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Variation of lattice parameters in some sedimentary dolomites

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Abstract

Lattice parameters and compositions were independently determined for 36 low-iron dolomites. The data for sedimentary samples reveal a bimodal distribution of compositions with each group showing different trends of lattice parameter variations. The a and c parameters show poor correlation with $CaCO_3$ content in the range $0.50 \leq X_{CaCO_3} \leq 0.525$ and little absolute change. Good linear correlation in the range $0.535 \leq X_{CaCO_3} \leq 0.562$ is found. Similar relationships occur for cell volume. Cation ordered, single crystal dolomites have cell parameters that are contracted relative to sedimentary samples.

The distinct trends in the different composition regions indicate a non-linear variation of cell parameters with composition in natural dolomites. The influences of cation disorder, structural defects, and cation substitution are discussed. The results suggest that compositional analysis by X-ray diffractometry may be insensitive for many sedimentary dolomites with low excess Ca.

Introduction

X-ray diffraction (XRD) represents a long-established technique for compositional determination in solid solution series. Ionic size differences between substituting and host cations result commonly in systematic variations in interplanar spacings which can be detected by XRD methods. As in other mineral systems, this approach has been used widely in the Ca–Mg carbonates. Chave (1952) was the first to determine the variation of $10\bar{1}4$ interplanar spacings for the magnesian calcite solid solution. His study was limited to biogenic materials with compositions up to 29 mol% $MgCO_3$. Goldsmith et al. (1955) also studied the relationship between $d_{10\bar{1}4}$ and Mg content using both biogenic and inorganic magnesian calcites. In a more comprehensive study, Goldsmith and Graf (1958a) measured both lattice parameters and $d_{10\bar{1}4}$ values for several dolomites and a series of synthetic magnesian calcites (up to 20 mol% $MgCO_3$). Compositions were determined spectrochemically and lattice parameters were measured using both a powder diffractometer and a powder camera. The magnesian calcites were found to exhibit an approximately linear variation of a, c, and $d_{10\bar{1}4}$ with increasing substitution of Mg in calcite. The dolomites they studied were all nearly stoichiometric, and yielded similar values for lattice parameters.

Later Goldsmith et al. (1961) reexamined lattice parameters for a new series of synthetic magnesian calcites up to the dolomite composition. Observed relationships between lattice parameters and composition differed significantly from those of their previous study, but the authors concluded that the values from the later study are preferred. In addition they reported lattice parameters for a stoichiometric dolomite synthesized at elevated T and P; values agree closely with those for the natural dolomites from the earlier study. More recently Bischoff et al. (1983) examined the relationship between cell parameters and composition for synthetic and biogenic magnesian calcites, generally confirming the results of Goldsmith et al. (1961).

In a separate study, Goldsmith and Graf (1958b) found significant variations in d-spacings for many natural dolomites, and attributed this to variable substitution of Ca for Mg. Today it is widely recognized that many natural dolomites contain as much as 7 mol% excess $CaCO_3$ (cf. Land, 1980; Lumsden and Chimahusky, 1980). Not surprisingly, X-ray powder diffractometer methods are now widely used to estimate the compositions of natural dolomites. While the actual procedures used to determine the composition from X-ray data may vary, most workers rely on the original method outlined by Goldsmith and Graf (1958b). Lacking an experimentally measured relationship between dolomite composition and lattice parameters (or other d-spacings), these workers assumed, as a working approximation, that d-spacings should lie on a straight line connecting the respective values for pure

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calcite and ideal dolomite[2]. The justification for this approximation derives from consideration that a line drawn between respective *d*-spacings for calcite and dolomite is nearly parallel to the analogous line between the same parameters for calcite and magnesite. Goldsmith and Graf constructed working curves for several reflections in this manner and then simply transformed observed *d*-spacings into composition. Their study was restricted to Fe-free dolomites.

We were unable to find in the literature, since these early studies, any systematic investigation of well-characterized natural dolomites that has corroborated the validity of this method. In the present study we have determined independently lattice parameters and compositions of natural, low-Fe dolomites over the approximate composition range $0.50 \leq X_{CaCO_3} \leq 0.56$. Part of the impetus for this study derived from the more recent observations of modulated structures in calcian dolomites (Reeder and Wenk, 1979a,b; Reeder, 1981; Blake et al., 1982). Although the actual nature of the periodic defect structure in these materials is not known, it was desired to ascertain whether its presence affected lattice parameters in any systematic way.

