

RELATION BETWEEN LATTICE CONSTANTS AND COMPOSITION OF THE Ca-Mg CARBONATES

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ABSTRACT

Synthetic magnesian calcites containing 4.94, 9.89, 14.83, and 19.78 mol per cent MgCO_3 in solid solution were prepared by solid-state reaction of pelletized mixtures of CaCO_3 and basic Mg carbonate at temperatures between 800° and 860° C. Spectrographic analyses of the Mg content of these solid solutions, using copper spark and *d.c.* arc methods, gave results which were, with one exception, within ± 7 per cent of the true values.

Dolomite crystals from five localities were analyzed by wet chemical methods, and gave molar compositions ranging from $\text{Ca}_{0.4940}(\text{Mg, Fe, Mn})_{0.5060}$ to $\text{Ca}_{0.5063}(\text{Mg, Fe, Mn})_{0.4937}$.

Values of a_0 and c_0 for magnesian calcites, the dolomites, and a synthetic magnesite were obtained from *x*-ray diffractometer and film measurements. The spacings of $d_{633(30-12)}$, the third order of the strongest reflection, measured on the diffractometer agree with those computed from measured values of a_0 and c_0 . The synthetic magnesite has $a_0 = 4.6330 \text{ \AA}$, $c_0 = 15.016 \text{ \AA}$, $a_{r1} = 5.6752 \text{ \AA}$, $\alpha = 48^\circ 10.9'$.

The average a_0 for the dolomites studied is 0.092 per cent less than one-half the sum of a_0 values for calcite and magnesite, and the average c_0 value, 0.21 per cent less than the analogous hypothetical c_0 value. If the magnesian calcite curves are extrapolated to 50 mol per cent MgCO_3 , the comparable numbers are 0.98 per cent for a_0 and 0.44 per cent for c_0 . The implied smaller mole volume for the hypothetical disordered equivalent of dolomite must be viewed with skepticism, however, because of the length of the extrapolation and the fact that cell constants of the magnesian calcites were measured at room temperature, from 500° to 800° C. below the minimum temperature at which they are stable.

Compositions of single-phase materials between calcite and dolomite can be determined from c_0 values to within about 2 mol per cent MgCO_3 if mixed-layer effects do not occur.

INTRODUCTION

In an earlier paper (Goldsmith, Graf, and Joensuu, 1955) *x*-ray and compositional data were used to prepare several curves showing spacing versus composition for a number of naturally occurring magnesian calcites. Wet chemical analyses consistently gave higher magnesium values than did spectrochemical analyses. The spectrochemical analyses were used, largely because the homogeneous single-phase samples available were frequently quite small. The validity of determinations of composition from *x*-ray spacing, given later in that paper, were thus dependent upon the spectrochemical data.

In order to examine further the validity of our curves showing spacing

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versus composition, several synthetic magnesian calcites have been prepared and examined by spectrochemical analysis and powder x -ray diffraction. In addition, compositions and spacings of synthetic magnesite and five carefully selected dolomites have been obtained in order to evaluate more accurately the composition-unit cell relationships in the Ca-Mg carbonates.

PREPARATION OF MAGNESIAN CALCITES

The synthetic magnesian calcites were prepared by reacting pelletized mixtures of C. P. basic magnesium carbonate and Johnson and Mathey's "Specpure" CaCO_3 in cold-seal pressure vessels using the apparatus described by Graf and Goldsmith (1955). The runs were held one or two days at temperatures of 800° to 860° C. under CO_2 pressures sufficient to prevent decomposition of dolomite, typically 20,000 to 24,000 lbs./in.² The temperatures chosen for individual runs were sufficiently high to insure complete solid solution of the mixture (Graf and Goldsmith, 1955).

Initially runs were made using mixtures of calcium carbonate with MgO and with magnesite. Ca-Mg carbonate solid solutions could be obtained with both these mixtures, but equilibrium was much more readily established and results were more consistent when basic Mg carbonate was used instead. Only those materials prepared with basic Mg carbonate as a source of Mg were used for analytical determinations. The MgO content of the basic carbonate was determined by dead-burning a portion of the material.

Mixtures equivalent to 4.94, 9.89, 14.83, and 19.78 mol per cent MgCO_3 were weighed out, hand-mixed under alcohol in an agate mortar, and pressed into cylindrical pellets $3/16$ inch in diameter by $1/8$ inch long. Several runs were made of each composition in order to obtain the desired amount of material. At the completion of a run the furnace was quickly removed and an air blast applied to the hot end of the bomb. Powder x -ray diagrams were taken of each batch of pellets, and in a few cases it was found that a small but detectable amount of dolomite had formed by exsolution during cooling. Pellets containing dolomite were not used for measurement of x -ray spacings.

SPECTROCHEMICAL METHODS

The spectrochemical method used by one of us (Joensuu) for determining Ca and Mg is essentially that described in Goldsmith, Graf, and Joensuu (1955). The beads from the 900° C. fusions were ground with graphite (1:2), and placed in $1/8$ inch O. D. graphite electrodes which had been drilled to a depth of 8 mm. with a #46 drill. The electrodes were arced at 6 amperes using the gas jet (Stallwood arc) with carbon dioxide (Stallwood, 1954), and the following lines used for analysis:

Element	Wavelength, Å	Internal Standard	Concentration range wt. per cent
Mg	2782.9	Co 3072.3	0.1- 5
Mg	3096.9	Co 3072.3	0.5-20
Mg	3336.1	Co 3334.1	2 -25
Ca	2997.3	Ba 3071.6	20 -50

The samples were also analyzed spectrochemically for Mg using the copper spark method (Chodos). A sample weighing 25 mg. was dissolved in 1 per cent HCl and 10 ml. of an internal standard solution containing 0.25 g. ammonium molybdate/liter was added. The volume of the solution was adjusted to 25 ml. with 1 per cent HCl, and 0.1 ml. of the solution was then transferred to the top of a copper electrode and evaporated under an infrared lamp. The residue was sparked for 30 seconds using a low resistance, low inductance, and low capacitance spark from the Jarrell-Ash Varisource, and the spectrum was photographed on III-O plates. The line pair Mg 3838.3/Mo 3903.0 was used. Standards were made from National Bureau of Standards Dolomite (#88) diluted with high-purity calcium carbonate.

MAGNESIAN CALCITE ANALYSES

The results of spectrochemical analysis of the synthetic magnesian calcites are given in Table 1. With only one exception, the average value for MgCO₃ obtained from multiple analyses differs less than ± 7 per cent from the actual amount present. The accuracy of these results would appear to be somewhat better than that usually attributed to spectrochemical analyses.

