure are: a = 4.8033(9), c = 15.984(4) A, V = 319.3(1) A^3.

Intensity data were collected at 24°C employing the θ–2θ scan technique with a scanning speed of 2.5°/min. Three standard reflections were measured every 47 reflections and showed a maximum random variation of ±1.3 percent. To reduce the amount of redundant data collected reflections were measured in the ranges: hkl to $hk\bar{l}$; $h\bar{k}l$ to $h\bar{1}l$; and $\bar{h}kl$ to $\bar{1}kl$. Lorentz and polarization corrections were applied to the observed structure factors.

The 17 variable parameters are: scale factor; inde-

Table 2. Chemical analysis of dolomite

Oxides	Weight Percent
CaO	30.77
MgO	21.54
MnO	.100
FeO	.008
SrO	.017
CO_2	47.38
Total	99.815

M. Batchelder analyst

pendent thermal parameters, two each for Ca, Mg, and C, and six for O; *x*, *y*, and *z* positional parameters for O, and the *z* positional parameter for C.

Structural refinement was performed on 178 unique reflections by the full-matrix least-squares method using the ORFLS (Busing *et al.*, 1962) program. Atomic scattering factors were taken from the Dirac-Slater calculations of Cromer and Waber (1965). The anomalous parts of the Mg and Ca scattering factors were obtained from the *International Tables for X-ray Crystallography*, Vol. 3 (1962).

The atom positions of Steinfink and Sans along with estimated isotropic temperature factors were used as starting values. A residual $R = 43$ percent indicated that their atom positions were based on a unit cell rotated 180° about the *a* axis chosen in this work. By transforming appropriate atom position signs, the absolute value of the Steinfink and Sans coordinates were again used as starting values. Weights were initially set equal to $1/\sigma_i(F_i)$. A final weighting scheme was chosen by an analysis of variance to make $|\Delta F|/\sigma$ independent of $|F_o|$. The following assignments for $\sigma(F_o)$ were made:

$$0 < |F_o| \leq 165.0 \qquad \sigma(F_o) = 0.0344|F_o| + 3.8$$

$$165.0 < |F_o| \qquad \sigma(F_o) = 0.1428|F_o| - 17.5$$

An absorption correction was made, but use of the corrected structure factors was discontinued because no improvement resulted.

With all atoms allowed anisotropic thermal parameters, the refinement converged to values of the residuals $R_F = 4.5$ and $R_w = 5.4$. Final positional and thermal parameters from the least-squares refinement and their standard deviations are listed in Table 1. Table 3 contains the observed and calculated structure factors. The interatomic bond lengths and angles are presented in Table 4 along with those of calcite and magnesite, and the thermal ellipsoid parameters are given in Table 5.

A final difference Fourier synthesis produced a general background of approximately 0.3 e A^{-3}, with no peaks greater than 0.5 e A^{-3}, confirming the proper location of all atoms and the absence of extra atoms.

Structural refinement of a magnesian calcite

For purposes of comparison, a magnesian calcite structure also was refined. The crystal used was a fragment from a single-crystal plate of an echinoid test supplied by Dr. Julian R. Goldsmith. Although the crystal was sieve-like and porous, it produced sharp diffraction maxima. This sample, containing approximately 10 mole percent $MgCO_3$ in solid solution, was previously used in Dr. Goldsmith's study of dolomite exsolution from calcite (1960). Although a common constituent of carbonate sediments, experimental work on the calcite–magnesite system (*e.g.* Goldsmith, 1960) indicates that magnesian calcite is metastable at surface temperatures.

The procedure used to refine the magnesian calcite was the same as that for dolomite. Again, the cell was chosen such that $khl = 104$ was the highest-intensity peak and thus compatible with previous work.

Fifteen medium-angle reflections were used for centering and least-squares refined yielding cell dimensions of: $a = 4.941(2)$, $c = 16.854(2)$ A, $V = 356.60(22)$ A^3 for a hexagonal cell in the $R\bar{3}c$ space group.

Intensity data were collected as for dolomite. Three standard reflections were measured every 47 reflections and showed a maximum random variation of ±3.3 percent. Lorentz and polarization corrections were applied to the observed structure factors.

The 12 variable parameters are: scale factor; independent thermal parameters, two each for Ca, Mg, and C, and four for O; and the *x* positional parameter for O.

Structural refinement was performed on 84 unique reflections. Calcite atom positions (Chessin *et al.*, 1965) were used as starting values. Weights were set equal to $1/\sigma_i(F_i)$ throughout the refinement, and no absorption correction was made.

The refinement converged to values of the residuals $R_F = 2.5$ and $R_w = 3.5$. At various points in the refinement the occupancies of Ca and Mg were allowed to vary. However, no improvement resulted, thus confirming that the 0,0,0 site indeed contained 90 mole percent Ca and 10 mole percent Mg. Final positional and thermal parameters from the least-squares refinement and their standard deviations are listed in Table 1. The interatomic bond lengths and angles and the thermal ellipsoid parameters are found in Tables 4 and 5 respectively. The observed and calculated structure factors are presented in Table 6.

A final difference Fourier synthesis produced a general background of 0.1 e A^{-3}, with no peaks greater than 0.3 e A^{-3}, confirming the proper location of all atoms and the absence of extra atoms.