Experimental

Samples

Two suites of sedimentary dolomites were selected, each of which shows compositional variation. Eighteen dolomites from Eocene rocks of the Floridan Aquifer constitute one suite. They exhibit differing textures (cf. Randazzo and Hickey, 1978) and a range of compositions ($0.501 \leq X_{CaCO_3} \leq 0.562$). The second suite consists of fourteen samples from the Ordovician Platteville Fm., S.W. Wisconsin. Again, these dolomites exhibit a variety of textures and compositions ($0.503 \leq X_{CaCO_3} \leq 0.553$). Data for two other sedimentary dolomite specimens (Triassic of Germany) are included since they were readily available.

It was also desired to have some examples of "ideal" dolomite for use as comparative standards. We selected two stoichiometric dolomites from previous studies which have been well characterized. The Eugui sample is taken from a large (3 cm), clear, colorless dolomite rhomb from a metamorphic complex in Spain. The sample was examined by transmission electron microscopy (TEM) by Barber et al. (1981) and Reeder and Nakajima (1982), and was shown to be homogeneous with very few dislocations. The latter authors report a wet chemical analysis which confirms that the stoichiometry is nearly ideal; this analysis is reported in Table 1. Reeder and Wenk (1983) have refined the crystal structure for this specimen using single-crystal X-ray data obtained from a four-circle diffractometer. Of particular interest to the present study is the refinement of site occupancies which shows essentially perfect cation ordering.

Table 1. Compositional and unit cell data for 36 natural dolomites

No	Sample	Composition (Mol%) $CaCO_3$	$MgCO_3$	$FeCO_3$	Cell Parameters a (Å)	c (Å)	V (Å^3)	c/a
1	EUGUI	50.06	49.32	0.52	4.8078(6)	16.002(3)	320.33(6)	3.328
2	LA	50.1	49.8	0.1	4.8069(2)	16.0034(6)	320.25(2)	3.329
3	CO53	55.7	44.3	0.0	4.831(1)	16.134(7)	326.02(18)	3.340
4	CO79	55.6	44.4	0.0	4.829(2)	16.140(7)	325.86(21)	3.342
5	CO50	55.6	44.4	0.0	4.829(1)	16.129(7)	325.74(19)	3.340
6	CO105	54.3	45.7	0.0	4.820(2)	16.085(8)	323.64(22)	3.337
7	RS126	53.8	46.2	0.0	4.819(1)	16.097(6)	323.80(15)	3.340
8	RS145	51.5	48.5	0.0	4.814(1)	16.031(5)	321.72(13)	3.330
9	RS154	51.6	48.4	0.0	4.813(1)	16.020(8)	321.34(18)	3.328
10	RS163	50.1	49.9	0.0	4.813(1)	16.023(5)	321.45(14)	3.329
11	12423	56.2	43.8	0.0	4.830(2)	16.143(8)	326.18(21)	3.342
12	12431	52.5	47.5	0.0	4.815(1)	16.035(5)	322.03(12)	3.330
13	12434	51.1	48.9	0.0	4.815(1)	16.030(5)	321.79(13)	3.329
14	12414	55.9	43.9	0.2	4.827(2)	16.130(7)	325.43(15)	3.342
15	10123	56.2	43.7	0.1	4.827(1)	16.136(6)	325.67(12)	3.343
16	10723	56.0	44.0	0.0	4.828(2)	16.152(10)	326.11(19)	3.345
17	1243	54.6	45.2	0.2	4.820(2)	16.079(7)	323.47(13)	3.336
18	10735	56.0	43.9	0.1	4.826(1)	16.142(6)	325.65(11)	3.345
19	1249	54.5	45.5	0.0	4.820(1)	16.117(6)	324.26(13)	3.344
20	ED1	55.8	44.1	0.1	4.825(2)	16.124(9)	325.07(18)	3.342
21	RI15	54.8	44.9	0.3	4.826(1)	16.122(7)	325.13(19)	3.341
22	WI30	52.0	47.9	0.1	4.814(1)	16.036(4)	321.92(11)	3.331
23	CG13	51.2	48.8	0.0	4.814(1)	16.030(6)	321.78(16)	3.330
24	WI13	50.8	49.2	0.0	4.814(1)	16.032(6)	321.70(16)	3.330
25	HH9	50.3	49.4	0.3	4.814(1)	16.018(6)	321.43(17)	3.327
26	WI9	50.5	49.3	0.2	4.815(1)	16.025(6)	321.74(11)	3.328
27	WI11	50.8	49.1	0.1	4.815(1)	16.030(6)	321.84(11)	3.329
28	WI13	50.8	49.2	0.0	4.816(1)	16.032(9)	322.01(18)	3.329
29	MI4	55.3	44.4	0.3	4.825(2)	16.123(10)	325.06(22)	3.342
30	HH26	54.0	45.3	0.7	4.818(1)	16.077(7)	323.25(13)	3.337
31	WI21	51.5	48.4	0.1	4.813(1)	16.028(7)	321.57(14)	3.330
32	RI5	51.8	47.5	0.7	4.814(1)	16.028(6)	321.66(10)	3.329
33	WI34	51.4	48.6	0.0	4.812(1)	16.024(6)	321.38(11)	3.330
34	EL13	52.1	47.0	0.9	4.814(1)	16.030(5)	321.69(9)	3.330
35	T3	50.9	48.7	0.4	4.813(1)	16.025(6)	321.44(11)	3.330
36	T6	51.1	48.7	0.2	4.813(1)	16.027(6)	321.48(11)	3.330