TABLE 1. SPECTROCHEMICAL ANALYSES OF SYNTHETIC MAGNESIAN CALCITES

Mol % MgCO ₃	Wt. % MgCO ₃	Wt. % MgCO ₃ *	Av.	Error (% of amount pres- ent)	Wt. % MgCO ₃ †	Av.	Error (% of amount pres- ent)	Wt. % CaCO ₃ ‡
4.94	4.50	5.10, 4.61, 4.51, 4.50	4.72	+4.9	4.8, 4.6, 4.5	4.6	+2.2	95, 96, 96
9.89	8.99	§(a) 7.28, 8.39, 8.08, 6.87	7.66	-14.8	10.0, 9.4, 9.4	9.6	+6.8	93, 86, 88
		§(b) 8.08, 8.84, 8.29, 8.95	8.53	-5.1				
14.83	13.48	(a) 13.70, 12.83, 13.00, 12.66	13.04	-3.3				
		(b) 14.22, 13.70, 13.18, 13.70	13.63	+1.1	13.6, 13.7, 13.8	13.7	+1.6	82, 84, 86
19.78	17.98	(a) 17.34, 19.76, 18.72, 20.63	19.10	+6.2				
		(b) 18.20, 19.07, 19.42, 17.34	18.52	+3.0	17.6, 18.2, 18.2	18.0	+0.1	80, 82, 85

* Reported as wt. per cent Mg. Analysis by A. A. Chodos.

† Reported as wt. per cent MgO. Analysis by O. I. Joensuu.

‡ Reported as wt. per cent CaO. Analysis by O. I. Joensuu.

§ The (a) (b) pairs for each composition represent different batches of pills prepared from the same original mixture.

CHEMICAL COMPOSITION OF SELECTED DOLOMITES

Five dolomites, from Serra das Eguas, Brazil, Hammondsville, Vermont, Gabbs, Nevada, Monroe County, New York, and Binnental, Switzerland, were selected for correlation of composition with unit cell dimensions. The criteria used in selecting these materials were the absence of extraneous phases, which would affect chemical analyses, relative freedom from cations in solid solution (especially Fe^{++} and Mn^{++}), which would affect unit cell size, and homogeneity throughout. The Hammondsville and Serra das Eguas materials were single cleavage pieces of water-clear material. The Binnental sample was made up of several water-clear crystals taken from the same cavity. The Gabbs material was obtained from a single somewhat milky cleavage piece, and the Monroe County sample was made up of a number of somewhat milky crystals taken from the same cavity.

In order to check the wet chemical procedures for Ca and Mg against an absolute standard, 1:1 and 4:1 molar mixtures of Illinois Geological Survey Spectrographic Standard CaCO_3 and Johnson and Mathey's "Specpure" MgO were prepared. The analytical results for these mixtures are shown in Table 2. The weight of material found gravimetrically (Column 2) was corrected for MgO in the CaO product and for $\text{Ca}_3(\text{PO}_4)_2$ in the $\text{Mg}_2\text{P}_2\text{O}_7$ to obtain the corresponding value in column 4.

TABLE 2. ANALYTICAL DATA ON SYNTHETIC CaCO_3 -MgO MIXTURES

1:1 molar Ca:Mg mixture					
gms. CaCO_3 taken†	gms. CaCO_3 found†	wt. % MgO in CaO §	corrected gms. CaCO_3 found (average)	average % error	
1.0027*	1.0076	0.60	1.0045	+0.18	
1.0027*	1.0063	0.62			
gms. MgO taken	gms. MgO found	wt. % CaO † in $\text{Mg}_2\text{P}_2\text{O}_7$	corrected gms. MgO found (average)	average % error	
0.4032	0.4005	0.20	0.4025	-0.17	
0.4032	0.4003	0.15			
4:1 molar Ca:Mg mixture					
gms. CaCO_3 taken	gms. CaCO_3 found	wt. % MgO in CaO	corrected gms. CaCO_3 found (average)	average % error	
1.0027*	1.0058	0.04	1.0075	+0.48	
1.0027*	1.0062	0.04			
gms. MgO taken	gms. MgO found	wt. % CaO † in $\text{Mg}_2\text{P}_2\text{O}_7$	corrected gms. MgO found (average)	average % error	
0.1008	0.1013	0.35	0.1007	-0.11	
0.1008	0.1011	0.45			

* Samples of 1.008 gm. CaCO_3 were weighed out. The figure 1.0027 is a corrected value which takes into account the actual CaO content of the material as determined by calcining a sample at 1200°C . and weighing as CaO.

† The CaO reported in these analyses was assumed to be present as $\text{Ca}_3(\text{PO}_4)_2$.

‡ Analysis by L. D. McVicker.

§ Analysis by O. I. Joensuu.

TABLE 3. CHEMICAL ANALYSES OF SELECTED DOLOMITES

	Cations/100 Cations																				
	Corrected for impurities in precipitates					Further corrected against standard mixtures, Table 2															
	Wt. % CaO found ²	Wt. % MgO found	Wt. % FeO found	Wt. % MnO found	Wt. % CO ₂ found	Wt. % SiO ₂ found	Wt. % Al ₂ O ₃ found	Total	MnO*	CaO*	Fe ₂ O ₃ **	Wt. % impurities in Mg ₂ P ₂ O ₇	Ca	Mg	Mn	Fe	Mn				
Gabbs	30.50	22.24	.07	.004	47.46	.0511	.000911	100.41	<.01	.05	<.04	<.01	49.53	50.30	0.09	0.08	49.40	50.43	0.09	0.08	
	30.46	22.25	.08	.0611	47.63				<.01	.06	.035	<.01									
Hammondsville	30.11	20.73	2.50	.12	47.11	.0811	.01311	100.67	.07	.065	.025	.19	49.56	47.03	3.23	0.18	49.43	47.16	3.23	0.18	
	30.00	20.73	2.52	.1611	47.24				.065	.05	.025	.18									
Binnental	30.71	22.20 ⁵		.0811	47.45	.0511	.01311	100.62	.03	.04	<.01	.06	49.80	50.02	0.10	0.08	49.67	50.15	0.10	0.08	
	30.72	22.24 ⁵			47.53				.04	.06	.015	.09									
	30.78 ⁷	21.79 ⁸		.0111	47.26			99.98 ⁸	.06	.08	<.01	.13	50.41	49.45	0.01	0.13					
	30.73	21.85 ⁸		.1011	47.30	.0211	<.0111														
Serra das Eguas ³	30.37	22.18	.27	.08	47.62			100.79	.04	.09	.01	.10	49.55	50.00	0.33	0.12	49.42	50.13	0.33	0.12	
	30.54	22.33	.25	.1111	47.74	.0511	.01511		.035	.07	.015	.10									
	30.45	21.95	.26	(.08)	47.36	.09	.24	100.51													
	30.46	21.99	.26		47.47																
Monroe County ³	30.90	21.41 ⁵	.23		47.47				.03	.05	.015	.09	50.76	48.56	0.58	0.10	50.63	48.69	0.58	0.10	
	30.98	21.41 ⁵		.4511		.0611	.3811		.03	.05	.015										
	30.94	21.29 ⁵	.44		47.44	.07	.17	100.59													
	30.96	21.32 ⁵		(.08)11	47.49	.12	.17														

¹ Includes spectrochemical values in instances where gravimetric determinations were not made.

