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LATTICE CONSTANTS OF THE CALCIUM-MAGNESIUM CARBONATES

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In an earlier publication (Goldsmith and Graf, 1958) lattice constants of several dolomites and of synthetic magnesian calcites containing up to about 20 mol per cent MgCO_3 were presented. Since these data appeared, the system $\text{CaCO}_3\text{-MgCO}_3$ has been investigated at higher temperatures and CO_2 pressures, and single phase solid solutions were successfully prepared over the whole range from CaCO_3 to $\text{CaMg}(\text{CO}_3)_2$ (Goldsmith and Heard, 1961). The present paper is based upon measurements made on some of the latter samples. The experimental conditions under which these samples were prepared are given in Table 1.

Powder x -ray diffraction patterns were taken of these samples using

TABLE 1. EXPERIMENTAL CONDITIONS UNDER WHICH THE SYNTHETIC CALCIUM MAGNESIUM CARBONATES DISCUSSED IN THIS PAPER WERE PREPARED

The samples were contained in sealed Pt capsules in an internally heated gas system, described elsewhere (Goldsmith and Heard, 1961).

Sample Number	Mol Per Cent MgCO_3	Temp. ($^{\circ}\text{C}.$)	CO_2 Pressure (Kb.)	Time (minutes)
C-213	10	945- 950	5.0	45
C-291	10	684- 686	2.0	180
C-214	20	945- 950	5.0	45
C-226	20	884- 892	4.0	90
C-217	30	978- 981	5.0	40
C-207	40	1074-1075	8.5	30
C-203	40	1140-1150	10.0	30
C-193	42.5	1144-1150	10.0	30
C-194	45	1144-1150	10.0	30
C-91	45	1093-1101	8.0	12
C-182	47.5	1146-1151	10.0	25
C-102	50	1150-1155	10.0	5
C-114	50	900- 901	5.0	60

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CoK α radiation, and a_0 and c_0 were obtained from $\cos^2 \theta$ extrapolations of the appropriate back-reflections. These data are plotted in Figs. 1 and 2. The scatter of the plotted points is partly attributable to two principal factors. Small amounts of a secondary phase, presumably produced by incomplete reaction or exsolution during quenching were noted in several runs, particularly in the composition range Ca₇₀Mg₃₀ to Ca₅₅Mg₄₅.

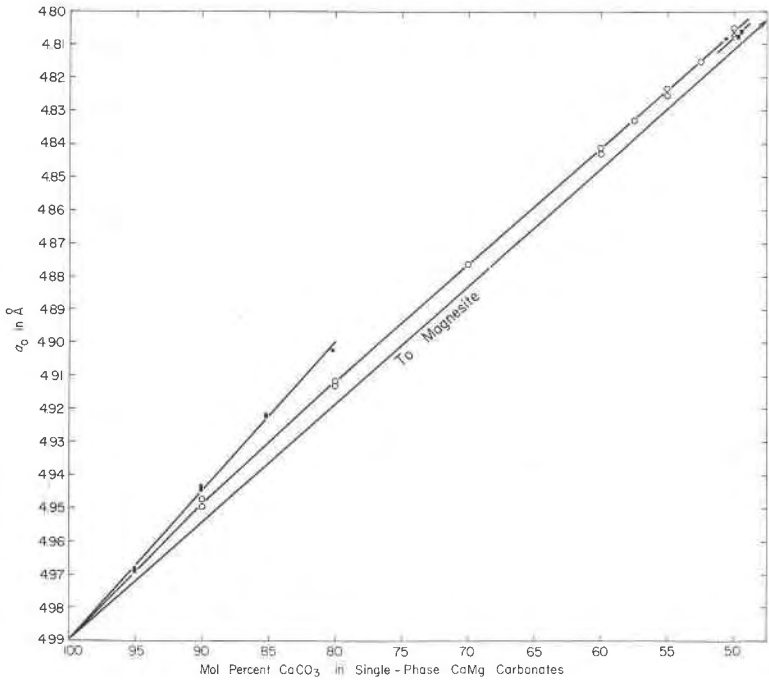


FIG. 1. The change in a_0 with composition for CaCO₃-rich phases in the system CaCO₃-MgCO₃. Open circles represent new measurements on disordered solid solutions; triangles, new measurements on phases with (cation-ordered) dolomite-type structures. Vertical bars are schematic representations of groups of closely similar measurements, published previously (Goldsmith and Graf, 1958).

Although runs obviously imperfect in this regard were discarded, lesser inhomogeneities may exist in some of the other samples. Secondly, some of the x -ray patterns have back-reflections that, although measurable, are not as sharp as would be desired for maximum accuracy.