Comparison of the carbonate structures

The dolomite structure is similar to that of calcite. Layers perpendicular to the *c* axis are composed alternately of cations or CO_3 groups. In magnesian calcite, the magnesium is unordered, substituting randomly in the structure for calcium. In contrast, dolomite is highly ordered. Calcium and magnesium alternate in the six-fold site along any three-fold axis. This arrangement eliminates the two-fold rotation axis which intersects the carbon atoms in calcite. In dolomite, each O in a carbonate group also coordinates with one Ca and Mg. The cations coordinate with six O, each from a different carbonate group (Fig. 1).

The predicted Ca–O bond length of 2.39 A, the sum of the Pauling ionic radii in six-fold coordination, is closely approximated in the dolomite structure but is considerably shortened in the calcite structure (Table 4). Similarly the O–M–O interatomic angles about both Ca and Mg in dolomite closely approach 90°, resulting in octahedra more ideal than those same octahedra in calcite and magnesite respectively (Table 4).

The M–O bond length in magnesian calcite (2.331 A) is exactly equal to the sum of 90 percent of the Ca–O bond length in calcite and 10 percent of the Mg–O bond length in magnesite, indicating distortion of the calcite octahedra. Again, in order to accommodate both Ca and Mg in the same site, the O–*M*–O interatomic angles in the magnesian calcite are the least ideal of the carbonates herein discussed (Table 4).

Table 3. Observed and calculated structure factors for dolomite

h	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c
l = 0				3	2	43	43	*l* = 9				2	-2	20	19
-1	2	53	50	*l* = 5				-4	-1	11	11	3	-4	6	6
1	4	36	35	-3	-2	19	19	-4	2	2	1	3	2	5	5
2	-4	49	46	-2	-4	14	15	-3	-3	12	13	4	0	24	25
3	-3	86	88	-2	-1	13	12	-2	-2	17	18	*l* = 14			
4	1	54	55	-1	-3	25	25	-2	1	48	47	-3	-2	25	26
l = 1				0	1	38	35	-1	-4	15	15	-1	-3	29	29
-4	-2	12	11	0	-2	11	8	0	-3	15	15	-1	0	25	25
-3	-1	13	13	1	-4	16	16	0	0	47	45	0	-2	36	36
-3	2	44	42	1	2	50	49	1	4	7	5	2	-3	48	49
-2	3	37	32	2	3	21	21	2	-1	31	29	2	3	20	20
-1	1	15	13	4	2	26	26	3	-3	26	26	3	-2	21	21
0	-4	12	12	4	-4	16	16	3	3	7	7	3	1	4	3
2	-2	43	40	*l* = 6				4	1	18	19	4	-4	5	5
2	4	4	3	-4	-1	12	12	*l* = 10				*l* = 15			
3	-4	4	4	-3	-3	27	27	-2	-3	44	46	-3	3	2	0
l = 2				-2	-2	41	42	-1	-2	38	38	-2	4	3	1
-4	3	4	4	-1	-4	31	31	-1	4	2	2	-1	-1	30	30
-3	-2	31	31	-1	-1	59	61	0	-4	3	3	0	0	19	18
-2	-4	23	23	0	0	54	51	1	0	25	24	0	3	7	7
-2	-1	45	43	1	1	80	86	2	-2	55	57	1	-2	9	9
-2	2	78	74	1	4	31	30	2	1	43	43	2	-4	12	11
0	1	23	20	2	2	38	37	3	-4	26	25	*l* = 16			
0	4	3	2	3	0	13	12	3	2	21	21	-3	2	29	29
2	-3	70	70	3	-3	15	14	*l* = 11				0	-4	44	45
2	3	43	43	3	3	25	25	-3	1	14	14	1	0	52	51
4	-1	34	36	4	1	14	14	-2	-1	22	22	2	-2	27	27
4	2	33	35	*l* = 7				-1	-3	5	5	3	-1	38	38
l = 3				-4	-2	26	26	-1	0	5	5	3	-4	34	35
-4	-1	11	11	-2	-3	16	16	0	4	4	4	4	-3	46	49
-3	-3	4	4	-1	-2	46	46	1	-4	4	4	*l* = 17			
-3	0	2	2	-1	4	3	2	2	0	24	24	-1	-3	20	20
-1	-4	2	1	0	-4	3	3	2	3	32	32	-1	3	5	5
-1	-1	76	80	0	-1	11	10	*l* = 12				0	1	23	23
0	0	3	2	0	2	6	4	-4	-1	42	44	1	-4	23	24
-2	1	51	45	2	1	15	14	-2	-2	33	32	1	2	23	23
-3	3	15	13	2	4	11	11	-2	1	25	22	*l* = 18			
-4	2	21	21	3	2	16	16	-1	-4	27	27	-2	-2	26	27
1	4	14	14	3	-4	17	17	0	-3	58	59	-1	2	21	21
3	3	10	11	*l* = 8				0	0	95	106	0	-3	12	12
l = 4				-4	0	61	68	1	4	30	29	0	0	4	4
-4	4	76	77	-3	-2	34	34	2	-1	51	50	1	1	44	45
-4	-2	27	27	-3	1	30	27	2	2	40	39	2	-4	19	20
-3	-1	81	87	-2	-4	31	31	3	-3	53	56	3	-3	15	16
-3	2	60	56	-2	-1	58	60	4	1	38	40				
-2	-3	23	21	-1	-3	41	41	*l* = 13							
-1	-2	50	47	0	1	85	92	-3	-1	23	24				
1	0	102	125	2	0	50	47	-2	-3	25	26				
2	-2	45	46	2	3	33	33	-2	3	12	11				
2	4	35	35	3	1	71	76	0	-1	19	18				
3	-4	52	51	4	2	18	18	1	-3	26	26				