² SiO₂ was shown spectrochemically to be <.01 wt. per cent in all of the samples, except for the second Binnental analysis where the CaO figure includes 0.02 wt. per cent SiO₂.

³ Independent analyses of the same Serra das Eguas and Monroe County samples, made several years ago, are shown for comparison.

⁴ Value given has been corrected for wt. per cent MnO determined spectrographically.

⁵ This analysis, as used by Richard Rolle in his Ph.D. thesis at the University of Chicago (1957), has MgO finally corrected to 21.54 wt. per cent and CO₂ corrected to 47.38 wt. per cent. The additional corrections are the amounts by which the analyst failed to duplicate the wt. per cent MgO reported for U. S. Bureau of Standards dolomite #88, and the wt. per cent CO₂ reported for U. S. Bureau of Standards dolomite #88.

⁶ CaO, MgO and CO₂ for the second Binnental analysis by M. C. Batchelder, other non-spectrochemical determinations by L. D. M.

⁷ Assumed to be present as Mn₂P₂O₇.

⁸ Assumed to be present as Ca₃(PO₄)₂.

⁹ Assumed to be present as Fe₂(PO₄)₃.

¹⁰ Spectrochemical determinations for the second Binnental analysis by A. J. Leoni, for SiO₂ and Al₂O₃ in the other analyses by Koza Nagashima, others by O.I.J.

The dolomites were similarly analyzed in duplicate for Ca and Mg by McVicker using the standard Ca oxalate and Mg ammonium phosphate precipitations, the latter in triplicate. The CaO and Mg pyrophosphate obtained after heating were analyzed spectrochemically by Joensuu for extraneous ions carried down with the precipitate. Spectrochemical determinations of MnO, FeO, and SrO in the dolomites were made. Where sufficient samples were available MnO was also determined colorimetrically and FeO gravimetrically. The results are summarized in Table 3. The differences in Ca and Mg content obtained with and without corrections based upon Table 2,

$$\left(\frac{0.48 + 0.18}{2} = 0.33 \text{ per cent for Ca, } \frac{0.17 + 0.11}{2} = 0.14 \text{ per cent for Mg} \right)$$

are less than 0.15/100 cations. The final CaCO₃ figures for four of the five samples are approximately 0.5 mole per cent below the ideal 50 per cent, but the Monroe County dolomite has about 0.5 per cent CaCO₃ in excess of that figure.

Some further information on the reliability of the various analytical determinations is furnished in Table 3 by analyses of the same Serra das Eguas and Monroe County samples made several years ago by McVicker, and by an independent analysis of the same Binnental sample for another purpose made by M. G. Batchelder of the Institute of Metals, University of Chicago, with spectrographic analyses of precipitates by A. J. Leoni. The three pairs of CaO determinations differ by a maximum of only 0.05 wt. per cent; the two pairs of CO₂ determinations, by 0.20 and 0.26 wt. per cent. The pairs of MgO determinations differ by 0.10, 0.29, and 0.44 wt. per cent. The discrepancy between MgO determinations is the reason for the difference in values (cations/100 cations) computed for the two Binnental analyses, a difference which is half the maximum difference observed among the several dolomites.

It may be noted that most of the analyses total somewhat high, and that moles of CaO+MgO+MnO+FeO exceed moles of CO₂ by from 0.009 (Monroe County) to 0.022 (Binnental, L. D. M.). This difference corresponds to a range of 0.37 to 0.87 wt. per cent MgO, for example, and is greater than the amount of material that could be combined with the small amounts of SiO₂ and Al₂O₃ present. The last two materials, furthermore, are at least partly derived from reagents, laboratory glassware, and the mullite mortar in which the samples were ground. The anomalies could be most easily resolved if MgO determinations were slightly high, but the analyses summarized in Table 2 indicate that correction for spectrographic analysis of precipitates seems to yield quite accurate results for MgO.

X-RAY METHODS

Spectrographically pure CaCO_3 , the synthetic magnesian calcites, the five chemically analyzed dolomites as well as U. S. Bureau of Standards dolomite #88, and a synthetic magnesite* were run on the General Electric XRD-3 *x*-ray diffractometer using Cu radiation. Because only small amounts of some of the materials were available, all mounts were prepared by spreading the finely ground powder evenly in *n*-butyl alcohol on a glass slide and then allowing the alcohol to evaporate. A similar mount of high-purity silicon having $a_0 = 5.4306_2 \text{ \AA}$ was used to prepare a graph of 2θ versus errors in *d*-values calculated from the observed maxima. This graph was then used to correct observed carbonate *d*-values. At moderate to low values of 2θ the correction incorporates not only instrumental error but also the effect of partial $a_1 a_2$ overlap.

The reflections used were $21\bar{3}$ (140)† which ranged from $2\theta = 109^\circ$ to 123° for the carbonates studied and from which a_0 can readily be obtained, 444 (00·12) at $2\theta = 65^\circ$ to 76° , the highest angle basal reflection available, and 633 (30·12) at $2\theta = 99^\circ$ to 115° , the third order of the strong 211 (104) reflection which lies at about 45° to *a* and *c*. The $30\bar{3}$ (330) reflection at $2\theta = 136^\circ$ could also be detected for calcite, and was used to obtain a_0 values. Diffraction angles were obtained from charts recorded at a rate of $1^\circ/5 \text{ min.}$ with a time constant of 1.0 second for 444 (00·12) and 633 (30·12), 3 seconds for the other two reflections.

The complete set of samples examined with the diffractometer was also run using standard 114.59 cm. Philips Straumanis-mount powder cameras and suitable radiations, in order to obtain an independent check. The Straumanis method of film shrinkage correction was used, and $\cos^2\theta$ extrapolations to $2\theta = 180^\circ$ were carried out to obtain a_0 and c_0 , except where otherwise noted. The various radiations and *x*-ray reflections used in determining a_0 and c_0 are summarized in Table 4. An upper limit to the accuracy of the extrapolations is set by the sharpness of the back reflections which can be obtained. The dolomites examined, even though macroscopically good single crystals, typically have somewhat more diffuse back reflections than do well crystallized single-cation carbonates such as calcite and magnesite. Attempts to obtain structurally more perfect dolomites by recrystallization in the presence of water and CO_2 at 700° C. yielded materials which were not significantly improved.

