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# Electron Optical Investigation of Sedimentary Dolomites

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**Abstract.** Transmission electron microscope studies demonstrate a structural distinction between stoichiometric and ancient calcian dolomites of sedimentary origin. A modulated or tweed structure similar in appearance to spinodal microstructures characterizes ancient calcian dolomites, whereas stoichiometric dolomites are homogeneous. Recent calcium-rich dolomites lack a modulated structure, but have a heterogeneous microstructure with high densities of growth defects. Electron and optical diffraction and lattice imaging suggest a fluctuation in interplanar spacing in a coherent lattice. In addition, lattice imaging also reveals discontinuous faults throughout the modulated structure. Ordering and possibly incipient exsolution are suggested. 'c' reflections in SAD patterns of calcian dolomites document a new superstructure in at least part of the lamellar structure and raise questions of different ordering states throughout the structure.

The results provide new insight regarding the formation of sedimentary dolomites

## Introduction

Transmission electron optical studies of natural minerals have documented a variety of microstructures which provide insight to the processes affecting mineral formation. Among these the modulated structure or tweed structure is frequently observed in minerals exhibiting ordering or limited miscibility. Some of the most notable examples of modulated structures in silicates have been attributed to exsolution by the spinodal mechanism (cf. Champness and Lorimer 1976). In fact this mechanism is not uncommon in silicate minerals in part due to the similarity of endmember structures in silicate solutions (Aaronson et al. 1974). Other modulated structures have been attributed to ordering behavior such as in adularia (McConnell 1965, 1971). The causes for modulated structures are not limited to these examples and other cases are reported in Cowley et al. (1979).

Recently Reeder and Wenk (1979a, b) demonstrated the characteristic occurrence of a modulated structure in sedimentary calcian dolomites using the transmission electron microscope (TEM). These preliminary reports stressed the morphologic similarity of the structure in calcian dolomites to spinodal microstructures in alloys and silicates. In fact spinodally decomposed minerals were in a sense adopted as a standard for comparison during much of these early investigations. The mere prospect of exsolution occurring at low temperatures was intriguing and warranted further investigation. The present communication reports on more complete studies of microstructural differences of ideal and non-ideal sedimentary dolomites. The results provide new information regarding the structure and origin of natural dolomites.

The crystal structure of ideal dolomite, $CaMg(CO_3)_2$, has been reviewed in some detail by Lippmann (1973) and X-ray structure refinements have been reported by Steinfink and Sans (1959), Althoff (1977), Reeder (1980), and Reeder and Wenk (in prep.) Dolomite has a superstructure in which Ca and Mg atoms are segregated onto alternating planes normal to the *c*-axis, thus distinguishing it from the calcite structure. Ordering of the cations lowers the symmetry from $R\bar{3}c$ (calcite) to $R\bar{3}$ (dolomite) and gives rise to extra 'superlattice' reflections in diffraction patterns.

It was first recognized by Goldsmith and Graf (1958) that many natural dolomites deviate from ideality. They found that many dolomites from Eocene to Ordovician in age contain up to 6 mol% excess $CaCO_3$ and have enlarged unit cells. X-ray powder diffraction showed these calcian dolomites have attenuated superlattice reflections and diffuse or bimodal basal plane reflections. Graf et al. (1967) suggested that both substitutional and mixed-layer disorder were necessary to account for the diffraction evidence. Further investigation was not undertaken, in part due to the difficulties presented by the fine grain size of the material.

Many of the characteristics observed in calcian dolomites were not unlike those described previously by Graf and Goldsmith (1956) for their synthetic protodolomites; the inference being that calcian dolomites might represent an intermediate, metastable stage during dolomitization.

Other experimental studies have also stressed the importance of intermediate phases during the formation of dolomite. Gaines (1974) observed disordered precursor phases which eventually ordered and became nearly stoichiometric (with aging) in his experimental synthesis of dolomite in aqueous solutions at 100° C. Katz and Matthews (1977) reported a disordered, calcium-rich, intermediate phase in hydrothermal experiments at 252° to 295° C involving dolomitization of calcite and aragonite. Sureau (1977) observed similar disordered, calcian, precursor phases in his study of hydrothermal dolomitization of calcite at 150° C. While the final products of such studies are invariably ideal dolomite, the intermediate or precursor phases are typically disordered and calcium-rich. Thus in nature it is not unreasonable to expect precursor phases with similar characteristics. The disordered carbonate cements reported by Barnes and O'Neil (1971) with compositions near that of dolomite suggest that such disordered phases may persist for many thousands of years.

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## Methods of Study

During the course of this investigation over 50 sedimentary dolomite samples were examined with the TEM to document microstructures on the scale of 10–1,000 Å. Localities, ages, compositions and references for the specimens are given in Reeder (1980). Samples range in stratigraphic age from Cambrian to Holocene and represent a broad spectrum of depositional and diagenetic environments. Many of the dolomites are from localities described in the literature and include both samples interpreted as primary (or early diagenetic) and secondary.

Mineralogy was checked by x-ray powder diffractometer scans and the attenuation in the superlattice reflections as well as the diffuseness of basal plane reflections was consistent with earlier findings of Goldsmith and Graf (1958).

Bulk compositions were routinely determined by electron microprobe analysis using a homogeneous dolomite standard for Ca and Mg. Compositions for some samples were taken from previous studies or, in a few cases, estimated by x-ray diffraction peak-shift methods from the curves of Goldsmith et al. (1961). The dolomite compositions varied from ideal stoichiometry to 6 mol% excess $CaCO_3$ with the most common nonstoichiometric composition between 55 and 56 mol% $CaCO_3$. These findings are in agreement with Goldsmith and Graf (1958) and Füchtbauer and Goldschmidt (1965) who also found the most prevalent nonstoichiometric compositions to be roughly 55 mol% $CaCO_3$.

TEM foils were prepared using conventional ion thinning techniques at 5 kv (cf. Barber and Wenk 1973). Powdered specimens were dispersed onto a Formvar film on 200 mesh grids. Specimens were examined using conventional brightfield (BF) and darkfield (DF) techniques on a JEM 100C in the Department of Geology and Geophysics at Berkeley. Lattice imaging was done on a JEM 100C with a high-resolution specimen holder at Lawrence Berkeley Laboratories and a JEM 200CX in the Department of Earth and Space Sciences at SUNY Stony Brook.