The greater regularity of the octahedra in dolomite is further demonstrated by the thermal ellipsoid of oxygen. In calcite the oxygen thermal ellipsoid is compressed along the *a* axis and is extremely elongated in one direction (Table 5). It has a similar but less attenuated configuration in dolomite, and indicates better cation shielding. In calcite, the Ca is not sufficiently shielded by O(Oh *et al.*, 1973). The oxygen thermal ellipsoid is most regular in magnesite because all octahedra are identical. In contrast, each O in the dolomite structure is a corner shared by a Ca octahedron and a Mg octahedron.

The thermal ellipsoids in magnesian calcite also reflect the disorder in that mineral. The thermal ellipsoid of calcium is flattened along the *c* axis, probably due to *c*-axis shortening, as Mg substitutes for Ca in the structure. Moreover, the thermal motions of the Ca, C, and O atoms are extremely large in comparison to those in the other carbonate minerals (Table 5). Exaggerated thermal motion of these ions about their rest positions causes periodic stretching and attendant weakening of the bonds in the structure. Certainly, this bond weakening is basic to the metastable nature of the magnesian calcite structure.

Unlike calcite and magnesite, the CO_3 group in dolomite is non-planar, as can be seen from the *z*

Table 4. Interatomic distances and angles in the calcium–magnesium carbonates

	Dolomite	Calcite*	Mg-calcite	Magnesite**
Ca-O	2.378(1)	2.356	2.331(1)	
O_1-Ca-O_2	87.66(5)	87.57	87.43(4)	
O_1-Ca-O_6	92.33(5)	92.43	92.56(4)	
O_1-Ca-O_5	180.00(0)	180.00	180.00(0)	
O_1-O_2	3.294(2)	3.261	3.222(3)	
O_1-O_6	3.432(3)	3.402	3.370(1)	
Mg-O	2.081(1)			2.105(1)
O_1-Mg-O_2	88.38(6)			88.25(2)
O_1-Mg-O_6	91.61(6)			91.75(2)
O_1-Mg-O_5	180.00(0)			180.00(2)
O_1-O_2	2.903(3)			2.931[a]
O_1-O_6	2.985(3)			3.022(1)
C-O	1.2835(15)	1.283(2)	1.276(3)	1.283(1)
O-C-O	119.95(1)	120.00	120.00(1)	120.00
O-O	2.222(2)	2.222	2.210(5)	2.222

Bond lengths are in Å, angles are in degrees. Values for dolomite and Mg-calcite were calulated employing ORFFE (Busing et al, 1964).

* Calculated from Chessin et al (1965) employing ORTEP (Johnson, 1965) except for the C-O bond length which they reported.

** Oh et al (1973)

a Oh et al (1975)

(See Figure 1 for atom designation.)

(Estimated standard deviations are given in parentheses and refer to the least significant figures.)

parameters of the C and O atoms (Table 1) and the O–C–O interatomic angles (Table 4). The C atom lies slightly above the plane of the three O, as in the orthorhombic carbonates (de Villiers, 1971), and again precludes the 2-fold axis of the $R\bar{3}c$ space group. Also, the carbon thermal ellipsoid is compressed along the *c* axis (Table 5) reflecting the slight out-of-plane location of carbon.

The C–O bond lengths in calcite, magnesite, and dolomite are equal (Table 4). However, in magnesian calcite, the C–O bond length is slightly shortened, as in another metastable carbonate, calcite (II), which has a C–O bond length of 1.274 A (Bassett and Merrill, 1973).

Distortion parameters were calculated for the octahedra in each of the four carbonates, using the appropriate bond lengths and angles in the "Distort" program written by Dr. Martha Hamil (personal communication) (Table 7, Fig. 2). All distortion parameters are greatest for the Ca–Mg octahedron in magnesian calcite.

Line *A–A′* on Figure 2 connects the octahedral distortion values of calcite and magnesite. Because of the known stability of these two minerals, line *A–A′* should represent the maximum amount of total octahedral distortion allowable for stability in the calcite–magnesite solid-solution series. Any value, averaged over all the octahedra in a structure, which falls above line *A–A′* indicates metastability. The individual Ca and Mg octahedra may be similarly evaluated. Specifically, the total distortion of the Ca octahedron in calcite and that of the Mg octahedron in magnesite must be the maximum allowable values for those octahedra in any hexagonal carbonate structure. For example, a value greater than 0.5145 for any Ca octahedron in a hexagonal carbonate indicates excessive distortion and thus instability. The distortion value for the Ca–Mg octahedron in magnesian calcite

Table 5. Root mean square component of thermal displacement along principal axis *R* of the thermal ellipsoids and the angles each makes with the *c* axis