* The magnesite was prepared by heating C.P. basic Mg carbonate to 300° C. for 15 hours in a Morey bomb in the presence of CO_2 and H_2O . Spectrographic analysis of this material by Juanita Witters of the Illinois State Geological Survey shows Ca equivalent to 0.38 mol per cent CaCO_3 and Fe equivalent to 0.013 mol per cent FeCO_3 .

† Rhombohedral indices h, k, l , are followed by the equivalent hexagonal indices $hk \cdot l$ throughout the paper.

TABLE 4. BACK REFLECTIONS USED TO DETERMINE a_0 AND c_0 FROM PHILIPS POWDER X-RAY FILMS OF Ca-Mg CARBONATES

Materials	Radiation	Constant desired	Reflections used†
Calcites and Mg-calcites	Co	a_0	21 $\bar{3}$ (140), 440(048), 41 $\bar{1}$ (324), 31 $\bar{2}$ (232), 400(404), 521(318)
Calcites and Mg-calcites	Co	c_0	642(22·12), 664(02·16), 653(12·14), 633(30·12), 644(20·14)
Calcites, 4.84 mol% and 9.89 mol% Mg-calcites	Fe	a_0	31 $\bar{2}$ (232), 521(318), 400(404), 420(226), 32 $\bar{1}$ (134)
14.83 mol% Mg-calcite	Fe	a_0	31 $\bar{2}$ (232), 30 $\bar{2}$ (321), 521(318), 400(404), 420(226), 32 $\bar{1}$ (134)
19.78 mol% Mg-calcite	Fe	a_0	400(404), 420(226), 32 $\bar{1}$ (134)
Dolomites	Co	a_0	21 $\bar{3}$ (140), 41 $\bar{1}$ (324), 31 $\bar{2}$ (232), 30 $\bar{2}$ (321)
Dolomites	Co	c_0	664(02·16), 653(12·14), 633(30·12), 655(10·16),* 654(11·15)*
Dolomites	Cr	c_0	Average c_0 extrapolation slope run through $c_0'_{543(11·12)}$
Magnesite	Cu	a_0	540(149), 33 $\bar{2}$ (054), 11 $\bar{4}$ (05 $\bar{2}$), 520(327), 440(048)
Magnesite	Co	c_0	Coincidences of 654(11·15)—30 $\bar{2}$ (321) and 655(10·16)—633(30·12)—31 $\bar{2}$ (232); fit of $a_0'_{540(149)}$ to a_0 extrapolation (see text)

† Tables of indexed d -spacings for the rhombohedral carbonates will be given in a separate publication (Graf, ms. in preearation).

* The 654(11·15) and 655(10·16) reflections of calcite and the magnesian calcites are too nearly coincident to be measured, but are resolved for dolomite.

Reflections with a strong c -axis component are more often broadened than are those from planes having a strong a -axis component, both for the dolomites and for the magnesian calcites.

It will be noted from Table 4 that the accuracy of $\cos^2\theta$ extrapolation is also restricted by the fact there are no basal reflections in the back reflection region, at least for the radiations commonly available. This has made it necessary first of all to carry out an a_0 extrapolation using the relation,

$$a_0' = d \sqrt{4/3(h^2 + hk + k^2) + \left(\frac{a_0}{c_0}\right)^2 l^2} \quad (1)$$

where the prime indicates that a_0' is in general not equal to a_0 except at $2\theta=180^\circ$. Greater reliance is placed upon the reflections from planes having no c -axis component, and those having a relatively small c -axis component so that a_0/c_0 in (1) need not be known too accurately.

With a_0 known, a series of c_0 extrapolations can be made using

$$c_0' = d \sqrt{4/3 \left(\frac{c_0}{a_0}\right)^2 (h^2 + hk + k^2) + l^2} \quad (2)$$

and a range of assumed c_0 values in order to determine which one best fits the several c_0' values to a straight line and which one most nearly gives an extrapolated c_0 equivalent to that assumed. Inasmuch as the several reflections used in making the c_0 extrapolation have varying a -axis components and thus varying contributions from the $(c_0/a_0)^2$ term in (2), an error in assumed c_0 will affect them unequally and tend to destroy the linearity of the plot. The extrapolated c_0 value obtained can be tested by using it in computing a_0' values for reflections containing small to moderate c -axis components, and seeing whether these a_0' values fall close to the line in the a_0 extrapolation.

The suggested c_0 extrapolation for dolomite in Table 4 using Co radiation is not possible for most of the dolomites studied because the reflections are too weak and diffuse to measure. Instead, $d_{643(11\cdot12)}$ at $2\theta=158^\circ$ can be measured quite accurately using Cr radiation, and c_0 then computed using equation (2) and a known value of a_0 . Inasmuch as c_0' and c_0 in (2) are not identical for $2\theta < 180^\circ$, it is necessary to establish the relationship between them. By determining the average of c_0 extrapolation slopes for some 20 carbonates which had been run previously, it was found that $c_0' \cong c_0 + 0.0009$ at $2\theta \cong 158^\circ$, for the particular Philips camera used. Thus the c_0 value for dolomite is changed by about 0.001 Å relative to that obtained if c_0' is assumed equal to c_0 .

The determination of c_0 for magnesite by $\cos^2\theta$ extrapolation is made difficult by the near-coincidence* of 654 (11·15)–30 $\bar{2}$ (321) and of 655 (10·16)–633 (30·12)–31 $\bar{2}$ (232). However, the synthetic material available is very well crystallized, and these multiple reflections can be observed in the back reflection region at $2\theta \cong 155^\circ$ using Co radiation. They do not appear broader than other back reflections of comparable intensity, indicating that coincidence is very closely approached. Using the accurately determined value $a_0 = 4.6330$ Å for magnesite, pairs of (2) can be solved simultaneously to eliminate c_0' and obtain c_0 . For the three pairs 654 (11·15)–30 $\bar{2}$ (321), 655 (10·16)–31 $\bar{2}$ (232), and 633 (30·12)–31 $\bar{2}$ (232) the same c_0 value, 15.013 Å, results. The two reflections with no c -axis component, 31 $\bar{2}$ (232) and 30 $\bar{2}$ (321), are weaker for calcite and dolomite than the reflections listed which have strong c -axis components but have appreciable intensity. Thus noticeable broadening of the multiple reflections would surely result if pairs of reflections from magnesite were separated by a fifth of the $\alpha_1\alpha_2$ separation in this 2θ region, and might be detectable at half this value. By leaving the reflections with no c -axis component fixed, and moving those with strong a -axis components these distances, it is possible to place limits of ± 0.008 and ± 0.004 Å respectively on the 15.013 value.

