

TEM observations and X-ray crystal-structure refinement of a twinned dolomite with a modulated microstructure

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ABSTRACT

X-ray precession photographs of a single crystal of natural dolomite reveal a pseudo-mirror in reciprocal space indicating twinning by merohedry. A single-crystal X-ray diffraction crystal-structure refinement carried out on 687 observed reflections from the twinned crystal shows the twin operation to be a mirror across the a^*c^* plane or $(2\bar{1}10)$ in direct space. Refinement on F^2 converged to $R = 0.025$ and $\omega R = 0.038$, and refinement on F yielded $R = 0.0314$, $\omega R = 0.0507$ after corrections were made for the twin operations. Bond distances and angles and atomic parameters agree well with previous determinations. The refinement indicates that cation positions are well ordered and that the composition is stoichiometric. The twin operation does not disturb cation sites, but the anions have a mirror relationship across the composition plane. Anion disorder is not present except at the twin boundaries.

This stoichiometric, well-ordered dolomite displays a modulated microstructure in TEM. The twin domains, however, are represented as features distinct from the modulated microstructure. The 100–200-Å-wide domains that define the modulations do not differ in composition, cation ordering, or anion orientation. Instead, the contrast in this dolomite may be due to lattice strain about the smaller domains that give rise to “c” reflections in electron-diffraction photographs. These domains scatter X-rays incoherently and do not contribute to the observed intensities. The strain can give rise to enlarged unit-cell parameters without necessarily an increase in Ca content.

A replacement origin for the twinning and the modulated microstructure is not indicated. Both microstructures are growth defects that have developed in a pore-filling dolomite cement.

INTRODUCTION

Many dolomites and some calcites display a very finely modulated microstructure when examined with transmission electron microscopy (TEM). This enigmatic microstructure, when found in dolomite, is commonly recognized in samples containing at least 1 mol% excess CaCO_3 , and in most ancient samples with an excess of 4% (Reeder, 1980) and has been ascribed to strain due to small-scale compositional fluctuations (Reeder, 1981). Originally proposed to be an exsolution phenomenon, it now appears to be a growth defect (Reeder et al., 1984; Miser, 1985; Reeder and Prosky, 1986). The exact nature of this microstructure is unknown. Since similarly appearing features occasionally occur in calcite, the possibility of domains with different anion orientations has been proposed (Gunderson and Wenk, 1981). Other suggestions have included highly localized or periodic cation substitutional disorder (Blake et al., 1982; Reeder and Nakajima, 1982) or some combination of the above (see e.g., Wenk et al., 1983).

We report here TEM observations and an X-ray structure analysis on a single crystal of dolomite that showed these modulations but was well ordered and stoichiometric.

MATERIAL STUDIED

An outcrop sample from the Troy member of the White Limestone Formation (Eocene, Jamaica) was found to contain large (up to 0.3 mm) crystals of optically clear dolomite (Fig. 1). In TEM, all crystals show a modulated microstructure. The reasonably heavy oxygen isotopic composition ($\delta^{18}\text{O} = +2.1\text{‰}$ PDB) as well as field relations (Zans et al., 1962) suggest that the unit has never been deeply buried.

An optically clear, rhomb-shaped crystal of volume $2.5 \times 10^{-3} \text{ mm}^3$ was extracted for X-ray analysis. Both Weissenberg and precession photographs indicated that the diffraction intensities are consistent with the space group $R\bar{3}$ in agreement with the known dolomite structure. However, an $hh(2\bar{h})l$ precession photograph dis-

played pseudo-mirror relations among intensities that are inconsistent with $R\bar{3}$. A structure refinement was, therefore, justified.

After completion of the X-ray and TEM work on this crystal, an attempt was made to perform an electron-microprobe analysis on the thicker portions of the previously ion-milled crystal. The analyses, assuming anion stoichiometry, yielded a composition of 49.3 ± 0.8 mol% MgCO_3 . Although Fe and Mn were not analyzed in this crystal, other crystals from the same sample had Fe and Mn contents below detection limits.