Atom	R	Dolomite	Calcite*	Mg-calcite	Magnesite**
	1	0.069(10)		0.1489(21)	
Ca	2	0.069(14)		0.1520(10)	
	3	0.070(6)		0.1520(10)	
	1	0.0606(44)		0.0471(1)	0.072(4)
Mg	2	0.0608(56)		0.0471(489)	0.072(4)
	3	0.0751(87)		0.0597(482)	0.083(4)
	1	0.039(26)		0.1285(63)	0.077(8)
C	2	0.0667(13)		0.1288(145)	0.077(8)
	3	0.0667(126)		0.1406(100)	0.077(8)
	1	0.053(11)	0.032	0.1363(59)	0.063(7)
O	2	0.082(4)	0.089(7)	0.1827(46)	0.084(5)
	3	0.116(4)	0.155(4)	0.2300(45)	0.099(3)
	1	90		0	
Ca	2	90		90	
	3	0		90	
	1	90		90	90
Mg	2	90		90	90
	3	0		0	0
	1	0		90	90
C	2	90		90	90
	3	90		0	0
	1	91.3(6.7)	90	89.9(2.6)	90
O	2	125.2(12.5)		141.7(4.2)	
	3	35.2(12.7)	47.8(2.1)	51.7(4.2)	19(2)

Displacements are in Å, angles are in degrees. Values for dolomite and Mg-calcite were calculated employing ORFFE (Bussing et al, 1964).

* Chessin et al (1965)

** Oh et al (1973)

(Estimated standard deviations are given in parentheses and refer to the least significant figures.)

falls well above line *A–A′*, as well as above the values for individual Ca and Mg octahedra (dashed lines on Fig. 2), indicating instability. However, in dolomite both the Ca and Mg octahedral distortion values fall below their respective maxima, and their average value falls below the maximum-distortion-for-stability line *A–A′* (Fig. 2). It is evident, therefore, that the Ca and Mg octahedra in dolomite are each less deformed than those same octahedra in calcite and magnesite respectively—further evidence for the greater suitability of the dolomite structure to contain each ion. Moreover, the octahedra in magnesian calcite are excessively distorted and thus unstable.

The above structural refinements reveal interatomic bond lengths and angles in the dolomite structure which are more ideal than those in the other structures examined. The octahedra in dolomite are the least distorted and provide the best cation shielding for both Ca and Mg in a carbonate mineral. In short, dolomite is the most ideal and stable common carbonate structure. In contrast, distortion of the octahedral site, exaggerated thermal motion of ions, and bond weakening are characteristic of the metastable magnesian calcite.

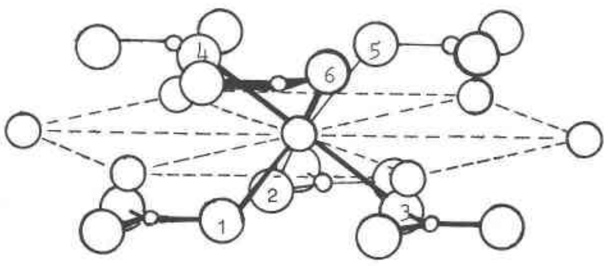
It is herein proposed that the metastable nature of magnesian calcite, together with the suitability of the dolomite structure to contain both Ca and Mg has great bearing on the problem of dolomite formation in the marine environment and will now be discussed.

Discussion of dolomite formation

Thermodynamic investigations on dolomite formation in the marine environment indicate that dolomite is more stable in sea water than calcite and aragonite (Berner, 1971) and should precipitate spontaneously (Hsu, 1967). However, primary dolomite forming today in marine environments has not been positively identified. Furthermore, dolomite in the rock record is considered to be secondary. Indeed, most ancient carbonate rocks are composed of low-magnesian calcite and dolomite, yet modern carbonate sediments contain high-magnesian calcite and aragonite (Berner, 1971). Single phase biogenic calcites contain up to 29 weight percent $MgCO_3$ (Chave, 1952). Because magnesian calcite is metastable, as seen above, it should recrystallize to a more stable form such as dolomite. The ideality of dolomite as a structure and its suitability to contain both Ca and Mg have already been demonstrated. However, metastable arrangements are common when minerals are grown rapidly at low temperature (Fyfe, 1964) and may persist indefinitely under static conditions. Clearly, to form dolomite from calcite, the process