## Occurrence and Description of Modulated Structure

Examination of the foils in the TEM revealed that microstructures of ancient calcian dolomites with roughly 3–6 mol% excess $CaCO_3$ were characterized by a pervasive modulated or tweed structure (Fig. 1) as noted by Reeder and Wenk (1979a). On the other hand stoichiometric dolomites show homogeneous microstructures with only dislocations and growth defects (Fig. 2). Those dolomites with intermediate compositions, in the range 1–3 mol% excess $CaCO_3$, show both regions of modulated and homogeneous microstructure suggesting a mixture of stoichiometric and calcian regions.

The tweed structure strongly resembles exsolution microstructures due to spinodal decomposition (cf. Champness and Lorimer 1976). Lamellar wavelengths, although somewhat irregular, average between 100 and 200 Å, just several tens of unit cell dimensions. Longer wavelengths (up to 400 Å) are observed in some of the Lower Paleozoic samples, but present data are insufficient to support any age relationship. Lamellae of the modulated structure typically have diffuse boundaries and are discontinuous in their long dimension.

The modulated structure is in strong contrast both in BF and in DF imaging fundamental (*a*) reflections and superlattice (*b*) reflections ($h\bar{h}Ol$, $l=2n+1$). The morphology may vary locally and with different reflections operating; however, the basic lamellar morphology is remarkably similar in all but a few unusual samples discussed separately. In fact, its occurrence and similarity in samples interpreted as primary and as secondary seem to suggest an origin that disregards that distinction.

Trace analysis using pairs of corresponding BF micrographs and selected-area diffraction (SAD) patterns indicates the tweed structure is oriented roughly parallel to the cleavage rhomb face,

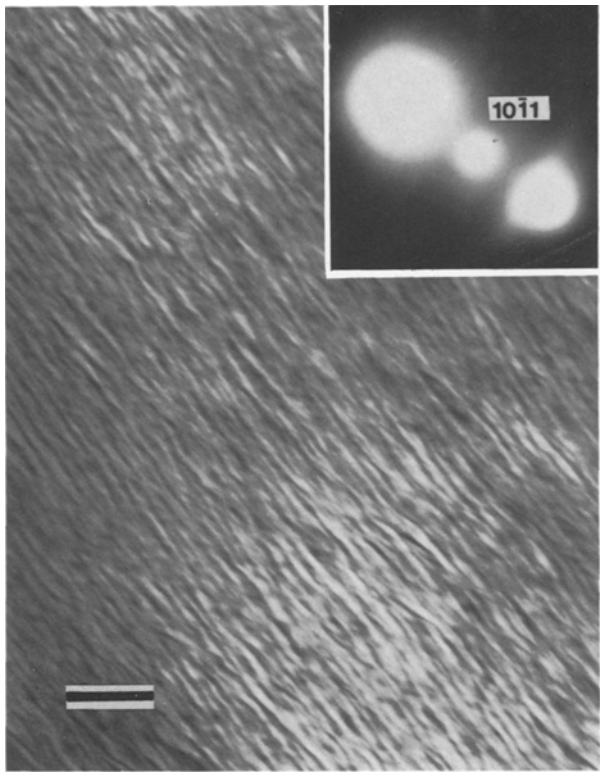


**Fig. 1.** DF micrograph ($g=10\bar{1}1$) showing modulated structure typical of ancient calcian dolomites. Note diffuse boundaries of lamellae. Bar scale in this and all subsequent micrographs represents 0.1 μm

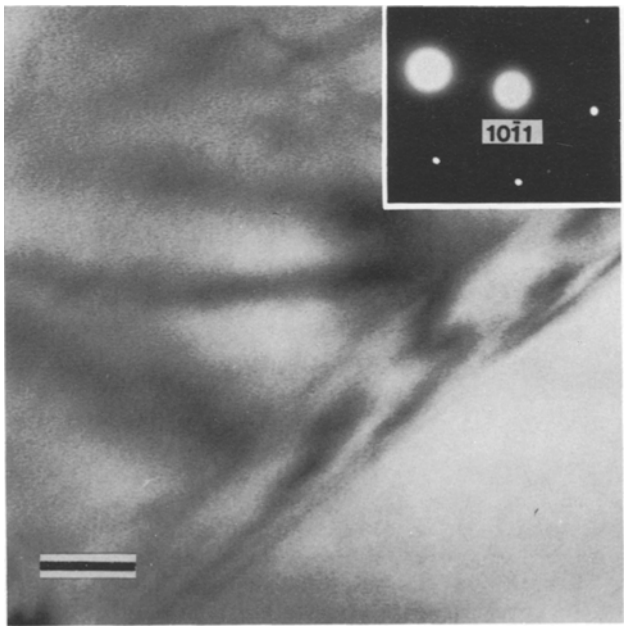


**Fig. 2.** BF micrograph ($g=10\bar{1}1$) of stoichiometric dolomite showing bend contours in homogeneous microstructure. Bar scale 0.1 μm

$r=\{10\bar{1}4\}$. The structure is generally observed occurring in only one orientation throughout an individual crystal. However in some cases the structure was observed in adjacent regions in different, but crystallographically equivalent orientations. Occasionally a subordinate modulation or banding with erratic spacing is superimposed on the fundamental tweed pattern (Fig. 3). This secondary structure is never pervasive and may vary from

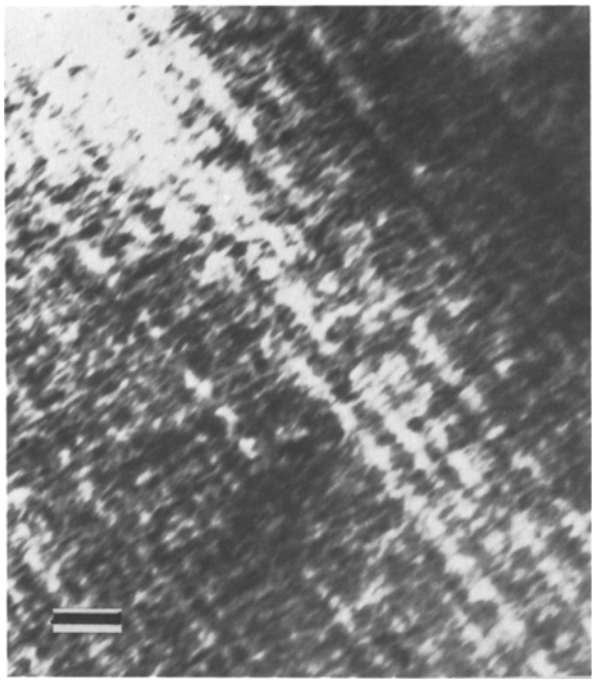

**Fig. 3.** BF micrograph ($g=01\bar{1}5$) of an Eocene calcian dolomite from the Floridan Aquifer showing the irregular secondary modulation (trending NW-SE) superimposed on the normal structure. Bar scale 0.1 μm