STRUCTURE REFINEMENT

The crystal was mounted on a Syntex P2₁ automated single-crystal diffractometer, and data were collected to $\sin \theta/\lambda = 0.70$, $-6 \leq h \leq 3$, $0 \leq k \leq 6$, $0 \leq l \leq 22$, using $\text{MoK}\alpha$ radiation monochromatized with a graphite crystal, $\lambda = 0.71069$. The diffractometer was operated in the ω -scan mode with scan rates varying from 1.5 to 5° min^{-1} . Omega scans of several peaks were symmetric with peak widths at half height of about 0.3°. A least-squares refinement of 15 reflections whose 2θ values were precisely determined in the range 26 to 29° yielded the lattice parameters $a = 4.811(1)$ and $c = 16.047(6)$ Å. The 687 measured intensities were transformed in the usual manner to structure amplitudes and included an absorption correction $\mu_1 = 15.2$ cm^{-1} based on stoichiometric dolomite. The transmission factors ranged from 0.81 to 0.84. Estimated errors of the intensities were calculated from

$$\sigma(F^2) = S[I_p + 1/R^2(I_{b1} + I_{b2}) + (pI)^2]^{1/2},$$

where I_p = number of counts accumulated during the scan of the peak, I_{b1} = background counts on the low 2θ side, S = speed of scan in $\text{deg} \cdot \text{min}^{-1}$, R = ratio of total background counting time to scan time, and $p = 0.02$. Equivalent reflections from the 687 measured reflections were averaged to give 215 unique reflections with $R_{\text{int}} = 0.0132$. All structure amplitudes were considered observed on the basis that $F > 2\sigma_F$.

Initially, an attempt was made to refine the data using published positional and anisotropic thermal parameters for dolomite (Beran and Zemann, 1977). Least-squares refinement using SHELX-76 (Sheldrick, 1976) converged to a conventional $R = 0.132$, with a nonpositive definite U tensor for carbon. Comparison of the calculated intensities with observed values revealed that all reflections of the type $hkil$, all nonzero indices, matched poorly. A difference electron-density map revealed extra electron density in the oxygen plane at x, y, z coordinates of 0.215, 0.301, 0.242, respectively. This extra electron density is 1.29 Å away from C and implies a reasonable C–O distance. This interpretation is consistent with rotated anions and/or the presence of a twin structure. The previously mentioned pseudosymmetry simulating $R\bar{3}m$ points to a twin by merohedry in which reflections $\bar{k}h\bar{l}$ from crystal 2 superimpose on $hkil$ from crystal 1.

To refine the structure using this twin model, the full

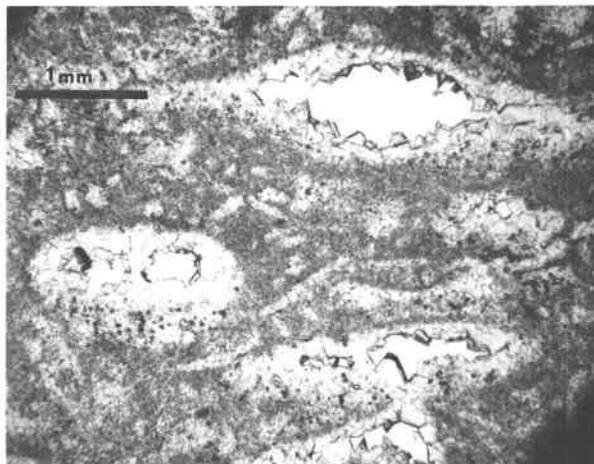


Fig. 1. Thin section of Troy dolomite. Coarse crystals, such as the one used in the refinement, are void-filling cement. In TEM, both the coarse spar and the fine-grained matrix contain a modulated microstructure.