A probable value for c_0 within the ranges mentioned may be obtained in at least two ways. Using the rather accurately measured reflection 540 (149), which lies at $2\theta = 165^\circ$ for Cu radiation and has about 75 per cent a -axis component, it is found that an assumed c_0 of 15.016 $_5$ Å is required in (1) in order to make a_0' for 540 (149) fall on the line in the a_0 extrapolation. Values of c_0 of 15.013 and 15.019 Å (average 15.016) were obtained by running average c_0 extrapolation slopes through c_0' values derived from measurements of $d_{542(12\cdot11)\alpha_1}$ and $d_{542(12\cdot11)\alpha_2}$ at $2\theta = 145^\circ$ using Fe radiation. A probable c_0 value of 15.016 Å is therefore chosen for magnesite.

The x -ray measurements were made in laboratories whose temperatures varied from 23° to 29° C. Thus if one ignores the possible heating-up inside the Philips cameras during long exposures, the measurements are valid for $26 \pm 3^\circ$ C. The correction in a_0 for these materials resulting from a temperature difference of 5° C., based upon available thermal expansion data for calcite, dolomite, and magnesite, is about 0.0001 Å, which is much less than error from other sources and is ignored. The value for c_0 is about 0.002 Å, which is

* The indexing of x -ray reflections in this paper is based upon tables of calculated d -values which are presented in a separate paper (Graf, ms. in preparation).

comparable to the experimental error from other sources in the more favorable cases. Correction of individual c_0 values to 26° C. does not change any of the conclusions reached in the remainder of the paper.

X-RAY MEASUREMENTS

The x-ray measurements are summarized in Table 5 and shown graphically in Figs. 1-4. Figure 1 gives a complete picture of the results, and Figs. 2, 3, and 4 are more detailed plots of the a_0 , c_0 and $d_{211(104)}$ data, respectively. The relationships shown in these figures supplant the preliminary ones suggested in Fig. 6 of Goldsmith, Graf, and Joensuu (1955). The values given are the most probable in each instance, but no attempt is made to specify probable error because of the difficulty of taking into

TABLE 5. MEASURED VALUES OF c_0 , a_0 , AND $d_{211(104)}$ FOR THE Ca-Mg CARBONATES

Sample Number	Materials	$d_{211(104)}$ from $d_{033(10-12)}$ Spectrometer Cu rad.	c_0 from $d_{033(10-12)}$ Spectrometer Cu rad.	c_0 from $\cos^2\theta$ Extrapolation Co rad.	a_0 from $d_{211(104)}$ Spectrometer Cu rad.	a_0 from $\cos^2\theta$ Extrapolation Co rad.	a_0 from $\cos^2\theta$ Extrapolation Fe rad.
	Illinois Geological Survey Spectr. Standard CaCO ₃ Johnson-Mathey "Specpure" CaCO ₃	3.0356	17.059	17.065	4.9894 4.9898* 4.9903 4.9899*	4.9900	4.9896
G-680	(4.94 mol% MgCO ₃)	3.0196	16.951	16.955	4.9676	4.9697	4.9691
G-684		3.0197	16.952		4.9679		4.9693
G-694		3.0198	16.950	16.956	4.9679	4.9682	4.9693
G-698	(9.89 mol% MgCO ₃)	3.0018	16.852	16.852	4.9428	4.9430	4.9440
G-700		3.0030	16.845	16.855	4.9448	4.9443	4.9449
G-714		3.0021	16.850	16.852	4.9435	4.9430	4.9443
G-696	(14.83 mol% MgCO ₃)	2.9854	16.735	16.734	4.9216	4.9220	4.9219
G-661		2.9857	16.736	16.738	4.9213	4.9226	4.9223
G-663		2.9864	16.735	16.741	4.9219	4.9215	4.9218
G-672	(19.78 mol% MgCO ₃)	2.9712	16.636	16.638	4.9022	4.9025	4.9019
	Dolomite, Gabbs	2.8842	16.004	16.002† 15.997	4.8056	4.8064	
	Dolomite, U.S.B.S. #88	2.8850	16.004	16.007†	4.8073	4.8068	
	Dolomite, Monroe County	2.8857	16.014	16.013†	4.8084	4.8080	
	Dolomite, Serra das Eguas	2.8843	16.004	16.000†	4.8065	4.8054	
	Dolomite, Hammondsville	2.8862	16.008	16.009† 16.011	4.8078	4.8070	
	Dolomite, Binnental	2.8857	16.015	16.014†	4.8070	4.8082	
	Synthetic magnesite	Interf. ¶	15.013	15.016§	4.6333	4.6330‡	

* a_0 from $d_{303(310)}$ at $2\theta = 136^\circ$.

† c_0 from extrapolation through c_0' (11-12), Cr rad.

‡ a_0 from $\cos^2\theta$ extrapolation, Cu radiation.

§ See text.

¶ Computed from $a_0 = 4.6630 \text{ \AA}$ and $c_0 = 15.016 \text{ \AA}$ to be 2.7412 \AA .