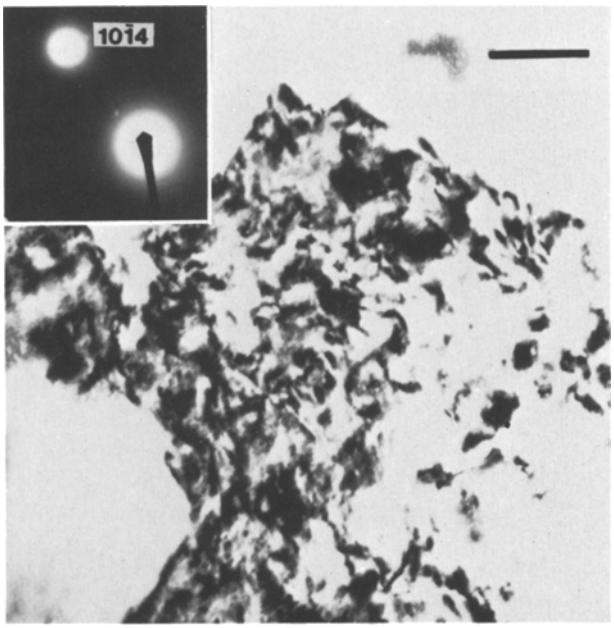


**Fig. 4.** BF micrograph ($g=10\bar{1}4$) of dolomite crystal from Deep Springs Lake, CA, showing strong contrast in a heterogeneous microstructure. No modulated structure was observed. Bar scale 0.1 μm

being only poorly developed to entirely absent. It also appears to favor an orientation nearly parallel to $\{10\bar{1}4\}$.

Several Recent and Late Pleistocene dolomites were examined in the TEM for comparison with the ancient samples described above. These young samples included dolomites from the well-known localities of Deep Springs Lake, CA, the Persian Gulf, Coorong, Australia and the Great Salt Lake. Although these dolomites are all calcium-rich they lack a modulated structure; however, they are by no means homogeneous. Fig. 4 shows the

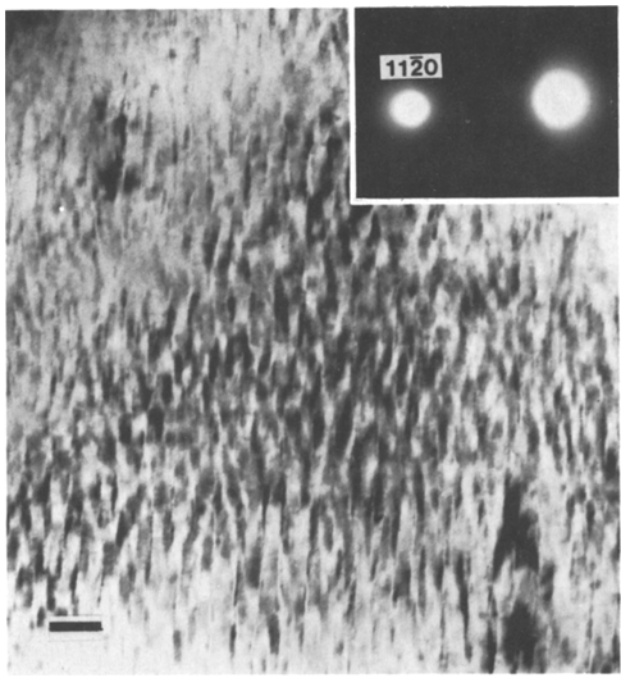


**Fig. 5.** BF micrograph ($g=11\bar{2}0$) of a Triassic calcian dolomite from Northern Italy. Lamellar boundaries are sharp and well-defined in contrast to most calcian dolomites. Bar scale 0.1 μm

strong contrast in the heterogeneous microstructure of a typical Recent calcium-rich dolomite. The structure reflects high densities of defects probably due to growth processes. These observations indicate that the youngest dolomites, all forming in the near surface environment, are structurally distinct from calcian dolomites commonly found in the ancient rock record. Having made this distinction, subsequent references to 'calcian dolomites' in this communication will exclude such Recent (and Late Pleistocene) calcium-rich dolomites.

Another unusual microstructure encountered in this study is worth mentioning at this point. A Triassic calcian dolomite from the thick Haupt-Dolomit sequence in N. Italy shows a coarse modulated structure (Fig. 5) intermixed with homogeneous regions. The boundaries of the lamellae in the modulated area are sharp and well defined while wavelength is roughly 400 Å. The morphology somewhat resembles exsolution lamellae in some silicates. This sample may have been subjected to somewhat elevated temperatures during burial possibly influencing the resulting microstructure.

### Contrast Analysis of Modulated Structure

During the course of the investigation of the modulated structure in calcian dolomites BF and DF images were observed for those reflections corresponding to $d$-spacings from $d_{0003}$ through $d_{03\bar{3}0}$. The structure was found to be in contrast for all reflections indicating that a unique displacement vector, $R$, does not characterize the structure. The strength of contrast and detail of the microstructure varied with different reflections operating; strongest contrast was obtained for $g=10\bar{1}4$, and the lamellae appeared more continuous in this orientation.

BF-DF reversal-of-contrast experiments using fundamental and superlattice reflections indicate that the modulated structure does not result simply from a fine intermixing of ordered and disordered domains, although the possibility of different degrees of ordering is certainly not discounted.

