STRUCTURAL REFINEMENTS OF DOLOMITE AND A MAGNESIAN CALCITE

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ABSTRACT OF THE THESIS

Structural Refinements of Dolomite and a Magnesian Calcite

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The structures of dolomite and a calcite containing 10 mol % $MgCO_3$ were anisotropically refined using single-crystal x-ray techniques. Cell constants and bond lengths were determined as: $\underline{a}$ = 4.803 Å, $\underline{c}$ = 15.984 Å,, $\underline{V}$ = 319.3 Å^3, Ca-O = 2.378 Å, Mg-O = 2.081 Å, and C-O = 1.283 Å for dolomite; and $\underline{a}$ = 4.941 Å, $\underline{c}$ = 16.864 Å, $\underline{V}$ = 356.6 Å^3, M-O = 2.331 Å, and C-O = 1.276 Å 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 calcium and magnesium in dolomite than in the other carbonate structures. Substitution of magnesium into the calcite structure distorts the octahedra diminishing cation shielding. This results in exaggerated thermal motion of the ions and bond weakening.

Acknowledgements

I would like to thank Dr. Roger Lalancette of the Chemistry Department at Rutgers, Newark for his assistance with the crystallographic aspects of this work, and Dr. Martha Hamil for serving as my advisor on this project. Thanks are also extended to Dr. Edward Olsen and Dr. Julian R. Goldsmith for their donation of samples which were used for crystal refinements.

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INTRODUCTION

Despite the abundance and economic importance of dolomite, the origin of this mineral is not well understood. Although thermodynamics, kinetics, and chemical activities have been considered in an effort to understand the origin of dolomite, crystal chemical aspects have been neglected. Most ancient carbonate rocks are composed of low-magnesium calcite and dolomite but modern carbonate sediments contain high-magnesium calcite and aragonite (Berner, 1971). Therefore, the crystal structures of dolomite and magnesian calcite are examined and compared to those of calcite and magnesite.

STRUCTURAL REFINEMENT OF DOLOMITE

Introduction

Steinfink and Sans (1959) performed the most recent refinement of the dolomite structure. They reported hexagonal cell constants of $\underline{a}$ = 4.815 Å, and $\underline{c}$ = 16.119 Å, and determined that dolomite belongs in space group $R\bar{3}$. They assigned calcium to site 3(a), magnesium to site 3(b), carbon to site 6(c) and oxygen to site 18(f). Atom positions were given as in Table 1. Also reported were bond lengths (Table 2). However, bond lengths calculated using Steinfink and Sans' cell parameters and atom positions disagree with those they reported (Table 2).

Every effort was made to reproduce their bond lengths, including sign changes and transposition of their oxygen $\underline{x}$ coordinate from 0.2374 to 0.2734. This transposition of their $\underline{x}$ coordinate produced an oxygen atom position very similar to that herein determined (Table 1) but did not result in bond lengths Steinfink and Sans reported. Perhaps they transposed their numbers such that the C-O bond distance was reported as 1.283 Å instead of 1.238 Å, a value closer to that calculated using their atom positions (Table 2). The Ca-O bond length they reported equals the sum of the ionic radii; the Mg-O bond length is spurious. Attempts to contact Steinfink and Sans also were unsucessful.

Since Steinfink and Sans' refinement was only two-dimensional, based on single crystal film data, and their bond lengths were inconsistent with their atom positions, a new refinement was justified.

Experimental Procedure

A cleavage rhomb 0.18 mm X 0.20 mm X 0.25 mm of dolomite from

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

		Dolomite	Dolomite[1]	Calcite[2]	Mg-calcite	Magnesite[3]
Ca	x	0	0	0	0	
	y	0	0	0	0	
	z	0	0	0	0	
	β11	0.0055(5)			0.0249(4)	
	β33	0.00038(7)			0.00153(4)	
Mg	x	0	0		0	0
	y	0	0		0	0
	z	$\frac{1}{2}$	$\frac{1}{2}$		0	0
	β11	0.0041(9)			0.002(3)	0.0063(4)
	β33	0.0004(1)			0.0002(3)	0.00060(3)
C	x	0	0	0	0	0
	y	0	0	0	0	0
	z	-0.2423(2)	0.2435(3)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	β11	0.0050(15)			0.0178(17)	0.0072(8)
	β33	0.0001(1)			0.0013(1)	0.00052(6)
O	x	0.2829(3)	0.2374(6)	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)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	β11	0.0041(19)		0.00524(59)	0.027(1)	0.0059(3)
	β22	0.0100(15)		0.01775(90)	0.049(2)	0.0091(4)
	β33	0.0008(1)		0.00104(5)	0.0028(1)	0.0083(3)
	β12	0.0041(15)				
	β13	-0.0003(1)				
	β23	-0.0009(1)		-0.00218(19)	-0.0026(4)	-0.00027(9)