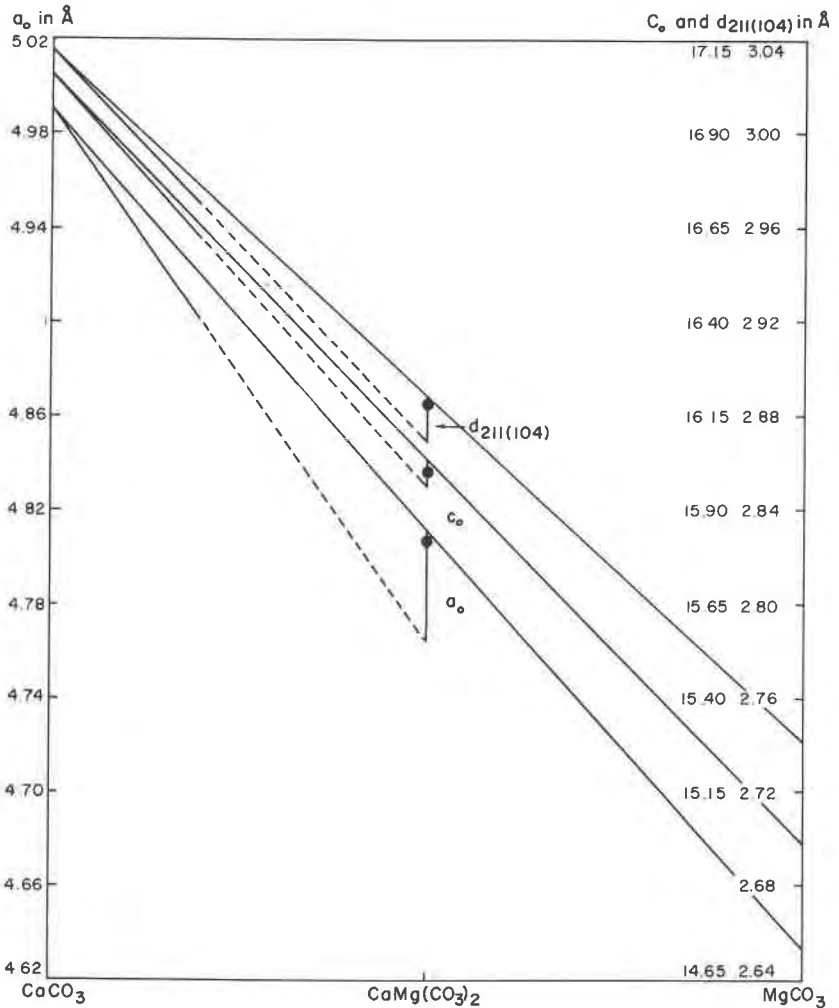


FIG. 1. Variation of a_0 , c_0 , and $d_{211(104)}$ for the Ca-Mg carbonates. The dots indicate the range of measured spacings for the several dolomites studied. Individual measurements for the dolomites and magnesian calcites are shown in Figs. 2, 3, and 4.

account such factors as variable line broadening and consequent variable $\alpha_1\alpha_2$ interaction.

The cell constants of calcite have been accurately determined by a number of workers (see discussion by Graf and Lamar, 1955, p. 643). At 20° C. $d_{211(104)} = 3.0357 \text{ \AA}$ and $\alpha(\text{cleavage rhomb}) = 101^\circ 54'3''$, from which one obtains $a_0 = 4.9900 \text{ \AA}$, and $c_0 = 17.0615 \text{ \AA}$. Using the thermal expansion data of Austin et al. (1940), the comparable values at 26° C.

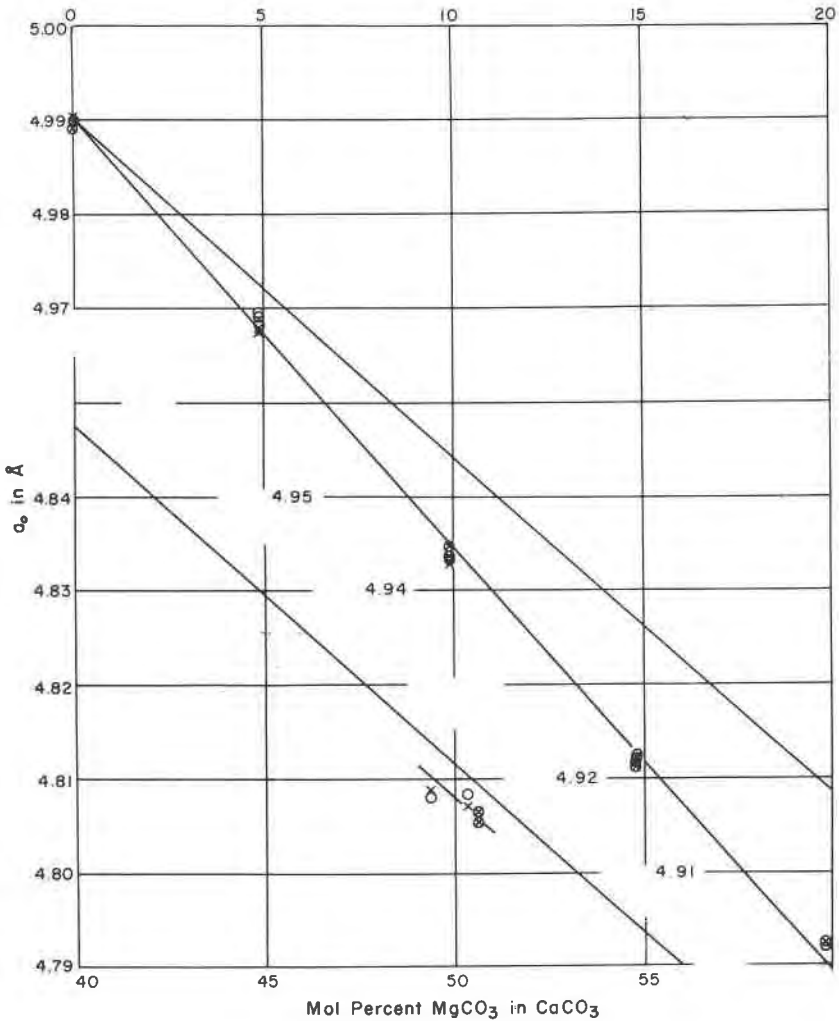


FIG. 2. Variation of a_0 for the Ca-Mg carbonates. Circles represent measurements obtained with Philips powder cameras; crosses show x -ray diffractometer results. The small dot is the literature value for calcite. The extension of the magnesian calcite line through the dolomite region has been inadvertently omitted, but passes through points 4.8085 \AA , $40 \text{ mol } \%$ MgCO_3 , and 4.7900 \AA , $44.08 \text{ mol } \%$ MgCO_3 .

are $a_0 = 4.9899 \text{ \AA}$ and $c_0 = 17.064 \text{ \AA}$, from which $d_{211(104)}$ is computed to be 3.0359 \AA . These literature values are plotted at the left-hand sides of Figs. 1-4 for comparison with our experimental determinations (Table 5).