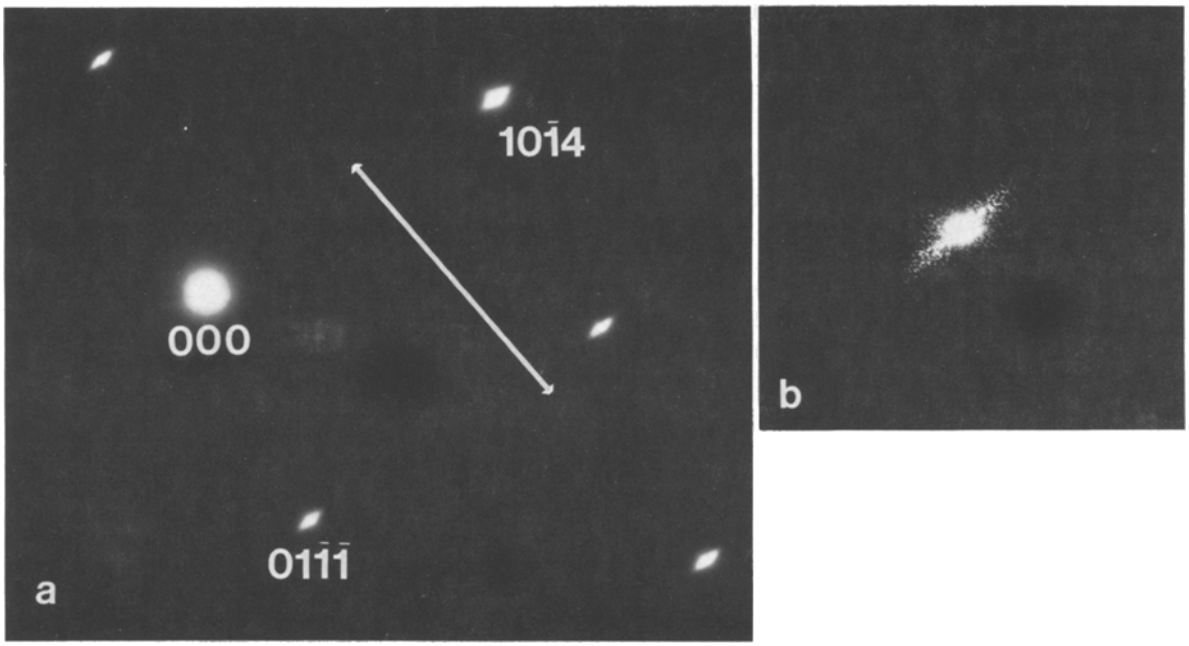


**Fig. 6.** **a** Enlarged SAD pattern (symmetric orientation) from a calcian dolomite modulated structure. Diffracted spots are streaked in a direction normal to the trace of the lamellae (shown by *arrow*). **b** Optical diffraction pattern of the modulated structure. The main spot is streaked as in the SAD pattern

### Electron Diffraction

Selected-area diffraction (SAD) patterns of the modulated structure in calcian dolomites show a single reciprocal lattice without splitting of spots (Figs. 1, 6a, 7). Thus the structure is coherent and the diffuseness of the lamellar boundaries suggests some gradual change between adjacent lamellae. Coherency is also discussed in a following section on direct lattice images.

Uniformly modulated structures generally show sideband reflections or satellites where the separation of the satellite from the diffracted spot is inversely proportional to the wavelength of the modulation. No satellites were observed in any of the SAD patterns of calcian dolomites. However, diffracted spots are streaked or broadened in a direction normal to the modulation (Fig. 6a). The streaking is typically diffuse and short and is most pronounced when the structure is oriented vertically with respect to the electron beam. Since the lamellae are irregularly spaced in calcian dolomites discrete sideband reflections do not occur, replaced instead by diffuse, short streaks. Similar streaks in diffraction patterns were attributed to this cause by McConnell (1969), Owen and McConnell (1971, 1974), and Laughlin (1976).

Evidence from optical diffraction (Fraunhofer diffraction) supports this conclusion. Optical diffraction patterns were obtained from original negatives of the modulated structure using a HeNe laser light source and selective apertures. One advantage of optical diffraction is that it can be used to "analyze" very small regions on a micrograph. The resultant optical diffraction pattern shows a short, diffuse streak through the main spot in a direction normal to the modulations, just as in the SAD patterns (Fig. 6b).

### 'c' Reflection

SAD patterns of the calcian dolomites contain extra reflections not due to the dolomite structure. These extra spots, termed 'c' reflections by Reeder and Wenk (1979a) are extremely weak and are only observed in strongly exposed diffraction patterns. The spots have been found in three systematic positions in the reciprocal lattice – midway between normal dolomite spots in the 01$\bar{1}$2, 10$\bar{1}$4 and 11$\bar{2}$0 reciprocal directions (Fig. 7). In all cases the spots only occur in one orientation of an equivalent set indicating a preference for a unique orientation in the crystal. In addition preliminary findings show the 'c' spots always have a systematic orientation with respect to that of the modulated structure suggesting a genetic relationship.

'c' spots may be either sharp or diffuse, and even streaked. DF imaging using 'c' reflections has been unsuccessful thus far in part due to the extremely long exposure times necessary. Extra spots were never observed in stoichiometric (i.e. homogeneous) dolomites of either high or low temperature origin.

The positions of the extra spots are such that an explanation by twinning, higher-layer reciprocal lattice effects, or double diffraction is unsatisfactory; hence, the spots apparently indicate a new superlattice associated with the tweed structure. The 'c' reflections double the *a* unit cell dimension (and, hence, the unit cell) and because they occur in a unique orientation within a crystal the 'c' superstructure is orthorhombic. At this point observations regarding the extra reflections are too limited to support any model of a new superstructure. However, the 'c' reflection probably indicates a slight periodic structural distortion since its intensity is too weak to be explained by periodic planar defects like APBs (as first suggested by Reeder and Wenk, 1979a). Quite a few structural variants are possible in dolomite, one of which might lead to a periodic distortion. One example might be some sort of rotational disorder in the $CO_3$ groups. Evidence of such disorder has been reported by Reeder (1980) in thermally disordered dolomites. Further efforts are being concentrated on these questions now.