Table 6. Observed and calculated structure factors for magnesian calcite

h	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c	*h*	*k*	F_o	F_c
$l = 0$				1	0	136	139	2	3	25	26	$l = 14$			
1	1	60	63	2	1	51	51	4	2	22	21	-1	0	22	23
1	4	39	40	3	2	30	30	$l = 9$				0	-2	37	38
2	2	43	44	4	0	67	67	-2	1	33	33	1	2	29	29
3	3	23	23	$l = 5$				$l = 10$				1	-4	13	12
3	0	83	82	-1	-3	5	5	-3	-1	16	16	2	3	20	19
$l = 1$				1	2	31	32	-1	1	29	30	3	-2	28	29
-3	-1	4	4	2	3	12	14	0	2	49	49	-4	0	6	5
-3	2	37	36	$l = 6$				1	-3	42	42	$l = 15$			
3	2	17	17	-4	2	37	37	2	4	18	18	1	1	14	14
3	-1	37	36	0	-3	22	21	3	2	24	23	$l = 16$			
$l = 2$				0	0	43	37	$l = 11$				0	-1	46	46
-2	-4	21	21	1	-2	77	76	-3	1	18	18	0	2	32	32
-1	-3	17	17	1	4	17	17	2	3	9	9	1	3	31	30
-1	0	31	31	3	-3	18	19	$l = 12$				3	-1	27	27
2	0	86	84	3	3	21	21	-4	2	31	31	3	2	19	20
2	3	29	32	4	1	15	16	-2	1	39	39	4	0	34	34
3	-2	58	60	$l = 7$				0	0	101	104	$l = 17$			
4	2	22	21	1	-3	26	25	0	3	50	49	-2	-1	7	8
$l = 3$				3	2	14	14	1	4	27	27	$l = 18$			
1	-2	62	58	$l = 8$				3	0	47	47	-2	1	26	26
2	2	4	5	-4	0	57	57	3	3	19	19	0	0	7	7
$l = 4$				-3	1	46	45	4	1	30	29	0	-3	13	13
-4	-2	22	21	-1	0	103	103	$l = 13$				0	3	12	11
-3	-1	62	61	1	-4	51	52	-3	2	13	12	2	2	18	17
-2	0	58	58	2	0	45	45	3	2	10	9				



○ = M SITE

Fig. 1. Sketch of the octahedral site in the calcium–magnesium carbonates (after Oh *et al.*, 1973).

presumed to take place, the right side of a reaction such as:

$$2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+} \quad (1)$$

must be favored with respect to temperature, pressure, and chemical environment.

The problems surrounding dolomite formation are two-fold: First, why doesn't dolomite precipitate from sea water as thermodynamics predicts, and second, how does dolomite form as a secondary mineral?

Lippmann (1973) produced an exhaustive study on the sedimentary carbonates. Therein he considered hydration of Mg to be the kinetic barrier preventing the precipitation of dolomite, as well as magnesite, from sea water. However, the larger Ca ion is less tightly bound to water dipoles and is therefore more available than Mg for incorporation into anhydrous carbonate structures.

Unable to synthesize dolomite at low temperatures, Lippmann chose to approach dolomitization by analogy to norsethitization, that is, the formation of norsethite, $BaMg(CO_3)_2$. Based on these experiments and his work on the magnesite problem, Lippmann concluded that the presence of activated CO_3^{2-} in solution helps overcome the Mg hydration barrier. Thus dolomitization proceeds in the presence of Mg and excess CO_3^{2-} at the expense of preexisting calcium carbonate by the reaction:

$$CaCO_3 + Mg^{2+} + CO_3^{2-} \rightarrow CaMg(CO_3)_2 \quad (2)$$

via solution of calcium carbonate and precipitation of dolomite (Lippmann, 1973). CO_3^{2-} is consumed and calcium is not liberated by this process.

However, hydration of Mg is only one of the barriers to the formation of dolomite. Another crucial consideration heretofore overlooked is the process of ordering Mg and Ca in the dolomite structure. Indeed, the analogy between norsethite and dolomite breaks down, because the Ba and Mg sites in the two minerals are very different. In norsethite, Mg is octahedrally coordinated as in dolomite, but Ba is surrounded by 12 oxygens. Mg cannot fill the dodecahedral-Ba site and Ba cannot substitute into the octahedral-Mg site. In contrast, calcite and dolomite may be considered as a solid-solution series with a disorder–order phase change. Before ordering takes place, the 0,0,0-Ca site and the 0,0,½-Mg site are identical. Moreover, Mg and Ca are geochemically similar. Both are divalent, very mobile, and suitable for six-fold coordination, although Ca is at the upper ionic size limit accepted in that site. The principal difference between the two atoms is size. Ca (ionic radius = 0.99 A), is 50 percent larger than Mg (ionic radius = 0.66 A), and thus not within the size range

Table 7. Distortion parameters for the octahedra in the calcium–magnesium carbonates

Polyhedral	Calcite	Dolomite		Magnesite	Mg-calcite
	Ca	Ca	Mg	Mg	Ca-Mg
Quadratic elongation	1.0017	1.0016	1.0008	1.0009	1.0020
Longitudinal strain	0.0053	0.0049	0.0024	0.0028	0.0060
Shear strain	0.5092	0.4883	0.3394	0.3666	0.5374
Total distortion	0.5146	0.4932	0.3418	0.3694	0.5434

Values were calculated using the "Distort" program written by Dr. Martha Hamil (personal communication).

of normal substitution. Mg, being the smaller ion, should be favored over Ca to enter the structure. However, the hydration of Mg (Lippmann, 1973) largely prevents this, and only minor amounts are incorporated. Because Mg and Ca are similar, and the two lattice sites are identical before ordering, no site preference is ordained unless ionic size becomes important. Consequently, Mg enters the structure randomly and disordered magnesian calcite results—the phase found in modern carbonates. Nevertheless, if ordering of the two ions could be induced, some dolomite would result. The key to dolomite formation may therefore be the preexistence of metastable magnesian calcite.

We have already seen that dolomite is the most ideal carbonate structure, but hydration of Mg and the problem of ordering the Ca and Mg within the structure combine to prevent dolomite precipitation. However, once metastable magnesian calcite is formed, an increase in pressure may cause sufficient additional disequilibrium to produce dolomite. In other words, a pressure increase could induce ordering of the Ca and Mg to form dolomite from magnesian calcite.