Diffractometer and Philips camera determinations of a_0 and c_0 for the magnesian calcites are plotted in Figs. 2 and 3 respectively. The lower

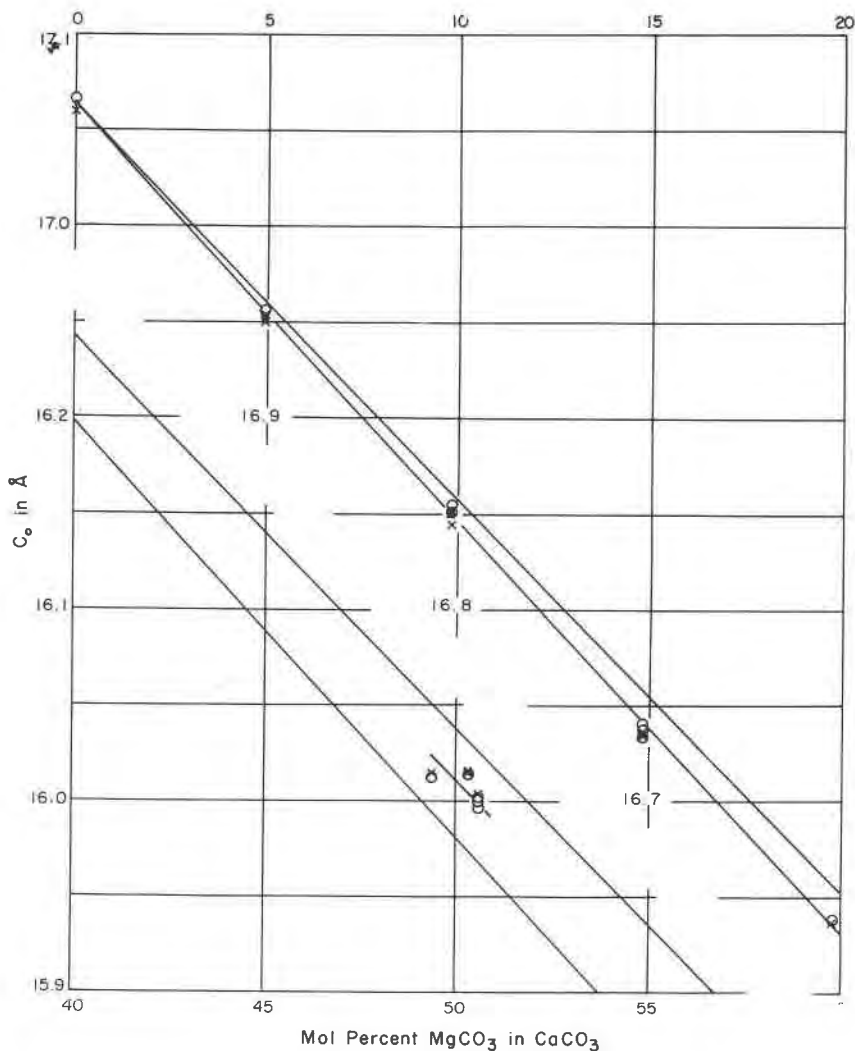


FIG. 3. Variation of c_0 for the Ca-Mg carbonates. Circles represent measurements obtained with Philips powder cameras; crosses show x-ray diffractometer results. The small dot is the literature value for calcite.

of the two straight lines in each figure is drawn through these values. The values of a_0 and c_0 for a calcite containing 20 mol per cent MgCO_3 , as determined by the straight lines through the plotted points, have been used to compute $d_{211(104)}$ for this composition. The calculated $d_{211(104)}$ has been used to determine the slope of the lower of the two lines in Fig. 4,

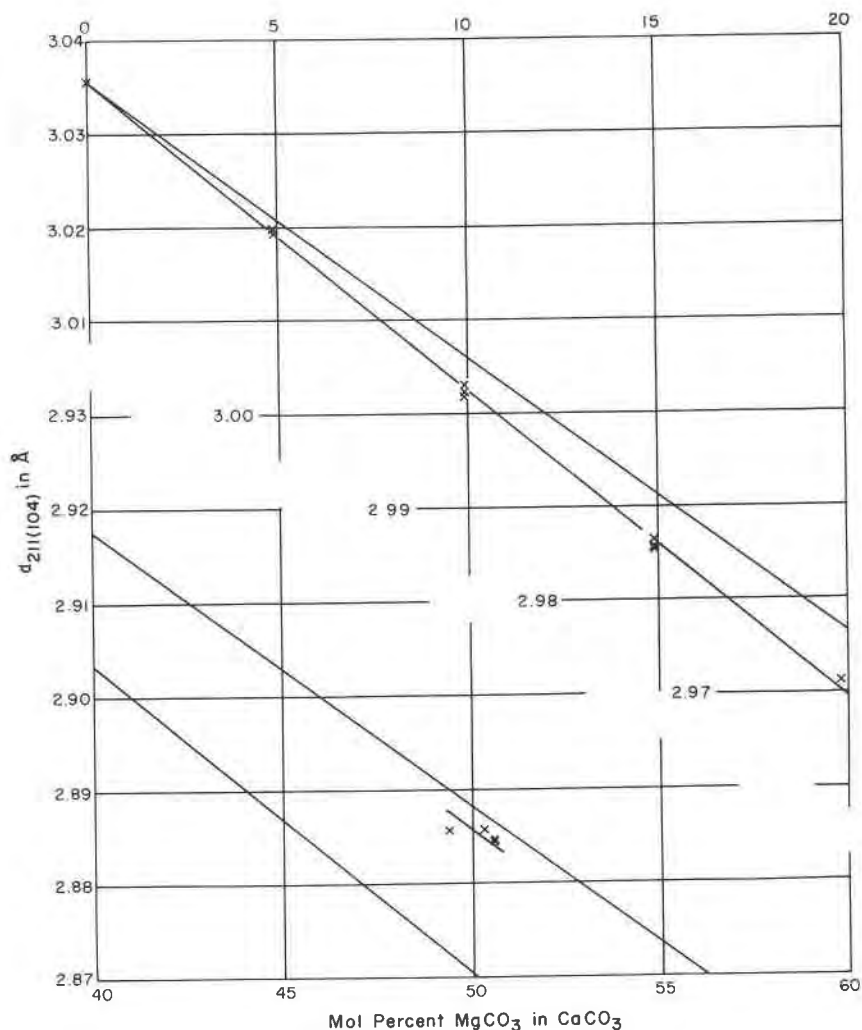


FIG. 4. Variation of $d_{211(104)}$ for the Ca-Mg carbonates. Crosses indicate measurements made with the x-ray diffractometer. The small dot is the literature value for calcite. The straight line through the plotted points was computed from the analogous a_0 and c_0 lines in Figs. 2 and 3.

which is seen to pass satisfactorily through the plotted experimental points. The curvature suggested in the a_0 and $d_{211(104)}$ plots is less convincing if one ignores the single point at 19.78 mol per cent $MgCO_3$, and with the amount of information available does not justify drawing anything but straight lines.

The a_0 , c_0 and $d_{211(104)}$ values for the Gabbs, Serra das Eguas, Binnental, and Monroe County dolomites are also plotted using McVicker's analyses together with the calcite-magnesite and extended magnesian calcite lines indicated in the dolomite region for reference. For these plots Mn^{++} and Fe^{++} are totalled with Mg^{++} . The short lines through these points in Figs. 2, 3, and 4 have been drawn so that they connect with the measured values for calcite if extended. This construction assumes that the contraction in a_0 and c_0 of dolomite relative to the averages of these values for calcite and magnesite results from the segregation of Ca and Mg into separate cation layers, as required by the dolomite structure. Ordered near-dolomites with some extra Ca in solid solution in Mg layers would have cation layers somewhat more alike, and would correspondingly retain only a proportionate part of the added packing efficiency gained by segregating cations. The fit of the plotted points to the short lines is a possible one, in view of the uncertainty in chemical analysis discussed earlier, but the points are too few and too close to 50 mol per cent to prove or disprove the assumption made in drawing the lines.