matrix least-squares program NUCLS (1974) was modified to permit refinement of intensity data from a twin consisting of two individuals of differing volume. The quantity minimized was

$$D = \sum \omega [F_o^2 - (kF_c)^2]^2,$$

where

$$\omega = [\sigma(F^2)]^{-2},$$

and

$$F_c^2 = xF_{\text{hkl}}^2 + (1-x)F_{\bar{k}h\bar{l}}^2.$$

F_{hkl} is the structure factor from individual 1, $F_{\bar{k}h\bar{l}}$ is the structure factor from its twin, and x is the volume fraction of individual 1. Refinement with full occupancies for all atoms converged to $R = 0.025$, $\omega R = 0.038$, where

$$R = \frac{\sum |F_o^2 - (kF_c)^2|}{\sum F_o^2}$$

and

$$\omega R = \frac{\sum \omega (F_o^2 - kF_c^2)}{\sum \omega F_o^2}.$$

When the occupancy factors for both Ca and Mg were varied simultaneously with all other parameters, the value of R decreased but not significantly. The occupancy factors for Ca and Mg were unity within the error limits. The twinning fraction for the full occupancy refinement was 0.606(3). The final positional and thermal parameters are shown in Table 1. The scattering factors were for neutral atoms corrected for the real and imaginary parts of dispersion (*International Tables for X-Ray Crystallog-*

Table 1. Atomic positional and thermal parameters ($\times 10^4$) for dolomite

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{∞} (\AA^2)
Ca	0	0	0	108(2)	108	113(2)	$\frac{1}{2}U_{11}$	—	—	110(1)
Mg	0	0	$\frac{1}{2}$	69(2)	69	98(4)	$\frac{1}{2}U_{11}$	—	—	79(2)
C	0	0	2430(1)	99(5)	99	80(7)	$\frac{1}{2}U_{11}$	—	—	93(4)
O	2476(2)	9650(2)	2441(1)	96(4)	140(4)	167(4)	72(3)	-23(3)	-30(3)	128(3)

Note: The anisotropic thermal parameters in \AA^2 are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. $U_{\infty} = \frac{1}{3}\sum_i U_{ij}a_i^*a_j^*$. Numbers in parentheses are estimated standard deviations.

raphy, 1974). Table 2¹ contains a list of observed and calculated F^2 .

The value of $F_o(hkl)$ from a single individual in the twinned crystal was calculated from

$$F_o^2(hkl) = [F_o^2(hkl) - vF_o^2(\bar{k}hl)]/(1 - v^2),$$

where

$$v = (1 - x_1)/x_1.$$

Refinement based on $F(hkl)$ converged to $R = 0.0314$, $\omega R = 0.0507$, $\omega = [\sigma(F)]^{-2}$. A difference Fourier was featureless with highest and lowest values of $|0.5| \text{ e \AA}^{-3}$. Positional and anisotropic thermal parameters were $\leq 3\sigma$ of those shown in Table 1.

TEM OBSERVATIONS

The same crystal on which the X-ray structure determination was done was ion milled and examined by transmission-electron microscopy using a JEOL 200 CX TEM. In spite of the ordered, stoichiometric nature of the crystal, a pervasive modulated microstructure is observed. The modulated domains seen in this crystal differ from those of typical calcian dolomites only in that the contrast is somewhat weaker, and the wavelength of the domains, although quite variable, is sometimes much coarser. Dark-field images revealed the twin domains as relatively large (up to several micrometers in width), separated by straight boundaries, and superimposed on the modulated microstructure. Figure 2(a) shows a twin boundary in a dark-field image produced with $\mathbf{g} = \bar{1}3\bar{2}2$ under two-beam conditions. This intensity is a superposition of $I(\bar{1}\bar{3}\bar{2}2)$ from individual 1 and $I(\bar{3}122)$ from individual 2. Figure 2(b) shows the same area but using $\mathbf{g} = \bar{3}122$, which contains an intensity contribution $I(\bar{3}122)$ from individual 1 and $I(\bar{1}\bar{3}\bar{2}2)$ from individual 2. The change in overall intensity between opposite halves of the two figures is the result of the large difference in structure-factor amplitude for these two superimposed reflections. Figure 2c shows the same area imaged with $11\bar{2}0$. The twin boundary is invisible because the intensities of $11\bar{2}0$ from individual 1 and $\bar{1}\bar{1}20$ from individual 2 are identical and the boundary is viewed edge-on. The modulated

microstructure, however, is still visible in this orientation. Figure 2d shows an electron-diffraction pattern of the same area but oriented so that the reciprocal lattice net containing the operating reflections indicated above is centered. None of the spots are doubled in this or any other orientation, confirming the twinning by merohedry. Slight streaking, parallel to the $[11\bar{2}0]$ direction, can be seen. This direction is perpendicular to the operational twin plane as well as to the composition plane shown in the dark-field photographs after corrections for image rotation have been made.