1. Steinfink and Sans (1959)
2. Chessin et al (1965)
3. Oh et al (1973)

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

Table 2. Bond lengths in dolomite

Bond	Reported*	Calculated**
Ca-O	2.390(4) Å	2.413 Å
Mg-O	2.095(4) Å	2.121 Å
C-O	1.283(4) Å	1.235 Å

* Bond lengths reported by Steinfink and Sans (1959).
** Bond lengths calculated using cell parameters and atom positions reported by Steinfink and Sans (1959) in ORTEP (Johnson, 1965).
(Estimated standard deviations are given in parentheses and refer to the least significant figures.)

Binnenthal, Switzerland was mounted on the end of a glass fiber with epoxy cement for data collection using a Syntex $P2_1$ four-circle computer-controlled automatic diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. Dr. Edward Olsen of the Field Museum supplied this sample. Table 3 contains the chemical analysis of this dolomite.

In this work, a right-handed hexagonal unit cell orientation was chosen so that the highest-intensity reflection could be indexed as $hkl = 10\bar{4}$, thus having the same orientation as in the calcite (Chessin, Hamilton and Post, 1965) and magnesite (Oh, Morikawa, Iwai and Aoki, 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: $a = 4.8033(9)$ Å, $c = 15.984(4)$ Å, $V = 319.3(1)$ Å^3. (Standard deviations in the least significant figures, in the text and tables, are given in parentheses.)

Intensity data were collected at 24°C employing the θ-2θ scan technique with a scanning speed of $2\frac{1}{2}°$/min.. Three standard reflections were measured every 47 reflections and showed a maximum random variation of $\pm 1.3\%$. 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; independent thermal parameters, two each for calcium, magnesium and carbon, and six for oxygen; x, y and z positional parameters for oxygen, and the

Table 3. Chemical analyses 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

z positional parameter for carbon.

Structural refinement was performed on 178 unique reflections by the full-matrix least squares method using the ORFLS (1962) program. Atomic scattering factors were taken from the Dirac-Slater calculations of Cromer and Waber (1965). The anomalous parts of the magnesium and calcium 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% indicated that their atom positions were based on a unit cell rotated approximately 180° about the a axis chosen in this work. By transforming appropriate atom position signs, the absolute values 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 (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 4 contains the observed and calculated structure factors. The interatomic bond lengths and angles are presented in Table 5 along

Table 4. Observed and calculated structure factors for dolomite.