The data of Goldsmith and Graf (1958) are also plotted in Figs. 1 and 2. There is a significant discrepancy between the two sets of data for the calcites containing up to 20 mol per cent MgCO₃. As a further check, Miss Juanita Witters of the Illinois Geological Survey has redetermined

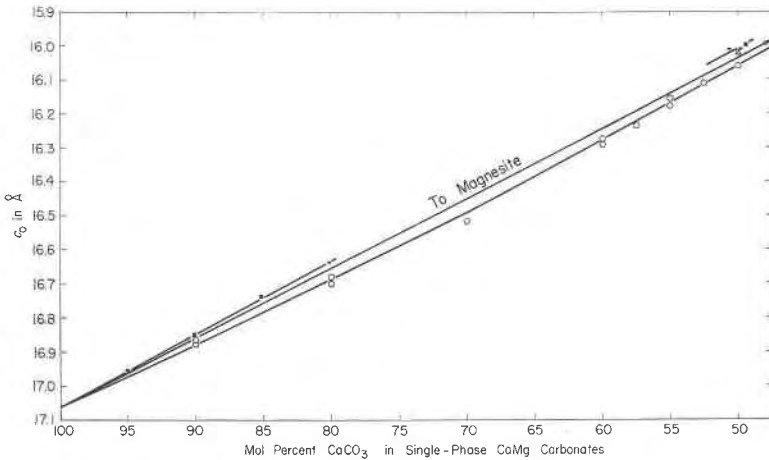


FIG. 2. The change in c_0 with composition for CaCO_3 -rich phases in the system CaCO_3 - MgCO_3 . The symbols used have the same meaning as in Fig. 1.

the compositions of the approximately 20 mol per cent MgCO_3 mixture used by Goldsmith and Graf (1958) and of the 20 mol per cent MgCO_3 mixture used by Goldsmith and Heard. Her results, given in Table 2, are within 1.0 mol per cent of the composition (by synthesis) of the Goldsmith-Heard magnesite-calcite mixture, and indicate a probable difference in composition between the mixtures of 0.4 mol per cent. A difference of three mol per cent would be required to explain the discrepancy in Figs. 1 and 2. We can offer no explanation, but prefer the

TABLE 2. EMISSION SPECTROGRAPHIC ANALYSES OF THE TWO SYNTHETIC MIXTURES USED IN PREPARING CaCO_3 SOLID SOLUTIONS CONTAINING APPROXIMATELY 20 MOL. PER CENT MgCO_3

The calibration curves were adjusted for each plate, using standards run on that plate—Juanita Witters, analyst.

	Goldsmith and Graf (1958)		Goldsmith and Heard (This paper)	
	MgCO_3	CaCO_3	MgCO_3	CaCO_3
First Trial	17.7	82.3	18.1	81.9
Second Trial	18.0	82.0	18.0	82.0
Third Trial	18.0	82.0	18.7	81.3
Average (Wt. Per Cent)	17.9	82.1	18.3	81.7
Mol Per Cent	20.6	79.4	21.0	79.0

TABLE 3. CELL CONSTANTS FOR SOME SYNTHETIC AND NATURAL
 CALCIUM CARBONATE SOLID SOLUTIONS (SEE ALSO TABLE 1)

The cell constants used for the ordered Gabbs and Serra das Eguas dolomites in the Guinier Δa_0 and Δc_0 determinations are those published by Goldsmith and Graf (1958); for the Lee, Massachusetts, dolomite, the mean of the published values, $a_0=4.8079 \text{ \AA}$, $c_0=16.010 \text{ \AA}$, was assumed; for the synthetic mixture of equimolar amounts of CaCO_3 and MgCO_3 , the a_0 and c_0 values given below for C-114 were used. The values given in this table are the most probable ones based upon $\cos^2 \theta$ extrapolations; the final figure is obviously not significant for some samples, but it is difficult to assign probable uncertainties.