DISCUSSION

The twin is operationally a mirror across the $\mathbf{a}^*\text{-}\mathbf{c}^*$ plane or ($2\bar{1}\bar{1}0$) in direct space. Since the inversion center is preserved, this twin operation is equivalent to a rotation about the direct space \mathbf{a}_2 axis. It is shown schematically in Figure 3. The cation sites on either side of the twin plane are identical; however, the anion planes have an antiphase relationship. This type of twinning is not visible in plane-polarized light.

Reeder and Nakajima (1982), on the basis of both TEM dark-field experiments and X-ray precession photographs, proposed a twinning mechanism in experimentally heated dolomites quenched from 1150 and 1200°C. Their model (Fig. 4b in Reeder and Nakajima, 1982) shows the cation layers offset in the two individuals whereas the CO_3 groups are undisturbed. They specify that "the twin axis is the zone axis containing co-linear carbon atoms parallel to \mathbf{a} ." The twin mechanism determined in this investigation is not equivalent to the Reeder-Nakajima model. Their two-fold twin axis passes through the C atom, whereas in our twin, the two-fold axis passes through a cation that lies on a center of symmetry. Thus, the composition plane is a mirror plane. We suggest that the observations reported by Reeder and Wenk (1983) of residual electron density in Fourier difference maps obtained from X-ray intensity data of dolomite crystals heated and quenched from 1150 and 1200°C are due to the twinning described by us.

The X-ray structure refinement is interesting in light of the presence of the modulated domains in this crystal. The atomic coordinates agree well with those published previously (Steinfink and Sans, 1959; Beran and Zemmann, 1977; Althoff, 1977; Reeder and Wenk, 1983). The anisotropic thermal ellipsoids, particularly along the \mathbf{c} axis,

¹ To obtain a copy of Table 2, order document AM-87-326 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