### Direct Lattice Imaging

Much useful information about the fine detail of the modulated structure was obtained from lattice images. Several Eocene specimens from the Floridan Aquifer were chosen. Bulk compositions

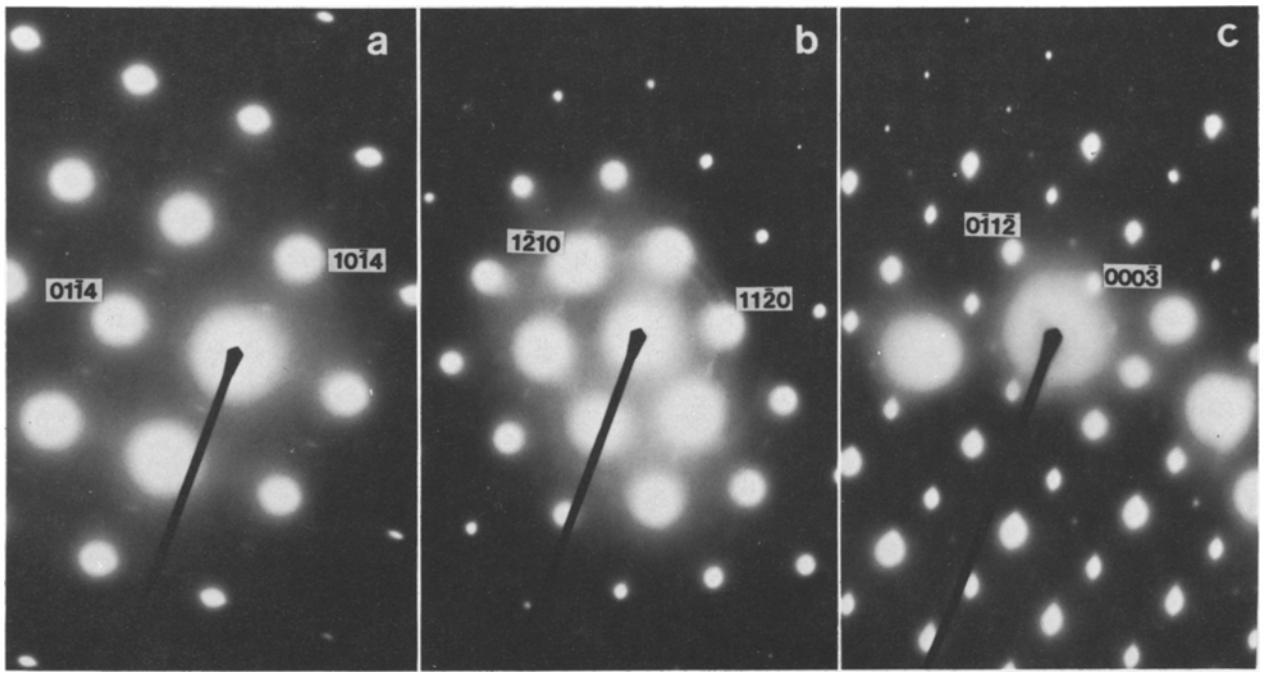


**Fig. 7a–c.** SAD patterns of modulated structures in calcian dolomites showing the weak 'c' reflections between normal dolomite spots in **a** the $10\bar{1}4$, **b** $2\bar{1}\bar{1}0$, and **c** $0\bar{1}1\bar{2}$ reciprocal directions

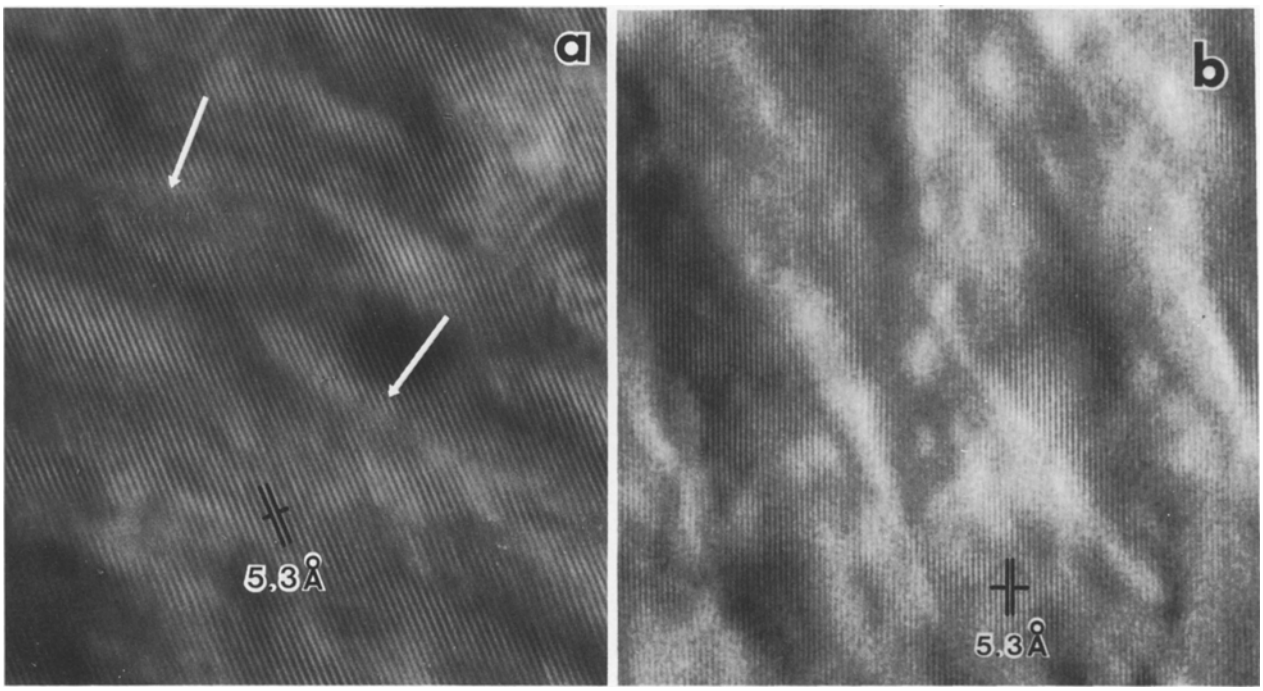


**Fig. 8a, b.** Direct lattice images of basal superlattice fringes (0003) in an Eocene calcian dolomite of the Floridan Aquifer. **a** shows several discontinuous APB-like faults (*arrows*), **b** clearly shows the individual lamellae of the modulated structure

are approximately 56 mol% $CaCO_3$, and with pervasive modulated structures they are representative of the calcian dolomites described herein. For purposes of the present study only the 0003 (superlattice) fringes were resolved. In addition to being the largest interplanar spacing in dolomite ($d_{0003}=5.3$ Å), the 0003 basal planes show the greatest change in spacing due to compositional changes. Several different orientations were used for imaging; all were either symmetric or such that only the 0003 systematic row was excited. Two different diffraction conditions were used, wherein the objective aperture included, in one case, the 0003 and $000\bar{3}$ spots and, in a second case, the 0006 and $000\bar{6}$ spots as well. All imaging was done in BF and through-focus series micrographs were routinely taken. The specimens clearly damage more rapidly during high-resolution work and it is noteworthy that the two lamellar domains appear to damage at different rates. This tends to suggest a structural or compositional difference between the domains.