H	K	FO	FC
L= 0			
-1	2	53	50
1	4	36	35
2	-4	49	46
3	-3	86	88
4	1	54	55
L= 1			
-4	-2	12	11
-3	-1	13	13
-3	2	44	42
-2	3	37	32
-1	1	15	13
0	-4	12	12
2	-2	43	40
2	4	4	3
3	-4	4	4
L= 2			
-4	3	4	4
-3	-2	31	31
-2	-4	23	23
-2	-1	45	43
-2	2	76	74
0	1	23	20
0	4	3	2
2	-3	70	70
2	3	43	43
4	-1	34	36
4	2	33	35
L= 3			
-4	-1	11	11
-3	-3	4	4
-3	0	2	2
-1	-4	2	1
-1	-1	76	80
0	0	3	2
-2	1	51	45
-3	3	15	13
-4	2	21	21
1	4	14	14
3	3	10	11
L= 4			
-4	4	76	77
-4	-2	27	27
-3	-1	81	87
-3	2	60	56
-2	-3	23	21
-1	-2	50	47
1	0	102	125
2	-2	45	46
2	4	35	35
3	-4	52	51
3	2	43	43
L= 5			
-3	-2	19	19
-2	-4	14	15
-2	-1	13	12
-1	-3	25	25
0	1	36	35
0	-2	11	8
1	-4	16	16
1	2	50	49
2	3	21	21
4	2	26	26
4	-4	16	16
L= 6			
-4	-1	12	12
-3	-3	27	27
-2	-2	41	42
-1	-4	31	31
-1	-1	59	61
0	0	54	51
1	1	80	86
1	4	31	30
2	2	38	37
3	0	13	12
3	-3	15	14
3	3	25	25
4	1	14	14
L= 7			
-4	-2	20	20
-2	-3	16	16
-1	-2	46	46
-1	4	3	2
0	-4	3	3
0	-1	11	10
0	2	6	4
2	1	15	14
2	4	11	11
3	2	16	16
3	-4	17	17
L= 8			
-4	0	61	68
-3	-2	34	34
-3	1	30	27
-2	-4	31	31
-2	-1	56	60
-1	-3	41	41
0	1	89	92
2	0	50	47
2	3	33	33
3	1	71	70
4	2	18	18
L= 9			
-4	-1	11	11
-4	2	2	1
-3	-3	12	13
-2	-2	17	18
-2	1	48	47
-1	-4	15	15
0	-3	15	15
0	0	47	45
1	4	7	5
2	-1	31	29
3	-3	26	26
3	3	7	7
4	1	18	19
L=10			
-2	-3	44	46
-1	-2	38	38
-1	4	2	2
0	-4	3	3
1	0	25	24
2	-2	55	57
2	1	43	43
3	-4	26	25
3	2	21	21
L=11			
-3	1	14	14
-2	-1	22	22
-1	-3	5	5
-1	0	5	5
0	4	4	4
1	-4	4	4
2	0	24	24
2	3	32	32
L=12			
-4	-1	42	44
-2	-2	33	32
-2	1	25	22
-1	-4	27	27
0	-3	58	59
0	0	95	106
1	4	30	29
2	-1	51	50
2	2	40	39
3	-3	53	56
4	1	38	40
L=13			
-3	-1	23	24
-2	-3	25	26
-2	3	12	11
0	-1	19	18
1	-3	26	26
2	-2	20	19
3	-4	6	6
3	2	5	5
4	0	24	25
L=14			
-3	-2	25	26
-1	-3	29	29
-1	0	25	25
0	-2	36	36
2	-3	48	49
2	3	20	20
3	-2	21	21
3	1	4	3
4	-4	5	5
L=15			
-3	3	2	0
-2	4	3	1
-1	-1	30	30
0	0	19	18
0	3	7	7
1	-2	9	9
2	-4	12	11
L=16			
-3	2	29	29
0	-4	44	45
1	0	52	51
2	-2	27	27
3	-1	38	38
3	-4	34	35
4	-3	46	49
L=17			
-1	-3	20	20
-1	3	5	5
0	1	23	23
1	-4	23	24
1	2	23	23
L=18			
-2	-2	26	27
-1	2	21	21
0	-3	12	12
0	0	4	4
1	1	44	45
2	-4	19	20
3	-3	15	16

Table 5. Interatomic distances and angles in the calcium-magnesium carbonates

	Dolomite	Calcite[1]	Mg-calcite	Magnesite[2]
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*
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 calculated employing ORFFE (Busing et al, 1964).
1. Calculated from Chessin et al (1965) employing ORTEP (Johnson, 1965) except for the C-O bond length which they reported.
2. Oh et al, (1973)
* Oh et al (1973) reported this distance as 2.850 Å which is the distance between two oxygen atoms in positions: x,0,$\frac{1}{4}$ and 2/3 -x, 1/3 -y, 1/3 -z and thus not the O_1-O_2 atoms which must be co-planar in the z plane.
(See Figure 1 for atom designation.)
(Estimated standard deviations are given in parentheses and refer to the least significant figures.)

Table 6. Root mean square component of thermal displacement along principal axis R of the thermal ellipsoids and the angle each makes with the c axis

Atom	R	Dolomite	Calcite[1]	Mg-calcite	Magnesite[2]
Ca	1	0.069(10)		0.1489(21)	
	2	0.069(14)		0.1520(10)	
	3	0.070(6)		0.1520(10)	
Mg	1	0.0606(44)		0.0471(1)	0.072(4)
	2	0.0608(56)		0.0471(489)	0.072(4)
	3	0.0751(87)		0.0597(482)	0.083(4)
C	1	0.039(26)		0.1285(63)	0.077(8)
	2	0.0667(13)		0.1288(145)	0.077(8)
	3	0.0667(126)		0.1406(100)	0.077(8)
O	1	0.053(11)	0.032	0.1363(59)	0.063(7)
	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)
Ca	1	90		0	
	2	90		90	
	3	0		90	
Mg	1	90		90	90
	2	90		90	90
	3	0		0	0
C	1	0		90	90
	2	90		90	90
	3	90		0	0
O	1	91.3(6.7)	90	89.9(2.6)	90
	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 (Busing et al, 1964).