Material	a_0 in \AA	c_0 in \AA
A. Cation disordered or largely so		
C-213, CaCO_3 containing 10 mol per cent MgCO_3	4.9494	16.876
C-291, CaCO_3 containing 10 mol per cent MgCO_3	4.9473	16.863
C-214, CaCO_3 containing 20 mol per cent MgCO_3	4.9128	16.699
C-226, CaCO_3 containing 20 mol per cent MgCO_3	4.9115	16.698
C-217, CaCO_3 containing 30 mol per cent MgCO_3	4.8760	16.514
C-207, CaCO_3 containing 40 mol per cent MgCO_3	4.8410	16.291
C-203, CaCO_3 containing 40 mol per cent MgCO_3	4.8428	16.274
C-193, CaCO_3 containing 42.5 mol per cent MgCO_3	4.8328	16.235
C-194, CaCO_3 containing 45 mol per cent MgCO_3	4.8255	16.178
C-91, CaCO_3 containing 45 mol per cent MgCO_3	4.8233	16.156
C-182, CaCO_3 containing 47.5 mol per cent MgCO_3	4.8152	16.111
C-102, CaCO_3 containing 50 mol per cent MgCO_3	4.8050	16.061
B. Cation ordered		
C-114, Dolomite containing 50 mol per cent MgCO_3	4.8067	16.025
C. Dolomite cell-size changes on cation disordering		
	Δa_0 in \AA	Δc_0 in \AA
Synthetic mixture (C-102, C-114), 900° vs. 1155° C.		
Straumanis-mount powder x -ray films	-0.0017	+ 0.036
Adjacent strips on film taken with Guinier-type camera	-0.0026	+ 0.016
Dolomite, Lee, Mass., Unheated vs. 1155° C. (Guinier)	-0.0033	+ 0.037
Dolomite, Serra das Eguas, Brazil, Unheated vs. 1152° C. (Guinier)	-0.0048	+ 0.033
Dolomite, Gabbs, Nevada, Unheated vs. 1155° C. (Guinier)	-0.0033	+ 0.030

latest set of measurements because the initial starting materials were anhydrous end members and because of the concordance between results for the magnesian calcites and synthetic and natural dolomites. The previous magnesian calcite values were available only to 20 mol per cent MgCO_3 and had to be extrapolated to the dolomite composition. They led to the improbable conclusion that ordered material of dolomite composition had a larger unit cell volume than its disordered counterpart.

The new data give, for the first time, direct information on the change in cell size accompanying cation disorder in dolomite, which is summarized in Table 3 together with cell constants for the synthetic disordered solid solutions and for several natural dolomites. Disorder of dolomite results in a very slight decrease in a_0 and a somewhat greater increase in c_0 . Considering all of the data of Table 3, $\Delta a_0 = -0.003 \text{ \AA}$, $\Delta c_0 = +0.035 \text{ \AA}$, and $\Delta V = +0.3 \text{ \AA}^3$ or $+0.09\%$ of the dolomite cell volume. A material of dolomite composition with complete cation disorder has not thus far been obtained; the materials here described are substantially but not completely disordered (Goldsmith and Heard, 1961). The comparable values for fully disordered cadmium magnesium carbonate, $\text{CdMg}(\text{CO}_3)_2$ (Goldsmith, 1958, and in preparation) are $\Delta a_0 = -0.0024 \text{ \AA}$, $\Delta c_0 = +0.037 \text{ \AA}$, and $\Delta V = +0.42 \text{ \AA}^3$ or $+0.14\%$ of the $\text{CdMg}(\text{CO}_3)_2$ cell volume.

Goldsmith and Heard (1961) show that the maximum amount of excess CaCO_3 that can be contained in the (ordered) dolomite structure at high temperatures is approximately 7 mol per cent. Thus the composition versus cell edge curves shown for ordered materials in the dolomite region in Figs. 1 and 2 must merge with the curves for disordered materials at the approximate molar composition $\text{Ca}_{57}\text{Mg}_{43}$, and the zone between such curves corresponds to a region of intermediate cation order. The measurable effect is, of course, quite small, and the available data do not justify drafting the bifurcation in Figs. 1 and 2.

ACKNOWLEDGMENTS

This investigation was supported in part by a grant-in-aid from the California Research Corporation and by ONR Contract 233 (28) to Professor G. C. Kennedy of the Institute of Geophysics.

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Dr. Esper S. Larsen, Jr. died in Washington, D. C., on March 8, 1961, at the age of 82. Dr. Larsen was a member of the faculty at Harvard for many years. He was President of the Mineralogical Society of America in 1928, and received the Roebling Medal in 1941. A memorial will appear in a later issue.

BORNITE FROM CHESHIRE

Dr. R. A. Howie of the University, Manchester, England, writes the following comments.

In the "Second find of euhedral bornite crystals on barite."

Living as I do in Cheshire, England, I was interested in the article "Second find of euhedral bornite crystals on barite" (*Am. Mineral.* **45**, 1062, 1960), which states that such an association had been previously reported from the "Cheshire locality in England." Barite is in fact known from Alderley Edge, where there is considerable copper mineralization, but there is no record of bornite in association with barite. However, Dana—System of Mineralogy, 6th edition, page 78, states that "bornite occurs at the copper mine in Bristol, Conn., abundant, and often in fine crystals. At Cheshire sparingly in cubes, with barite, malachite and chalcocite." It therefore seems evident that the Cheshire locality which Kullerud, Donnay and Donnay refer to is Cheshire, Connecticut.