Representative images are shown in Fig. 8a and b. Several

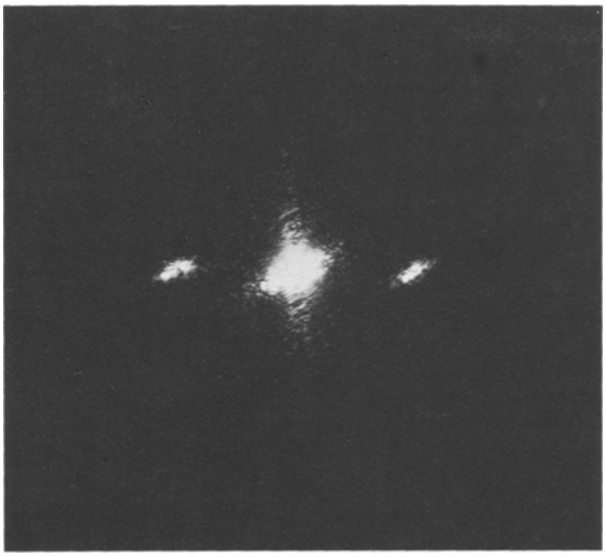

**Fig. 9.** Optical diffraction pattern of the lattice image in Fig. 8b. Diffracted spots are streaked or broadened normal to the modulations rather than to the fringes. Spikes radiating from the main spot are artifacts due to the aperture used

distinct features are apparent. The lamellar contrast of the modulated structure is still visible at high magnification (up to 500,000X on the screen) and the wavelength although somewhat irregular is roughly the same as in conventional micrographs, 100–150 Å. The lamellae appear short and discontinuous, and not perfectly aligned but only subparallel.

The fringes (superlattice fringes) are continuous through the boundaries of the lamellae except at localized regions with linear contrast as shown in Fig. 8a (arrow). These regions are roughly parallel to the lamellar domains of the modulated structure and resemble superlattice dislocations (SD) such as those described by Sinclair et al. (1975) in $Cu_3Au$. The fringes are continuous and undisturbed on either end of the defect, but become progressively offset (or bent) toward the center region where APB (antiphase boundary) contrast is observed. In some orientations of the foil the termination of a fringe at the defect is visible such that the number of fringes is different on either side of the defect. It should be noted, however, that there is no simple relationship between fringes and planes in the vicinity of a defect, and a terminating fringe does not necessarily spatially correlate with a terminating plane (Cockayne et al. 1971). In some cases along these defects the fringe image may become diffuse or even lose contrast, perhaps due to beam damage or an artifact of the foil.

These defects do not always uniformly coincide with lamellar domains either in frequency of occurrence or spatially and the overall structure is coherent. The APB-like defects, however, clearly contribute to the lamellar contrast of the modulated structure.

In the absence of strong double diffraction, the superlattice fringes indicate that both lamellar domains, have a dolomite-like superstructure. This confirms that the modulated structure is not simply due to ordered and disordered domains.

No evidence of cation stacking disorder was found in the specimens imaged. Such a defect where the alternating Ca–Mg–Ca, etc. sequence might be disrupted to allow extra or out of place Ca-dominated planes was suggested by Graf et al. (1967). Recently Reeder and Nakajima (in preparation) have observed evidence of stacking disorder in thermally disordered and quenched dolomites using lattice imaging techniques.

Optical diffraction from lattice images was done for comparison with electron diffraction which showed diffuse streaking normal to the modulations. The techniques used were similar to those described by Sinclair et al. (1976) who used optical diffraction to document a fluctuation of interplanar spacing in a spinodally decomposed alloy. It should be noted that due to lens aberrations the fringe spacings in lattice images may not correspond exactly to those in the crystal (Spence et al. 1979), but do reflect relative differences. Aperture size was chosen so as to cover ~750 Å or roughly five wavelengths of the modulation. The optical diffraction pattern corresponding to Fig. 8b is shown in Fig. 9. First-order diffracted spots occur in a direction normal to the lattice fringes. Diffraction "spikes" radiating from the main spot are an artifact of the method due to the aperture. The diffracted spots are always streaked in a direction normal to the modulation rather than the lattice fringes, in agreement with the effects observed in electron diffraction patterns. The streaking in the optical patterns is diffuse and somewhat poorly defined which may be due in part to the misorientation between the lamellae and the fringes. The evidence from electron and optical diffraction suggests a fluctuation in interplaner spacing coincident with the lamellae of the modulated structure.

## Discussion

The evidence presented thus far suggests that the modulated structure reflects the presence of at least two, and possibly three, types of defects: a roughly periodic fluctuation in interplanar spacing in a basically coherent lattice, localized discontinuous APB-like faults, and possibly a 'c' superstructure. The relative effects of each on image contrast and lattice strain are at best difficult to interpret. However, it is not unreasonable to comment on possible causes for these defects and implications.

Fluctuations in interplanar spacing in a coherent lattice may result from a variety of effects including small composition fluctuations, differences in ordering, and differences in structure. These factors are not necessarily independent of one another since compositional differences require differences in ordering and structural differences may require differences in ordering and composition.

As mentioned previously, modulated structures are not infrequently observed in some silicate solid solutions due to spinodal decomposition. Reported wavelengths of the structure typically range from 50–200 Å and the lamellar domains reflect slight compositional variations (cf. Yund and McCallister 1970). A modulated structure due to local differences in Si-Al ordering has been reported in adularia (McConnell 1965, 1971). Here the microstructure reflects the incipient development of triclinic domains in a monoclinic host.

In sedimentary calcian dolomites small variations in either the degree of cation ordering or the Ca/Mg ratio may conceivably result during growth (from aqueous solutions) or during subsequent reorganization in the solid state. Two observations argue against an origin of the domain structure due to growth. Preliminary studies of Recent and Late Pleistocene calcium-rich dolomites fail to show a modulated structure. And in ancient calcian dolomites where the structure is present, the regularity of the lamellae on the scale of 100–200 Å pervasively throughout a sample would be difficult to explain as an aqueous growth feature, particularly in view of the diverse depositional and diagenetic environments represented over broad periods of geologic time. Furthermore, the independent evidence cited earlier, that first precipitates are largely disordered, would seem to indicate that subsequent ordering has occurred since calcian dolomites exhibit considerable long-range order.