1. Chessin et al (1965)
2. Oh et al (1973)

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

with those of calcite and magnesite, and the thermal ellipsoid parameters are found in Table 6.

A final difference Fourier synthesis produced a general background of approximately 0.3 e $Å^{-3}$, with no peaks greater than 0.5 e $Å^{-3}$, confirming that the atoms are properly located and no extra atoms are in the structure.

STRUCTURAL REFINEMENT OF A MAGNESIAN CALCITE

Introduction

For purposes of comparison, a magnesian calcite structure was also 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 mol % $MgCO_3$ in solid solution, was previously used in Dr. Goldsmith's study of dolomite exsolution from calcite (1960). Although magnesian calcite is a common constituent of carbonate sediments, experimental work on the calcite-magnesite system (Goldsmith, 1960; Graf and Goldsmith, 1955, 1958; Harker and Tuttle, 1955; and Goldsmith and Graf, 1958) indicates that magnesian calcite is metastable at surface temperatures.

Experimental Procedure

The procedure used to refine the magnesian calcite was as described above for dolomite. Again, the cell was chosen such that $\underline{hkl} = \underline{10\bar{4}}$ 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: $\underline{a} = 4.941(2)$ Å, $\underline{c} = 16.864(2)$ Å, $\underline{V} = 356.60(22)$ Å 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 $\pm 3.3\%$. Lorentz and polarization corrections were applied to the observed structure factors.

The 12 variable parameters are: scale factor; independent thermal parameters, two each for calcium, magnesium and carbon, and four for oxygen; and the $\underline{x}$ positional parameter for oxygen.

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 calcium and magnesium were allowed to vary. However, no improvement resulted thus confirming that the 0,0,0 site indeed contained 90 mol % calcium and 10 mol % magnesium. Final positional and thermal parameters from the least-squares refinement and their standard deviations are listed in Table 1 along with those of calcite and magnesite. The interatomic bond lengths and angles and the thermal ellipsoid parameters are found in Tables 5 and 6 respectively. The observed and calculated structure factors are presented in Table 7.

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

Table 7. Observed and calculated structure factors for magnesian calcite

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

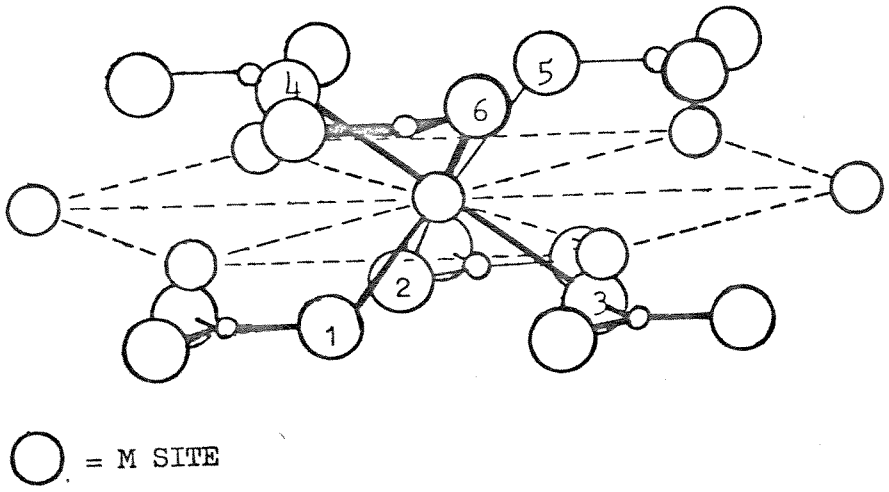
COMPARISON OF THE CARBONATE STRUCTURES

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. Dolomite, however, is highly ordered such that calcium and magnesium atoms alternate in the six-fold site along any three-fold axis, thus eliminating the two-fold axis of rotation which intersects the carbon atoms in calcite. In dolomite, each oxygen in a carbonate group also coordinates with one calcium and one magnesium. The cations coordinate with six oxygens, each from a different carbonate group (Figure 1).