The second sample (LA), from Lake Arthur, NM (G-1374 of Goldsmith and Graf, 1958b), occurs as clear, reddish, single crystals embedded in gypsum. Transmission electron microscopy confirms that the sample is homogeneous; an X-ray structure refinement (Reeder, 1983) again shows essentially perfect cation ordering. A microprobe analysis confirms that the composition is nearly stoichiometric (Table 1).

We do not maintain that these 36 samples are necessarily representative of the majority of dolomites occurring in the rock record, but rather that they exhibit the approximate limits of compositional variation commonly found in Fe-free dolomites. No Holocene dolomites have been included in the present study.

X-ray methods

Small portions of each sample were uniformly ground in a pestle and mortar. LiF was added to each powder sample for use as an internal standard, and the mixture was again ground until homogeneous. Care was taken so as not to overgrind the dolomite and possibly cause structural disorder. The high-purity LiF used in this study was annealed prior to use, and cell data were taken from the JCPDS file. Several drops of acetone were added to the powder and a smooth slurry was applied to a clean glass slide. Surface evenness was checked on each slide so as to minimize centering errors on the diffractometer.

All X-ray work was done on an automated Picker powder diffractometer using Ni-filtered Cu radiation and a diffracted-beam graphite monochromator. Intensities were collected using the step-scan mode with step intervals of 0.01 degrees two-theta. Counting times were varied from 20 to 60 seconds depending on the relative intensity of the reflection. Intensity profiles were

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[2] Strictly speaking, the assumption that two or more *d*-spacings co-vary in a perfectly linear manner with composition is not generally valid, since most *d*-spacings are related by non-linear functions. Exceptions are those which because of their orientations are independent of one another and include planes (000*l*) and *hki*0), proportional to *c* and *a*, respectively.

obtained for 10 to 13 reflections for each sample, including $10\bar{1}4$, 0006, $01\bar{1}5$, $11\bar{2}0$, $11\bar{2}3$, $02\bar{2}1$, $20\bar{2}2$, $02\bar{2}4$, $01\bar{1}8$, $21\bar{3}4$, $20\bar{2}8$, $11\bar{2}9$, and $03\bar{3}0$. Generally not all of these reflections were found to be suitable in a given sample. For example, the $03\bar{3}0$ dolomite reflection was frequently asymmetrical, and, if so, was deleted from the data set. The $11\bar{2}9$ reflection was sometimes not resolved by the peak-fitting program, and occasional overlap of the 200 LiF peak with the $02\bar{2}4$ dolomite peak prevented the use of either. Three reflections from the LiF internal standard (111, 200, 220) were also step-scanned for each sample. The positions of all peaks were determined by a least-squares curve-fitting program using a Lorentzian profile. The standard deviation of the least-squares fit of an observed intensity profile was typically less than 0.002 degrees two-theta; this represents the minimum error of the calculated peak position, however.

The peak positions for the LiF standard were used to construct a peak shift error *vs.* two-theta correction for each sample. The dolomite peak positions were then corrected accordingly. Corrected peak positions were used to refine *a* and *c* lattice parameters using C. T. Prewitt's least-squares cell refinement program CELRF. Standard deviations of the parameters were calculated from the least-squares method and do not reflect errors in the determination of peak positions. The latter are very small, however, owing to the use of the peak-fitting program. Reproducibility was tested by running the Eugui sample on four different occasions during the course of data collection. The observed variation in refined cell parameters was within the calculated error. The lattice parameters determined for Eugui dolomite agree closely with those reported by Reeder and Wenk (1983) using four-circle diffractometer data.