According to the Le Chatelier-Braun principle, an increase in pressure will favor an increase in density and a decrease in volume. Dolomite (2.85) is, of course, denser than calcite (2.72). The size difference between Ca and Mg allows closer packing in dolomite, because the two ions are segregated in discrete alternating layers. This closer packing more than compensates for the low atomic weight of Mg. Significantly, ordering the two ions in the magnesian calcite will produce some dolomite. Thus, in response to pressure increase, ionic size becomes important, because closer packing and density increase result when Ca and Mg are segregated into different lattice sites, producing dolomite.

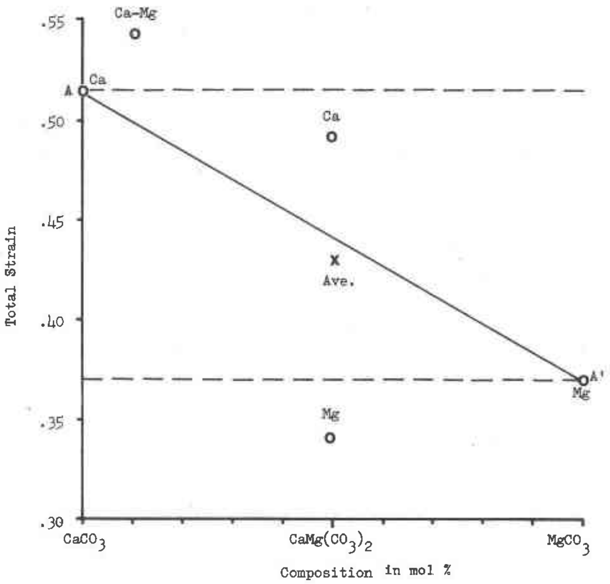


Fig. 2. Total distortion values (from Table 7) for octahedra are plotted against the mineral composition of the different carbonates. Line *A–A'* indicates the maximum amount of total octahedral distortion allowable for stability in the calcite–magnesite solid-solution series. Dashed lines represent maxima for individual calcium and magnesium octahedra in any hexagonal carbonate structure. The average value of the calcium and magnesium octahedra in dolomite is indicated with an *x*.

The ordering of Mg and Ca in the structure to form dolomite also results in a volume decrease. Consequently, ordering, and thus dolomite formation, is again favored by increased pressure. This volume decrease is illustrated in Figure 3. The volume of dolomite falls below the calcite–magnesite volume curve, and is also less than that of a disordered structure of dolomite composition. The volume of a mixture of 50 percent calcite and 50 percent magnesite (#5 on Fig. 3) is also greater than that of dolomite. Therefore, ordering Mg and Ca to form dolomite produces an even greater volume decrease than formation of calcite plus magnesite. Clearly the formation of dolomite from magnesian calcite with an attendant density increase and volume decrease would be favored by increasing pressure. The metastable nature of the magnesian calcite makes it sensitive to additional disequilibrium and thus susceptible to dolomitization.

Hydrostatic pressure leads to a change in volume. Biogenic or precipitated magnesian calcite which is formed in shallow water and subsequently removed to a higher-pressure environment by settling to the sea floor, reef subsidence and so on, can form dolomite by (1) ordering of the Mg already in the structure and (2) cation exchange of Mg from sea water for Ca in the structure. The resultant dolomite structure closely approaches an ideal atomic arrangement as seen above, is more dense, and occupies less volume than its precursor—metastable magnesian calcite.

Many previous workers have concluded that dolomitization must proceed by solution of preexisting $CaCO_3$ and subsequent precipitation of dolomite. This process presents problems, however. Several authors have suggested that an elevated Mg/Ca ratio, produced by evaporation of sea water to the point of gypsum precipitation, causes calcite to dissolve and dolomite to simultaneously precipitate. Upon evapo-