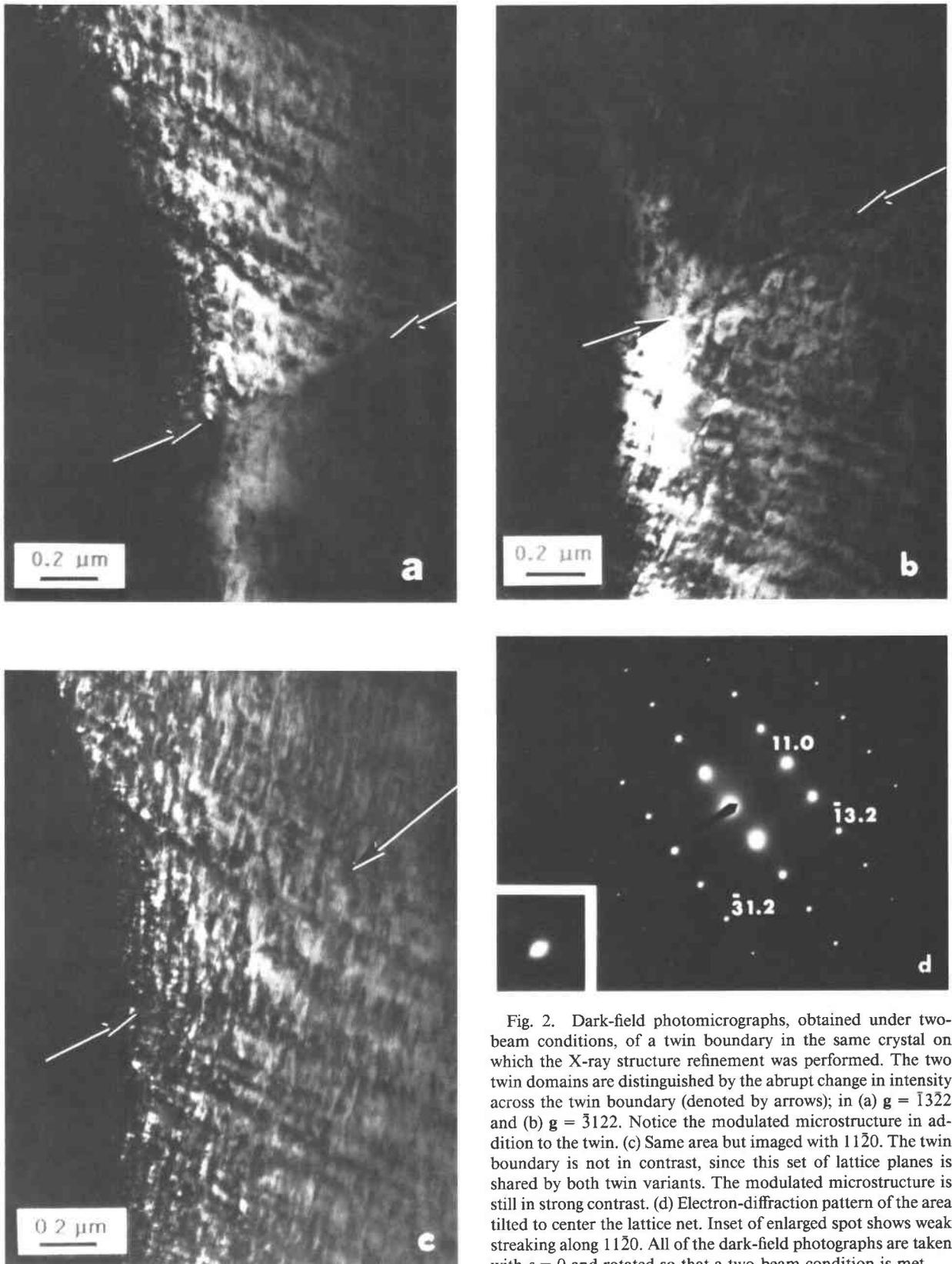


Fig. 2. Dark-field photomicrographs, obtained under two-beam conditions, of a twin boundary in the same crystal on which the X-ray structure refinement was performed. The two twin domains are distinguished by the abrupt change in intensity across the twin boundary (denoted by arrows); in (a) $g = \bar{1}322$ and (b) $g = \bar{3}122$. Notice the modulated microstructure in addition to the twin. (c) Same area but imaged with $11\bar{2}0$. The twin boundary is not in contrast, since this set of lattice planes is shared by both twin variants. The modulated microstructure is still in strong contrast. (d) Electron-diffraction pattern of the area tilted to center the lattice net. Inset of enlarged spot shows weak streaking along $11\bar{2}0$. All of the dark-field photographs are taken with $s = 0$ and rotated so that a two-beam condition is met.

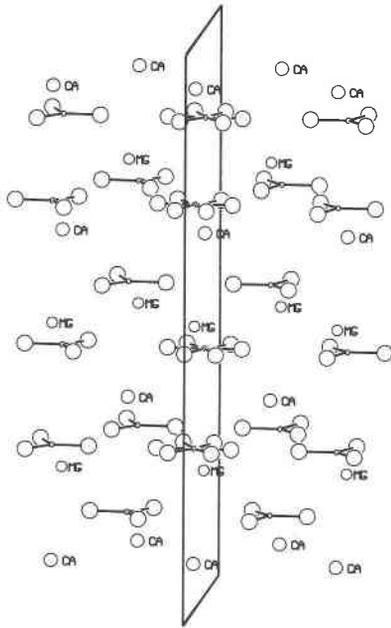


Fig. 3. Twinned structure of dolomite. The c axis is nearly vertical and a_2 is nearly horizontal. The mirror is perpendicular to a_2 . Anion disorder occurs only for the CO_3^{2-} groups lying in the composition plane.