The lattice parameters for one sample, LA, were determined by single crystal methods using a Picker four-circle diffractometer with graphite-monochromatized Mo*K*α radiation (Reeder, 1983). Centered peak positions of 30 reflections were used to refine lattice parameters with least-squares methods. The standard deviations using the single-crystal method are roughly an order of magnitude smaller than with the powder diffractometer method. However, this largely reflects the greater number of reflections used with the single-crystal method.

Compositional analysis

Ca, Mg, and Fe (and usually Sr and/or Mn) contents of the dolomites were determined using an automated electron microprobe operating at 15 kV. Sample current was monitored at either 0.01 or 0.015 μA on brass, and counting times varied from 20 to 30 seconds. Carbonate standards were used throughout, and incident beam diameters of 10–20 μm were used. Multiple analyses were made on each sample; averaged results are reported. Compositions have been normalized to give a sum of 100% carbonate. Errors are estimated to be a few tenths of one percent. The population of analyses for any given sample showed standard deviations ranging from 0.1 to 0.5 mol% MCO_3, although most were less than 0.3 mol%. No evidence for compositional zoning was found, based on the microprobe results and both light and cathodoluminescent microscopy.

Some of the sedimentary dolomites used in the present study are cloudy in thin section (Sheppard, 1982). Thus we were concerned that solid inclusions rich in Ca or Mg might influence the results of the microprobe analyses. In view of this, great care was taken to avoid placing the probe beam on or near visible inclusions. We believe that the generally small standard deviation of the population of analyses for each sample may be taken as evidence that solid inclusions were not a significant factor influencing the reported analyses.

Results

Compositions and unit cell data for the 36 natural dolomites studied are given in Table 1, and the relationships between them are shown in Figures 1–4. The composition range of the sedimentary dolomites studied is similar to that reported by other workers. As much as 56.2 mol% $CaCO_3$ is found. Among the samples analyzed, there appears to be a bimodal distribution in terms of $CaCO_3$ content. The population with compositions near the ideal 1:1 value has a range of $0.50 \le X_{CaCO_3} \le 0.525$. The range of composition for the more calcian group is $0.535 \le X_{CaCO_3} \le 0.562$. These two groups will be referred to here as the low-Ca and high-Ca populations. Similar bimodal distributions have also been reported by Goldsmith and Graf (1958b), Füchtbauer and Goldschmidt (1965), and Lumsden and Chimahusky (1980).

The $FeCO_3$ contents of all the dolomites are less than 1.0 mol% and usually less than 0.5 mol%. Where analyzed, $MnCO_3$ and $SrCO_3$ contents are less than 0.1 mol%, and have been disregarded in reporting compositions.

The relationships between lattice parameters and $CaCO_3$ content are shown in Figures 1 and 2. The open circles in

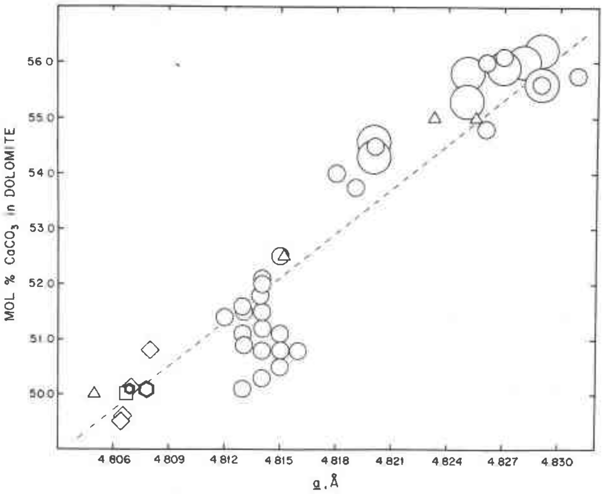

Fig. 1. *a* lattice parameters and $CaCO_3$ contents for 34 sedimentary dolomites (open circles) and other selected samples. The hexagons represent the ideally-ordered, single-crystal specimens, LA and Eugui. The diamonds represent four of the well-crystallized, stoichiometric dolomites from Goldsmith and Graf (1958a). The square and the triangles represent the synthetic dolomite and the largely-disordered synthetic carbonates, respectively, of Goldsmith et al. (1961). The diameters of the circles represent one standard deviation of the refined lattice parameter, while the "diameters" of the hexagons reflect two standard deviations. The size of other symbols are drawn arbitrarily, since no standard deviations were given by the reporting authors. The dashed line connects *a* lattice parameters for ideal dolomite and calcite.