The a_0 and c_0 values obtained for ideal dolomite by noting where the short lines cross the 50 mol per cent composition are 4.8079 Å and 16.010 Å respectively. The $d_{211(104)}$ value computed from these values, 2.8855 Å, is in good agreement with that read from Fig. 4, 2.8857 Å. The accuracy of these constants is principally dependent upon the chemical analyses. To the extent that Mg values are high, for example, these constants will be high.

Values for U. S. Bureau of Standards dolomite #88 and a dolomite from Hammondsville, Vermont, are also reported in Table 5. Sample #88 was studied because of the wide use of this material as a chemical standard, even though it is, strictly speaking, not a single-phase material. Its cell dimensions fall within the range of those for the other dolomites. The Hammondsville dolomite contains some $3\frac{1}{4}$ mol per cent $FeCO_3$ which might be expected to increase the dolomite cell size because of the larger cell of siderite relative to that of magnesite (Graf, ms. in preparation). The fact that the Hammondsville material has cell dimensions only slightly larger than those of the Gabbs and Serra das Eguas dolomites, which have the same $CaCO_3$ content, indicates how little the substitution of Fe^{++} changes the unit cell size of dolomite.

DISCUSSION

The a_0/c_0 ratios of calcite, dolomite, and magnesite differ significantly. The a_0 of magnesite is 7.15 per cent less than that of calcite, but c_0 is 12.00 per cent less than the calcite c_0 . For dolomite having $a_0 = 4.8079$ Å and $c_0 = 16.010$ Å, the comparable figures are 3.65 per cent and 6.18 per

cent. It is thus not surprising that substitution of Mg into calcite occasions an anisotropic contraction, e.g., a 1.82 per cent smaller a_0 but a 2.54 per cent smaller c_0 for calcite containing 20 mol per cent MgCO_3 in solid solution than for pure calcite. In all three of these cases the percentage c_0 contraction relative to calcite is greater than the decrease in a_0 . Comparisons between the data for magnesian calcite and dolomite can best be made by referring them to joins connecting c_0 and a_0 values for calcite and magnesite.

The data of Table 5 and Figs. 2 and 3 show that a_0 and c_0 of dolomite are quite close to one-half the sum of the corresponding values for calcite and magnesite. However, there remains a measurable contraction of both axes in dolomite. The graphically derived a_0 value for dolomite, 4.8079 Å, is 0.074 per cent less than the a_0 , 4.8114₅ Å, of an hypothetical material halfway between calcite and magnesite. Similarly, the c_0 for dolomite, 16.010 Å, is 0.18 per cent less than the hypothetical 16.039₅ Å.

If one extrapolates the a_0 and c_0 magnesian calcite curves to 50 mol per cent MgCO_3 , for comparison with dolomite, the a_0 and c_0 values obtained are 0.98 per cent and 0.36 per cent less than the hypothetical values. On the basis of the extrapolation, the a_0 and c_0 contractions for this magnesian calcite referred to the hypothetical values on the calcite-magnesite join are both greater than the corresponding contractions for dolomite. This would imply that the disordered equivalent of dolomite would have a smaller molar volume than dolomite itself, as measured at room temperature.

The extrapolation of the magnesian calcite curves must, however, be viewed with considerable skepticism. First of all, there may be no real physical significance in an extrapolation to the dolomite composition. Although increasingly high temperatures are needed to accommodate larger amounts of Mg in the calcite structure (Graf and Goldsmith, 1955; Harker and Tuttle, 1955), the composition and degree of Ca-Mg order of the equilibrium high-temperature phase or phases having a total composition of $\text{Ca}_{50}\text{Mg}_{50}$ are not known. It has not been established that the disordered equivalent of dolomite exists at any temperature below that at which melting or some other phase change occurs. Secondly, the lines through the a_0 and c_0 points for the magnesian calcities may actually be curved rather than straight, and of course may deviate even more in the extrapolated region. Furthermore, the magnesian calcite cell constants are measured on quenched samples, metastable at room temperature.* In view of the unknown thermal expansions of these materials, especially over a temperature range in excess of 800° C., compari-

* For example, 20 mol per cent MgCO_3 in calcite is stable only at temperatures greater than approximately 825° C.

son of molar volumes at other than the equilibrium temperatures could lead to erroneous conclusions.

The percentage contraction figures derived above also indicate that, with increasing substitution of Mg, a_0 values for the magnesian calcites deviate more rapidly percentage-wise from the calcite-magnesite a_0 join than do c_0 values from the c_0 join. Yet the a_0 value for dolomite is percentage-wise closer to the a_0 join than is the c_0 value to its join. This apparent reversal presumably results from the fact that Mg^{++} ions are accommodated in two different ways in these materials, by random cation substitution in the magnesian calcites and as separate cation layers in dolomite.

One practical consequence is that c_0 values may be used to define the composition of single-phase materials between calcite and dolomite, regardless of whether cations occur in random solid solution or in the ordered dolomite arrangement, with a maximum error of about 2 mol per cent $MgCO_3$ at 50 mol per cent $MgCO_3$ † and lesser errors toward $CaCO_3$. This statement is contingent upon retaining the assumption made earlier that the relation between $CaCO_3$ content and cell size of dolomites may be satisfactorily approximated by a line on the c_0 plot connecting calcite and the value for dolomite of 1:1 composition, and that this line may be used to determine composition of materials near dolomite which show order reflections of proper intensity. Materials with cation disorder would be referred to the extrapolated magnesian calcite line, which lies about 2 mol per cent $MgCO_3$ away for a given c_0 near the dolomite composition. The probable maximum errors using a_0 and the spacing of the strongest reflection, 211(104), or its higher orders, can be shown by similar reasoning to be 9 and 5 mol per cent $MgCO_3$ respectively.

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† Materials between calcite and dolomite in composition with hypothetical mixed layer effects, in which relatively Ca-rich and relatively Mg-rich cation planes occur in other than perfect alternation, would in some cases have c_0 values larger than those predicted from a join connecting the spacings for calcite and magnesite, and might even have bimodal intensity maxima for the basal reflections. Additional x -ray diffraction criteria are needed to describe these materials (Graf, Blyth, and Stemmler, ms. in preparation), and they are not considered in this discussion.

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