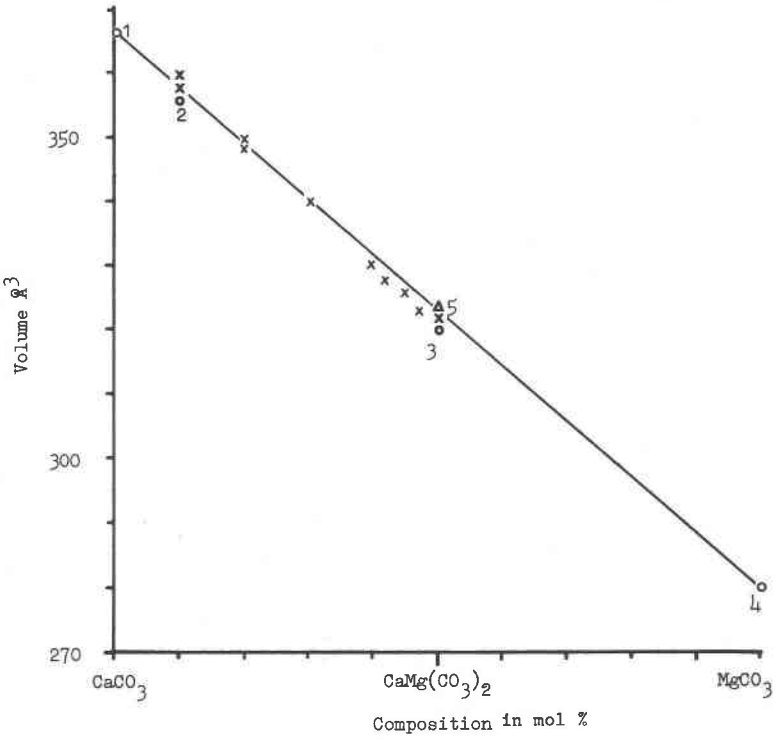


Fig. 3. Molar volumes of ordered and disordered calcium–magnesium carbonates. 1. Calcite calculated from Chessin *et al.* (1965). 2. Magnesian calcite, this paper. 3. Dolomite, this paper. 4. Magnesite calculated from Oh *et al.* (1973). 5. Mixture of 50% calcite and 50% magnesite. *x*. Disordered compositions calculated from Table 3 of goldsmith *et al.* (1961).

ration of sea water, carbonate is precipitated out early as $CaCO_3$, precluding Mg dehydration by activated CO_3^{2-}. Gypsum does not form until sea water has evaporated to about one-fifth of its original volume. It is, moreover, too soluble to secure a sufficiently low concentration of dissolved Ca to favor solution of $CaCO_3$ (Lippmann, 1973). It therefore seems unlikely that $CaCO_3$ will dissolve in supersaline brines. Similarly, it is unlikely that it will dissolve in sea water which is supersaturated with respect to calcite, aragonite, and dolomite. Solution of $CaCO_3$ as a precursor to dolomite precipitation is chemically unrealistic in most marine environments.

Another difficulty with a solution-precipitation mechanism is, again, dehydrating and ordering the Mg. As discussed above, ordering of the Mg and Ca in the dolomite structure is logical only when size becomes important, as in the case of increased pressure on a solid. In addition, Lippmann's mechanism of dehydrating Mg in the presence of activated CO_3^{2-} takes place only after an ion is adsorbed onto the crystal surface. Since Ca and Mg are both likely to be adsorbed, incorporation of Mg would be more favored as pressure increases. Mg would then be preferentially absorbed into the structure and ordered, and some Ca expelled, in response to increased pressure on preexisting metastable magnesian calcite.

By analogy to the norsethite experiments, Lippmann (1973) concluded that dolomitization proceeded according to reaction (2) from ionic species. It is noteworthy that he was unable to precipitate even norsethite directly from solutions containing sizable amounts of all component ions. Rather, he obtained norsethite by reacting solid $BaCO_3$ with Mg-bearing solutions in the presence of excess CO_3^{2-}. Increased pressure as a mechanism to induce ordering would be unnecessary because the Ba and Mg sites are so different. Perhaps Lippmann's analogous dolomite experiments failed partly because they were performed at a pressure of 1 atmosphere, which does not favor ordering. An additional problem with solution-precipitation according to equation (2) is the attendant volume increase of approximately 45 percent which Lippmann noted. Preservation of relic grain textures in dolomite crystals also is compelling evidence for solid-state transformation of magnesian calcite to dolomite.

Ion diffusion and exchange, which are essential for conversion of magnesian calcite to dolomite in response to pressure increase, are, of course, slow processes. Mg in calcite, however, distorts the structure. The resultant exaggerated thermal vibrations of ions (Table 5) reduce the firmness with which the atoms are bound within the structure. Because of weakened bonding, ion exchange and ordering occur more readily in magnesian calcite than in the more strongly bonded pure calcite.

Thermal vibrations in another structure containing Mg in six-fold coordination was investigated by Hazen (1976). He refined the periclase structure at elevated temperatures and pressures. As expected, increased temperature augmented thermal motion, but increased pressure did not alter the thermal parameters. It may not, therefore, be argued that increased pressure would also increase bond strength by reducing thermal vibration and thus bond stretching.

In addition to the weakened bonding, Sr, a minor constituent in calcite, further degrades the magnesian calcite structure because it is too large for six-fold coordination. With increased pressure it becomes even more unsuitable and would be replaced by Mg.

Sea water aids dolomite formation by supplying ample Mg and facilitating ion mobility. The open nature of the calcite structure allows ion migration throughout the structure. As dolomitization proceeds, however, the structure becomes more compact, making ion diffusion increasingly difficult and entrapping excess Ca. Naturally-occuring dolomites are not stoichiometric, but rather contain a slight excess of Ca.

Murray and Lucia (1967) noted a selective dolomitization of units which initially contained abundant carbonate mud. They suggested that the more soluble carbonate mud was dissolved and dolomite precipitated in its place. The greater ratio of surface area to volume in fine-grained crystals indeed does allow for greater solubility. However, the surface-area-to-volume ratio would also allow a faster rate of dolomite formation, since less ion diffusion is required. Therefore, fine-grained material may be selectively dolomitized by ion exchange and ordering rather than solution-precipitation, for reasons discussed earlier.

To summarize, Mg in calcite distorts the structure, rendering it metastable. The increased thermal vibrations of the atoms weaken bonding and facilitate ion mobility. An increased pressure, then, would favor ordering and ion exchange in magnesian calcite, forming dolomite, since the volume decreases, the density increases, and a better, undistorted structure results.