The predicted Ca-O bond length of 2.39 Å, the sum of the ionic radii in six-fold coordination, is closely approximated in the dolomite structure (Table 5) but is considerably shortened in the calcite structure (Table 5). Similarly the O-M-O interatomic angles about both calcium and magnesium in dolomite closely approach 90° resulting in octahedra more ideal than those same octahedra in calcite and magnesite respectively (Table 5).

The M-O bond length in magnesian calcite (2.331 Å) is exactly equal to the sum of 90% of the Ca-O bond length in calcite and 10% of the Mg-O bond length in magnesite. This indicates that magnesium occurs as magnesite molecules in the calcite structure. It is more correct to consider magnesian calcite as a mixed crystal rather than a solid solution. Again, in order to accomodate both calcium and magnesium in the same site, the O-M-O interatomic angles in the magnesian calcite are the least ideal of the carbonates herein discussed (Table 5).

Figure 1. Sketch of the octahedral site in the calcium-magnesium carbonates



(After Oh et al, 1973)

The greater regularity of the octahedra in dolomite is further indicated by the thermal ellipsoid of oxygen. In calcite the thermal ellipsoid is compressed along the a axis and is extremely elongated in one direction (Table 6). The oxygen thermal ellipsoid in dolomite has a similar configuration but with less pronounced extremes (Table 6). In calcite, the calcium is not sufficiently shielded by oxygen (Oh et al, 1973). However, the oxygen configuration in dolomite provides better cation shielding as evidenced by the thermal ellipsoids (Table 6). The oxygen thermal ellipsoid is most regular in magnesite (Table 6). However, each oxygen in the dolomite structure is a corner shared by a calcium octahedron and a magnesium octahedron whereas in magnesite all octahedra are identical.

The thermal ellipsoids in magnesian calcite further reflect that mineral's metastability. The thermal motions of the calcium, carbon and oxygen atoms are extremely large in comparison to those in the other carbonate minerals (Table 6). The thermal ellipsoid of calcium is flattened along the c axis. This reflects the shortening of the c axis by the substitution of magnesium for calcium in the structure. Moreover, the exaggerated thermal motion of the ions about their rest positions causes periodic stretching and attendant weakening of the bonds in the structure. 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 parameters of the carbon and oxygen atoms (Table 1) and the O-C-O interatomic angles (Table 5).

The carbon atom lies slightly above the plane of the three oxygens as in the orthorhombic carbonates (deVilliers, 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 6) reflecting its slight out-of-plane location.

The C-O bond lengths in calcite, magnesite, and dolomite are equal (Table 5). However, in magnesian calcite, the C-O bond length is slightly shortened resembling that of another metastable carbonate, calcite (II), which has a C-O bond length of 1.274 Å (Bassett and Merrill, 1973).