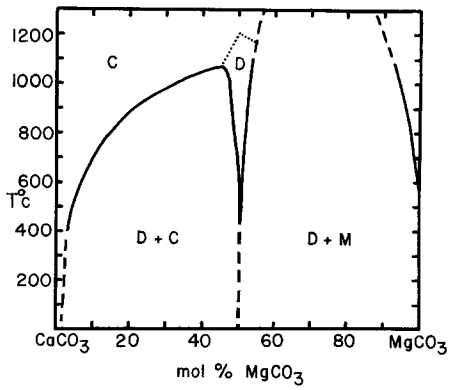


**Fig. 10.** Phase diagram for the $CaCO_3$-$MgCO_3$ system after Goldsmith and Heard (1961) (*solid line*) and extrapolated to low temperatures (*dashed lines*). Stability fields are indicated for calcite (*C*), dolomite (*D*) and magnesite (*M*)

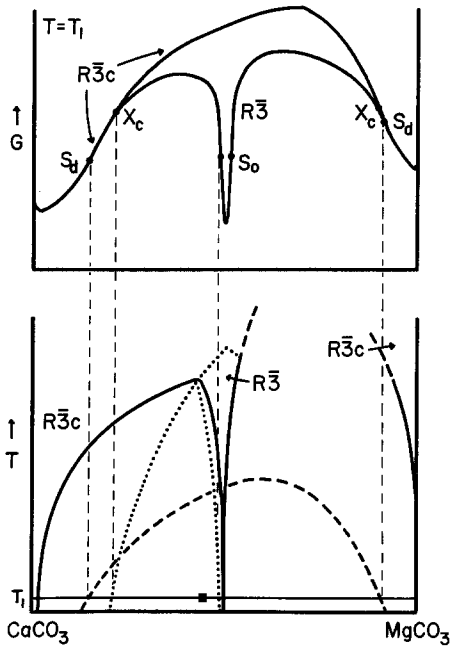


**Fig. 11.** Schematic $G-X$ and $T-X$ curves for the $CaCO_3$-$MgCO_3$ system showing spinodal relations following the example of Carpenter (1980). Relations are based on the phase diagram (*heavy solid line* on $T-X$ diagram) of Fig. 10. Free energy curves for disordered ($R\bar{3}c$) and ordered ($R\bar{3}$) phases join with continuous first derivatives, consistent with a higher order transition. Points $X_c$ and $S_o$ indicate limits of metastability for the ordered phase and determine points on the conditional spinodal (*dotted curves* within calcite-dolomite solvus), Points labelled $S_d$ indicate limits of metastability for the disordered phase and determine points on the disordered spinodal (*dashed curve*) which is drawn arbitrarily for illustration. The *black square* shows the approximate composition of calcian dolomites with pervasive modulated structures

## Phase Relations

An understanding of phase relations in the $CaCO_3$-$MgCO_3$ system is fundamental when considering the feasibility of exsolution or ordering in calcian dolomites. The currently accepted phase diagram for this system (Fig. 10) was established by Goldsmith and Heard (1961) following earlier work by Graf and Goldsmith (1955) and Harker and Tuttle (1955). Goldsmith and Newton (1969) later revised slightly the position of the calcium-rich limb of the solvus and demonstrated that pressure had a fairly small effect on the position of the solvus. Phase relations below 400° C have not been established largely due to the slow reaction rates and short times available in laboratory experiments. Most workers have simply extrapolated the solvus curves to low temperatures. Justification for this can be found in field evidence and hydrothermal experiments below 300° C (Graf and Goldsmith 1956; Gaines 1974; Katz and Matthews 1977, and Sureau 1977) where *final* products are calcite and stoichiometric dolomite. Accepting the extrapolated phase diagram, it is at once clear that the bulk compositions of calcian dolomites lie within a two phase region and hence a phase of such composition cannot be stable with respect to a mixture of calcite and dolomite. In fact the bulk compositions of calcian dolomites with a pervasive modulated structure lie within a narrow composition range from about 43 to 46 mol% $MgCO_3$ which coincides rather closely with the composition of the critical point of the solvus. Goldsmith and Graf (1958) concluded that calcian dolomites are metastable at low temperatures. As evidence these authors heated calcian samples at temperatures from 520° to 832° C with sufficient $CO_2$ pressure to prevent decomposition. In the presence of a flux ($Li_2CO_3$) the samples exsolved to a magnesian calcite and dolomite with compositions in agreement with the solvus.

Although exsolution in calcian dolomites is favored a consideration of ordering and spinodal relations is necessary to determine the likelihood of either exsolution or ordering by a continuous mechanism. In particular the nature of the ordering transformation in dolomite is crucial in determining viable mechanisms. Carpenter (1980) provides an excellent review of phase relations for binary systems which exhibit limited miscibility and an intermediate ordered phase.

In dolomite, disordering involves the cooperative exchange of Ca atoms from the A sublattice with Mg atoms from the B sublattice. Complete disorder is obtained when a random distribution occurs at which point the A and B sublattices are no longer distinct. Goldsmith and Heard (1961) investigated the thermally induced disordering in stoichiometric dolomite and presented evidence supporting continuous disordering indicating a higher-order or lambda transition. Recent studies of thermal disordering in dolomite by Reeder and Wenk (in preparation) also support a continuous disordering transition although experimental difficulties prevent precise determination of order parameters as a function of temperature. If one presumes that the ordering reaction is higher-order then there can be only one stable phase at any T and X above the solvus curves. The dotted line in Fig. 10 separating the dolomite field from the calcite(ss) field is merely the line of all lambda points at different compositions. Goldsmith and Heard (1961) have determined that the line of lambda points intersects the solvus very close to the critical point. This intersection has been called the tricritical point and several important relationships follow (Allen and Cahn 1976a, b; Carpenter 1980). First of all it should be noted that as long as there is a continuous free energy curve between calcite and magnesite then a spinodal region exists for the disordered phase irrespective of whether an ordered phase may occur (Fig. 11). Although the exact position of these spinodal limbs is not precisely known there can be little doubt that the bulk composition of a typical calcian dolomite ($Ca_{55}Mg_{45}$) is within that spinodal region. Thus a disordered, homogeneous phase within that spinodal region may exsolve by a continuous mechanism. However the disordered spinodal no longer applies as soon as the ordering reaction begins. If one assumes as a first approximation that ordering will proceed more rapidly than exsolution then spinodal relations in the calcite-dolomite miscibility