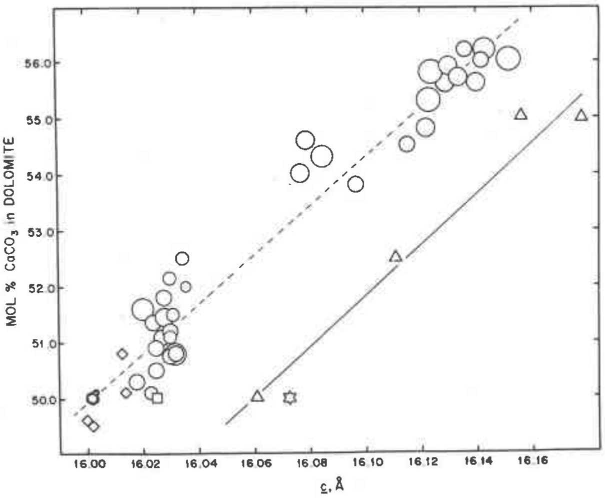

Fig. 2. c lattice parameters and $CaCO_3$ contents for the samples shown in Fig. 1. Symbols have the same meanings (in all figures) as in Fig. 1. The dashed line connects c parameters for ideal dolomite and calcite. The solid line is the best fit to the synthetic, largely-disordered carbonates of Goldsmith et al. (1961), and is analogous to the lower line in their Fig. 2. The star depicts the estimated c parameter for a completely disordered sample based on the data of Reeder and Wenk (1983).

both figures represent values for the two suites of sedimentary dolomites and the two additional sedimentary samples from Triassic rocks in Germany. The diameter of each circle reflects one standard deviation of the refined parameter. The remaining symbols represent other dolomites and will be discussed shortly.

The dashed lines in Figures 1 and 2 connect "best" lattice parameters for calcite and dolomite. Values used for calcite are a = 4.990Å and c = 17.061Å(Graf, 1961; Effenberger et al., 1981). Dolomite values are taken as the average of the Eugui and LA samples—a = 4.807Å, c = 16.003Å. In Figure 2 this dashed line nearly bisects the data points for the sedimentary samples (open circles). A similar relationship is found in Figure 1 over part of the composition range; a discrepancy is observed in the low-Ca population. In general both lattice parameters are found to increase with increasing $CaCO_3$ content. Thus it might seem that a linear relationship as suggested by Goldsmith and Graf is not an unreasonable *first approximation*. A careful examination of the data, however, seems to reveal distinctly different trends which are inconsistent with a *strictly* linear relationship. Both a and c lattice parameters for the low-Ca population show little or no correlation with composition; linear correlation coefficients are: R = −0.03 for a and R = 0.53 for c. Conversely, parameters for the more calcian samples exhibit a good linear correlation (R = 0.87 for both a and c). Equally important are the maximum variations of a and c for the low-Ca group which are only 0.004Å and 0.018Å, respectively. These values are small when compared with the same variations found for the high-Ca group—0.013Å and 0.075Å, respectively). In each population, roughly the same total variation of $CaCO_3$ content is represented (2.5 mol%).

The behavior of the high-Ca population is roughly consistent with the linear approximation for both a and c, although least-squares lines describing these data points in each case have slightly lower slopes than the dashed lines connecting values for pure calcite and dolomite. In the low-Ca population, although the correlation is poorer, the least-squares line for c is steeply inclined relative to that for the high-Ca population. For a there is little or no correlation (R = −0.03). Furthermore, the relatively small total variation of a and c with composition in the low-Ca group indicates an insensitivity of these parameters over this composition range. The poor correlation and low sensitivity are not simply artifacts due to fundamental differences between the two suites of dolomites studied. The samples of each suite not only span essentially the entire composition range of the study, but also show, as individual suites, the poor correlation with composition in the low-Ca samples and the good correlation in the high-Ca samples. It should be noted that the relationship between $d_{10\bar{1}4}$ and $CaCO_3$ content shows behavior similar to that seen in Figures 1 and 2.