GELATIN MOUNTS FOR MINERAL GRAINS

In the Sept.–Oct. 1960 issue of the *American Mineralogist*, Olcott described a method for mounting mineral grains which was a modification of the procedure of Marshall and Jeffries (*Soil Sci. Soc. Amer. Proc.*, **10**, 397–405). Dr. Jeffries writes that carbonates are decomposed by the formalin in the original solution B, and very satisfactory results are obtained when the formalin is omitted.

1960 PEACOCK MEMORIAL PRIZE

The Walker Mineralogical Club announces that it has awarded its Peacock Memorial Prize (1960) of two hundred dollars "for the best scientific paper on pure or applied mineralogy, including crystallography, mineralogy, petrology, ore genesis, and geochemistry," submitted by a graduate student, to Dr. Joseph E. Patchett.

Dr. Patchett's paper was entitled, "A Study of the Radioactive Minerals of the Uraniferous Conglomerate, Blind River Area." He did his work under Professor E. W. Nuffield and Professor W. W. Moorhouse at the University of Toronto (Toronto, Ontario, Canada). Dr. Patchett, a native of Middletown, New York, received his B.S. from Rutgers University, New Brunswick, New Jersey in 1952. He received his M.A. in 1954 from the University of Toronto and, following two years of service in the U. S. Army, he returned to Toronto to resume his studies. He received his Ph.D. in 1960. He is presently employed as a crystallographer with the Research Department of the Norton Company, Chippawa, Ontario.

The Walker Mineralogical Club announces also at this time that it is offering the Peacock Memorial Prize again in 1961. A copy of the announcement follows.

1961 PEACOCK MEMORIAL PRIZE

TWO HUNDRED DOLLARS—\$200.00

For the best scientific paper on pure or applied mineralogy, including crystallography, mineralogy, petrology, ore genesis and geochemistry.

Conditions

1. The author of the paper shall be any graduate student enrolled in a Canadian university, a Canadian graduate student enrolled in any university, or any graduate student on a Canadian subject.

2. The paper, written in French or English, will be accepted for competition up to two years after completion of the work, even though the author may be enrolled no longer as a graduate student.

3. The paper may be in the form of:

- (a) a thesis,
- (b) a paper ready for publication,
- (c) a printed publication.

4. The paper may offer new or refined observations; or a significant synthesis and interpretation of existing data; or some new or improved application of mineralogy to useful ends; or the results of other work of sufficient interest and value.

5. Each paper must be accompanied by a letter from the candidate's supervisor stating the nature and extent of the assistance he may have given to the work submitted.

6. The paper is to be addressed to—The Secretary, Walker Mineralogical Club, 100 Queen's Park, Toronto 5, Ontario.

7. CLOSING DATE OF THIS COMPETITION—December 31, 1961.

If no paper of sufficient merit is received, the prize will not be given. All papers submitted will be returned to their authors as soon as the judging is completed. Announcement of the award will be made in the appropriate publications.

BACK ISSUES OF *Contributions to Canadian Mineralogy*

The Walker Mineralogical Club now has complete sets of the University of Toronto Studies, Geological Series, "*Contributions to Canadian Mineralogy*" (26 issues with indexes) on microfilm, at less than one-third the cost of a set in book form.

AMERICAN CRYSTALLOGRAPHIC ASSOCIATION

The 1961 summer meeting of A.C.A. will be held at the University of Colorado, Boulder, Colorado, July 31–August 4. The local chairman is Dr. Walter M. MacIntyre, Chemistry Department, University of Colorado; and the program chairman is Dr. G. B. Carpenter, Department of Chemistry, Brown University, Providence 12, Rhode Island.

10TH ANNUAL CONFERENCE ON APPLICATIONS OF X-RAY ANALYSIS

This conference will be held immediately following the A. C. A. Conference, in Boulder, Colorado, on 7, 8 and 9 of August, 1961. (Note that this is Mon.-Tues.-Wed.) The sessions will be held in the new conference room of the Park Lane Hotel, Denver.

For additional information, write W. W. Mueller, Head, Metallurgy Division, Denver Research Institute, University of Denver, Denver 10, Colorado.

Erratum

In the January–February, 1961 issue of the *American Mineralogist*, the book review on page 238 of "ULTRAVIOLET GUIDE TO MINERALS" was credited to the wrong author. The author is Mr. Sterling Gleason.