are somewhat enlarged relative to those of other dolomites. Similarly, the c axis is larger than that expected for a stoichiometric dolomite. The origin of the modulated domains cannot be due to fluctuations in cation order or rotational anion disorder in regions that scatter X-rays coherently. We suggest that this modulation arises from smaller regions in the single crystal that scatter X-rays incoherently. These regions give rise to the "c" reflections in electron-diffraction patterns that cannot be attributed to the dolomite structure (Reeder and Wenk, 1979; Reeder, 1981) and may incorporate various structural defects (Wenk et al., 1983; Wenk and Zhang, 1985; Barber et al., 1985; Van Tendeloo et al., 1985). It is reasonable to expect that these regions will cause strain in the crystal structure that will manifest itself in an expanded lattice as seen in this crystal. Several authors have related unit-cell parameters or d spacing of the most intense dolomite reflection ($10\bar{1}4$) to composition (Goldsmith et al., 1961; Scholle, 1978; Reeder and Sheppard, 1984). Although these values generally increase with increasing Ca content, considerable scatter occurs. Dolomites quenched from elevated temperatures show partial disordering of the cations and expansion of the c axis (Goldsmith et al., 1961; Reeder and Wenk, 1983). The crystal of this study is, however, well ordered and stoichiometric, as shown by the X-ray structure refinement, and in addition possesses an expanded lattice. Apparently, the strain induced by the presence of the modulated microstructure is sufficient to cause this lattice expansion. Perhaps some of the scatter found in unit-cell parameters of natural dolomites is also due to similar strain.

Gunderson and Wenk (1981) have suggested that modulated calcite and perhaps dolomite may display anion disorder if they occur as replacement minerals, particularly if the precursor is aragonite. They further suggested that if replacement occurs across a thin, aqueous film, then disorder may be induced by the anion orientations of the mineral being replaced. However, the crystal refined in this study has no indication of a replacement origin. All coarse crystals in the sample occur as spar growing inward from the walls of voids left after dissolution of allochems (Fig. 1). The crystals, once nucleated, could not have grown in contact with precursor calcite or aragonite and therefore could not have been affected by their anion orientations. Thus, neither twinning nor the presence of a modulated microstructure requires a replacement origin. Phase transformations may produce twins in dolomite on quench from temperatures in excess of 1150°C (Reeder and Nakajima, 1982), but there is no indication that this sample experienced temperatures or pressures much above Earth surface conditions.

The twins in this dolomite are most likely growth defects. What initiated the twinning is unknown. It is possible that the crystal did not grow from a single nucleus, but perhaps from several nuclei with similar c -axis orientations but different a -axis orientations. Once initiated, the twin growth continued. No twin terminations were observed, suggesting that few, if any, new twins were added or old ones destroyed once the crystal had grown well away from the fine-grained pore wall. The modulated microstructure, as with twinning, is a growth defect. Its appearance in this void-filling spar suggests that it may precipitate freely from an aqueous solution, perhaps as a coprecipitate of dolomite and a phase that yields "c" reflections in electron-diffraction patterns.

CONCLUSIONS

A single crystal of dolomite from the Troy Formation of Jamaica is twinned by mirror reflection across $(2\bar{1}10)$. This operation leaves the cation positions unchanged, but the anions have a mirror relationship between twinned individuals.

This study documents the presence of a modulated microstructure in stoichiometric, well-ordered dolomite. From the X-ray structure-refinement results, it is concluded that the $100\text{--}200\text{-\AA}$ -wide domains of this microstructure do not differ in composition, cation ordering, or anion orientation. Instead, the contrast in this dolomite crystal may be due entirely to lattice strain about the domains that give rise to "c" reflections in electron-diffraction patterns. These domains occupy only a small volume of the crystal and do not diffract X-rays coherently. Strain associated with this microstructure can give rise to enlarged unit-cell parameters without necessarily an increase in Ca content. Neither the twinning nor the modulated appearance of dolomite requires a replacement origin of the dolomite. Both can form freely in a primary precipitate.

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