Even though cell volume is a non-linear function of the lattice parameters, the same general features just described are found for the relationship between cell volume and $CaCO_3$ content (Fig. 3). In the low-Ca group there is poor linear correlation with composition (R = 0.32) and little absolute change of cell volume (~0.7Å^3). In the high-Ca group a good linear correlation is observed (R = 0.91) and also a larger variation (~3.0Å^3).

Variations of a and c lattice parameters of individual samples are found to be highly correlated throughout the entire composition range studied. Samples with large values of c have commensurately large values of a, and *vice versa*. This correlation between lattice parameters is

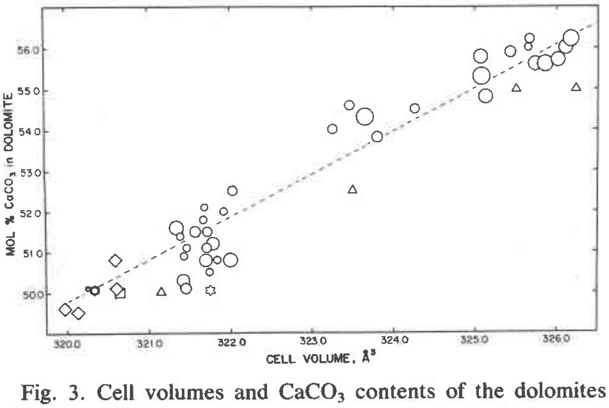

Fig. 3. Cell volumes and $CaCO_3$ contents of the dolomites shown in Figs. 1 and 2. The dashed line connects values of the cell volumes for ideal dolomite and calcite.

the reason for the similarity of behavior seen in Figures 1 and 2.

The maximum variation in the *a* lattice parameter over the entire composition range studied is rather small (0.019Å) compared to that for *c* (0.134Å). Thus in natural samples, increasing substitution of Ca ultimately affects the *c* parameter considerably more than *a*. This was recognized by early workers, as well. We have calculated axial ratios *c*/*a* for our samples (Table 1) and plotted them as a function of $CaCO_3$ content in the dolomites (Fig. 4) to show this relationship. Overall, the axial ratio *c*/*a* increases with $CaCO_3$ content. Although the correlations are less well defined, the bimodal distributions are apparent, as well as the distinct trends for each group.

Comparison of the lattice parameters of the sedimentary samples with those of the single-crystal specimens LA and Eugui proved to be interesting. The latter are represented as hexagons in Figures 1–4 ("diameters" here reflect two standard deviations of the respective parameter). There is a noticeable difference between lattice parameters for these single-crystal samples and those from the two suites of sedimentary dolomites, the latter being uniformly larger (see Figs. 1 and 2). This difference is especially pronounced for *a*, and not surprisingly, is also true for cell volume (Fig. 3). Goldsmith and Graf (1958a) determined cell parameters and compositions independently for several nearly stoichiometric dolomites These authors report that the samples occur as well-crystallized, cleavage rhombs or fragments, either clear or somewhat milky. We have taken values from four of these dolomites as reported by the authors;[3] they are included as diamonds in Figures 1–4. The size of the diamond does not reflect error in the parameter since none was reported. Thus we are unable to evaluate the relative importance of these observations, and must place more weight on the values for LA and Eugui. Furthermore cation distributions are not known in these other dolomites. Nevertheless, the data from Goldsmith and Graf (1958a) do tend to strengthen our observation. This hiatus in lattice parameters between single-crystal specimens and the nearly pure sedimentary samples may just reflect an artifact of sampling, which might be filled by additional specimens. Alternatively, it may indicate a structural difference characteristic of one group.

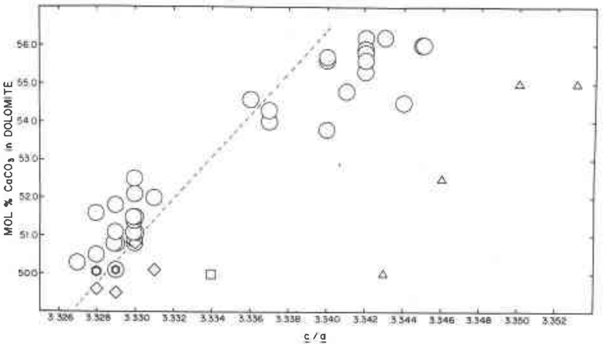

Fig. 4. *c*/*a* ratios and $CaCO_3$ contents of the dolomites shown in the previous figures. The dashed line connects values for ideal dolomite and calcite.