Of course, pressures attainable in the marine environment are generally less than 1 kbar. Because magnesian calcite is so metastable, increases in hydrostatic pressure of perhaps 20 bars over geologic time may be sufficient to produce dolomite. In fact, the dolomitization process discussed here is a low pressure and temperature metamorphic-type reaction between metastable magnesian calcite and sea water in response to an increase in pressure. Significantly, low temperature also favors ordered phases over disordered ones. Theoretically, then, magnesian carbonate rocks can indeed be dolomitized in sea water. In effect, increased pressure may render sea water a dolomitizing solution.

Similarly, dolomite can form under metamorphic conditions due to burial. Increased pressure would again favor volume decrease and density increase. Interstitial sea water would supply additional Mg for dolomitization. The increased temperature would increase thermal vibrations of the ions, further weakening bonds and promoting rapid ion exchange. Without the addition of Mg a magnesian calcite can still exsolve dolomite under metamorphic conditions (Goldsmith, 1960). A calcite containing 10 mole percent $MgCO_3$ can produce a final mineral composition of up to 20 mole percent dolomite and 80 mole percent calcite. Previously-formed dolomite could also recrystallize.

Exsolved dolomite in calcite has been observed in medium- and high-grade metamorphic rocks (Joplin, 1935; Coomaraswamy, 1902). Perhaps a modest increase in pressure in the marine environment might cause a similar exsolution of dolomite from magnesian calcite. Yet exsolution lamellae may be too fine to detect with the petrographic microscope; transmission or scanning electron microscopy might be needed. Exsolution lamellae may have been mistaken for the twinning commonly exhibited in dolomitized carbonate units. Exsolution textures have been mistaken for twinning in plagioclase (Smith, 1974). The absence of exsolution lamellae would not disprove pressure-induced dolomite formation in sea water. Many dolomitized units are so fine-grained that the dolomite can be detected only by X-ray analysis. The textural relationships between the dolomite and calcite are indeterminate and may be related, in part, to exsolution. In addition to cation-ordering exsolution, dolomitization can also involve replacement of calcite by ion diffusion. Calcite–dolomite textures closely resemble replacement textures in metamorphic rocks.

The vuggy nature of dolomitized rock is characteristic. Molar volume of a carbonate unit can be reduced 12.8 percent upon dolomitization. The reduction of bulk volume would increase void space and thus reduce pore pressure, particularly in a confined unit. Reduced pore pressure would promote or at least allow accumulation of hydrocarbons or ore fluids in these units. In the rock record, ores and hydrocarbons are commonly found in dolomitized units.

Without an increase in pressure on magnesian calcite, a very different reaction will result. A magnesian calcite formed in and remaining in shallow water will approach greater stability by expelling the Mg from the structure and replacing it with Ca. This occurs because a volume decrease and density increase is not favored. Chave (1952) noted that the Mg content of calcite falls to one or two percent within a few tens of millions of years under near-surface conditions. Similarly, magnesian calcite uplifted into the zone of fresh-water interaction rapidly loses Mg (Berner, 1971). Since fresh water contains greater concentrations of Ca than Mg, Mg diffuses out of the structure. Towe and Hemleben (1976) have observed Mg loss from skeletal magnesian calcite without alteration in the crystal morphology. They also suggest a cation exchange reaction. Again, since volume decrease and density increase are not favored, greater stability is achieved by normalizing the calcite structure.

Although dolomite is a more stable structure than calcite, calcite is still sufficiently stable to persist in most marine environments. Consequently, the amount of Mg in the calcite is undoubtedly important regardless of pressure conditions. A calcite containing less than a certain percentage of Mg can reach stability most easily by expelling the Mg from the structure. With increasing pressure it is probable that approximately 10 mole percent $MgCO_3$ in the calcite structure will favor formation of dolomite rather than low-magnesian calcite. The above refinement of magnesian calcite clearly indicates that 10 mole percent $MgCO_3$ is sufficient to produce an extremely metastable structure. This value is also suggested by the divergence between theoretical and experimentally-determined cell-dimension curves in the calcite–magnesite series established by Goldsmith *et al.* (1961). Structural refinements of additional low-magnesium calcites should establish a better threshold value.

Increased pressure has been theoretically considered here as an activating force for dolomite formation. Two other processes can be suggested for the marine environment. Locally-elevated water temperature due to volcanic activity may allow dolomite precipitation from sea water. The additional heat energy accelerates ion movement, which may in turn dehydrate Mg by bond stretching between Mg and H_2O dipoles and/or increased incidence of collisions dislodging H_2O dipoles. In this higher-energy environment, Ca and Mg would be ordered in the dolomite structure, simply because it is the best possible arrangement and the elevated temperature allows the two ions to reach their proper sites rapidly. The volcanic environment is the closest natural analog to dolomite formed in the laboratory at temperatures above 100°C. Dolomite may also form by shock-induced ordering caused by hurricane-force wave action on magnesian calcite in the supratidal zone. Wave activity and indeed water circulation may mechanically dehydrate Mg by collision dislodgement of H_2O dipoles. Both hypotheses merit further investigation.

The hypotheses discussed here are based on the crystal chemistry of the common carbonate minerals, in conjunction with basic geochemical concepts. Emphasis has been placed on the mechanisms or processes of dolomite formation in relation to pressure as well as temperature and chemical conditions probable in marine environments. It still remains to apply these theories to field data for corroboration.

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