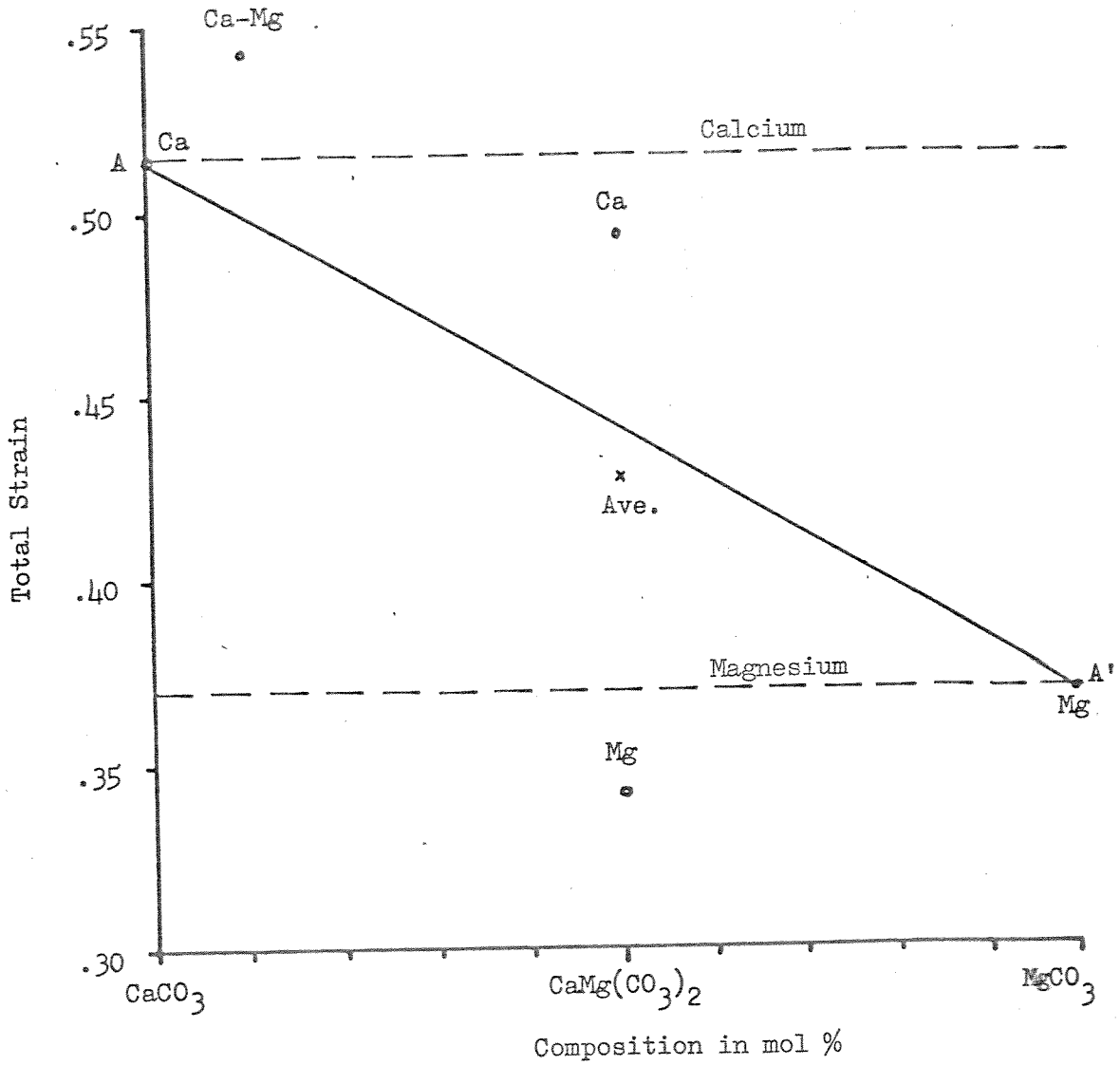
Distortion parameters were calculated for the octahedra in each of the four carbonates using the appropriate bond lengths and angles in the "Distort" program written by Dr. Martha Hamil (personal communication) (Table 8, Figure 2). All distortion parameters are greatest for the Ca-Mg octahedron in magnesian calcite. Because of the known stability of calcite and magnesite, the line A-A' on Figure 2, connecting their octahedral distortion values, should represent the maximum amount of total octahedral distortion allowable for stability in the calcite-magnesite solid-solution series. Any value, averaged over all octahedra in a structure, which falls above line A-A' indicates metastability. The individual calcium and magnesium octahedra may be similarly evaluated. Specifically, the total distortion of the calcium octahedron in calcite and that of the magnesium 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 calcium octahedron in a hexagonal carbonate indicates excessive distortion and thus instability.

Table 8. 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).

Figure 2. Total distortion of octahedra in the calcium-magnesium carbonates



Total distortion values (from Table 8) 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. Ca = calcium octahedron, Mg = magnesium octahedron, x = average value of the calcium and magnesium octahedra in dolomite.

The value for the Ca-Mg octahedron in magnesian calcite falls well above line A-A' as well as above the values for individual calcium and magnesium octahedra (dashed lines on Figure 2) and thus is metastable. However, in dolomite, both the calcium and magnesium octahedral values fall below their respective maxima, and their average value falls below the maximum-distortion-for-stability line, A-A' (Figure 2). Thus it is evident that the calcium and magnesium 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 both ions. 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 carbonate structures examined. The octahedra in dolomite are the least distorted and provide the best cation shielding for both calcium and magnesium in a carbonate mineral. On the other hand, distortion of the octahedral site, exaggerated thermal motion of ions and bond weakening are characteristic of the metastable magnesian calcite.

CONCLUSIONS

Examination of all structural parameters of the calcite, dolomite, magnesian calcite and magnesite structures indicate that dolomite can accomodate both calcium and magnesium in a more ideal structure than either of the single carbonate structures. Furthermore, magnesium substituting in the calcite lattice distorts the structure rendering it metastable. The metastable nature of magnesian calcite together with the suitability of the dolomite structure to contain both calcium and magnesium may be significant in understanding dolomite formation.

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