Discussion

In general, variations in lattice parameters may reflect changes in composition, site distributions, *T* and *P*, and other structural factors. In the present case, it is not possible to rigorously evaluate each of these aspects, since very little is known about either site distributions or structural disorder in natural dolomites. We regard *T* and *P* variations as insignificant in the present context. In the magnesian calcite solid solution, the lattice parameters determined by Goldsmith et al. (1961) exhibit a linear correlation with composition over the range $0.50 \leq X_{CaCO_3} \leq 0.70$ (R = 0.999 for *a* and R = 0.998 for *c*). These synthetic samples (triangles in Figs. 1, 2 and 3) are reported as being largely cation disordered. Nearer the calcite composition, their data show slight deviations from linearity, also confirmed by Bischoff et al. (1983). Over the composition range of the present study, however, the behavior of the dolomite lattice parameters is in marked contrast to that of the magnesian calcites.

In the calcite structure, there is one cation site, and it is generally assumed that substituting cations mix randomly on this site. There are strong site preferences in the dolomite structure, where Ca and Mg atoms preferentially occupy the A and B sites, respectively. Thus, assuming maximum order any excess Ca must occupy the smaller B site, and so distorts the local structure. Cation disorder also requires that Ca occupies the B site. There seems to be a common belief that many sedimentary dolomites have less than maximum ordering of cations (cf. Land, 1980; Carpenter, 1980). The data to support this seem to be rather qualitative, however, and no site occupancy determinations, except for LA dolomite (Reeder, 1983), have been published for sedimentary samples.

The effect of cation disorder on lattice parameters has been investigated by Goldsmith et al. (1961). They showed that *partial* disordering may result in an increase in *c* by as much as 0.03Å and a slight decrease in *a* (0.003Å). Reeder and Wenk (1983) also studied the effect, and showed that the change in *c* for complete disordering may be considerably larger (0.07Å); no measurable change in *a* was observed. We have illustrated the influence of cation disorder in Figures 1–3. The triangles represent parameters for the largely disordered, synthetic materials of Goldsmith et al. (1961). The stars in Figures 2 and 3 represent the *c* parameter and cell volume, respectively, for a completely disordered sample, using the data from Reeder and Wenk (1983). The symbol is not shown in Figure 1 since these authors detected no measurable change of *a*.

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[3] The other dolomite used by these authors contained $FeCO_3$ in excess of 3 mol%.

Based on the *c* lattice parameter data (Fig. 2), it might be argued that some of the sedimentary samples, those with compositions most nearly stoichiometric, are partially cation disordered. This is consistent with the observed differences in *c* between these and the ideally ordered samples LA and Eugui. Such a conclusion seems less tenable considering the data for *a* (Fig. 1). Here, *a* parameters for the low-Ca group, more specifically those nearest the ideal composition, are expanded relative to both the ideally ordered single-crystal dolomites and the largely disordered materials of Goldsmith et al. (1961). This observation is inconsistent with cation disorder being the major factor and suggests that something else is responsible for the expanded lattice parameters for these nearly stoichiometric dolomites, or else that the disorder is of a different kind. In this regard, the role of CO_3-group disorder has not been evaluated. If present, it might effect both *a* and *c* parameters. In any event, because the variations of the *a* and *c* lattice parameters are highly correlated with one another, the factors causing these variations must influence both.

Graf et al. (1967) proposed that basal stacking disorder might occur in some nonstoichiometric dolomites. If pervasive, this might also influence measured cell parameters. All of the samples from the Floridan Aquifer suite had previously been examined using the TEM by Reeder (1981). No evidence of mixed layering was found in any of these samples. We have also recently examined in the TEM several of the samples from the other suite, and failed to find any mixed layering. It should be noted that some type of basal stacking disorder has recently been found in other dolomite samples by H.R. Wenk (pers. comm.). We have no reason to believe, however, that it may be a factor in the present study.

Other structural aspects may be relevant to the study. The previously cited TEM work has shown that the samples in the high-Ca population typically have a modulated microstructure. The more stoichiometric samples generally lack this microstructure and are usually homogeneous. We found this to be true for the samples we examined as well. Thus it is observed that a good linear correlation between cell parameters and composition exists for those dolomites that have pervasive modulated microstructures, but a poor correlation for those lacking them. Unfortunately, we cannot yet evaluate whether this is merely coincidental, or if this is an important factor.

Lacking sufficient data regarding the other various contributing factors, the observed variations in cell parameters could simply be described with composition as the *predominant* controlling variable. For example, if a continuous curve were drawn through each complete data set in Figures 1 and 2, in both cases the different trends for the distinct populations would necessitate that it be manifestly non-linear. This would also be true for cell volume. Newton and Wood (1980) have discussed nonlinear behavior not unlike this for cell volumes in silicate solid solutions. They distinguish between two types of site-filling mechanisms, both of which may lead to sigmoid-shaped curves of cell volume *versus* composition. In their *non-equivalent site* model, the presence of distinct sites affects a change in volume behavior when, upon increasing substitution, the preferred site first becomes filled by that species, which only then must begin to fill the other site. In their *equivalent site* model characterized by the availability of only one site, nonlinearities in volume behavior are caused by the varying influence on the overall structure of local deformations resulting when "foreign" atoms begin filling a site. Newton and Wood argue for this case, as did Iiyama and Volfinger (1976), that the influence of increasing substitution on the structure only becomes pronounced when the locally-deformed regions begin to interact with one another as their "concentration" increases.

We are hesitant to draw any close analogy with the behavior described by Newton and Wood, not only because the present case concerns an intermediate, cation-ordered phase in a cation-disordered solid solution, but also because the total range of compositional variation is rather limited. Nevertheless, the site-filling mechanisms described by these authors might provide insight to the observed behavior. For example, if sedimentary dolomites are characterized by partial cation disorder, increasing substitution of Ca should favor the A site. A change in volume behavior (and also of lattice parameters) is then expected when the A site becomes completely filled by Ca (or nearly so). Obviously the point at which the site-filling behavior changes is dependent on the degree of disorder and is then limited, in the present case, by the narrow range of compositional variation. Unfortunately, the lack of reliable data on cation distributions in low-temperature dolomites precludes a complete evaluation of this model. Moreover, cation distributions may be influenced, not only by composition, but also by structural disorder as previously noted.

Alternately, if cation order is sufficiently near maximum so that only the B site is available for excess Ca, then a change in the behavior of volume and lattice parameters might also be expected. For this type of model, Newton and Wood found that upon *initial* substitution of the larger-cation component, less pronounced increases in cell volume occur than do for continued substitution. This type of anomaly was observed in several silicate solid solutions, usually manifested in the first 10 to 15 mol% substitution, and it commonly resulted in a negative excess volume of mixing over this interval.

If the data for the single-crystal samples are included with those from the sedimentary dolomites then we find no analogy with this latter model, since cell parameters and volumes for the sedimentary samples are expanded relative to the single-crystal specimens. We can offer no explanation for this difference that remains consistent with the data. If the sedimentary samples are considered alone, then the different trends shown by the high- and low-Ca groups are not inconsistent with the equivalent-site model, showing initially little or no response to increasing Ca, and after roughly 3 mol% excess, a more pronounced response occurs. In view of the uncertainty about cation disorder, however, we are hesitant to propose this except as a possible explanation. Very likely, several factors are responsible for the observed behavior.

In a practical sense, we find the assumption of a linear relationship, as used by Goldsmith and Graf, to be reasonably good only for natural dolomites with compositions $X_{CaCO_3} > 0.535$, and compositions for such dolomites can be *estimated* from our data. For dolomites with more nearly stoichiometric compositions serious discrepancies exist. For example, if *a* and *c* parameters were measured to determine $CaCO_3$ content, our data suggest that the error might be roughly 1 mol% $CaCO_3$ in the high-Ca region; however, in the low-Ca region, the error could be as large as 2.5 mol%. Similar errors are expected using cell volume. If factors allow, an independent determination of composition, such as by electron microprobe, is generally preferred. Furthermore, the X-ray method is likely to be unsuitable either for mixtures of crystals having different compositions or for crystals with significant compositional heterogeneities, such as zoning.

We are aware that many workers prefer to use the position of the $10\bar{1}4$ reflection for dolomite rather than the lattice parameters to estimate compositions. Since the same general behavior is also observed for $d_{10\bar{1}4}$ variations there is no benefit to this approach. Furthermore, we believe that better precision is obtained by refining lattice parameters since random error is minimized by the least-squares method and calculated standard errors give an indication of the uncertainty of the measurement. Lattice parameters also provide a unique description of the cell which is not available with $d_{10\bar{1}4}$. It should be pointed out that any error associated with the determination of peak position will further increase the expected overall error. In this regard, the use of least-squares peak-fitting programs reduces this error, and we recommend their use whenever good precision for parameters is required.

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