gap become the determining factor. Allen and Cahn (1976a, b) have shown that when the free energy curves for the ordered and disordered phases join with continuous first derivatives a spinodal exists within the miscibility gap which is "conditional" upon formation of the ordered phase. In Fig. 11, at low temperatures, the right-hand limb of the conditional spinodal must lie to the right of the tricritical point, very near to ideal dolomite composition. The left-hand limb is simply the metastable extension, into the miscibility gap, of the line of lambda points. It is evident that the composition $Ca_{55}Mg_{45}$ lies within this spinodal region and therefore homogeneous phases of this composition, whether disordered or slightly ordered, are *unstable* with respect to fluctuations in composition. Furthermore, a continuous mechanism exists for both ordering and exsolution. It should be noted that *final* exsolution products for the conditional spinodal are disordered and ordered phases. This analysis shows that the initially disordered phase ($Ca_{55}Mg_{45}$) is stabilized by continuous ordering and the development of fluctuations in composition.

Ordering or incipient exsolution in the solid state must rely on diffusion which at low temperatures is not generally regarded as a significant mechanism of mass transfer. Compositional zoning in crystals many million years old suggests that mass transfer on a scale as small as 10 μm (or less) is effectively precluded by slow diffusion rates. However, the scale on which diffusion might be called upon to explain is very much less in calcian dolomites. Ordering would require short-range diffusion on a scale of less than 5 Å and incipient exsolution would require diffusion over a distance of less than 100 Å. Diffusion in crystals at low temperature is perhaps too poorly understood to discount it as a viable mechanism in the present case.

In fact several observations seem to indicate that solid state ordering has occurred subsequent to formation. APBs typically result from ordering reactions (Amelinckx and Van Landuyt 1976) and it is very likely that the discontinuous APB-like defects observed in calcian dolomites indicate such. And although less is known about the 'c' superstructure it too may have formed during ordering.

Since there is a driving force to exsolve simultaneously with ordering it is quite possible that slight compositional fluctuations form, perhaps facilitated by the reorganization accompanying ordering. Direct confirmation of fluctuations in composition or degree of cation order is not possible. It is for this reason that the analogy with spinodal decomposition and simultaneous ordering is not drawn too rigidly. It will be seen that several criterion for spinodal decomposition cannot be unambiguously demonstrated with present information.

The development of fluctuations in a coherent lattice within a spinodal region has been described in detail by Cahn (1968) and Hilliard (1970). Early stages of spinodal decomposition are characterized by a preferential amplification of fluctuations with optimum wavelength. As amplitudes become large during later stages two things may happen – (1) wavelength increases due to coarsening and (2) coherence is gradually lost.

Coherency related to spinodal decomposition has two major consequences (Yund and McCallister 1970). Elastic strain in the lattice gives rise to a positive strain energy term which effectively limits the region within which spinodal decomposition may occur. This is usually calculated in terms of a temperature depression of the spinodal and results in a 'coherent spinodal'. The magnitude of the temperature depression varies depending on the orientation chosen and is a measure of the 'misfit' between the adjacent structures. In practice the actual calculation is rather difficult in all but simple systems. In the calcite-dolomite system, insufficient data are available for actual calculations; however it does not appear unreasonable to suggest that the steepness of the right-hand conditional spinodal makes it unlikely that any but an extremely large temperature depression would affect the low temperature spinodal region in question.

Another effect of coherency concerns the orientation of the modulated structure in the crystal. Modulations will preferentially form in that orientation where strain energy is minimized. Calculation of the optimum orientation requires a knowledge of elastic coefficients which have not been completely determined for dolomite. Although elastic coefficients for calcite are known, its vastly different physical properties preclude substituting elas-

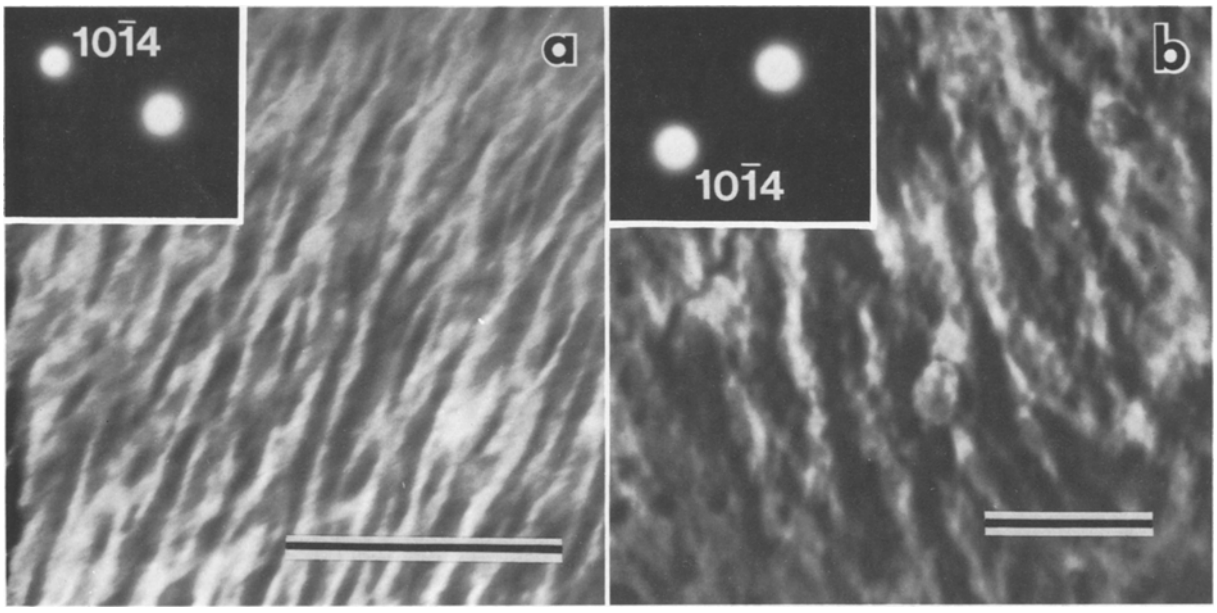


**Fig. 12a, b.** BF micrographs ($g = 10\bar{1}4$) of **a** An untreated calcian dolomite showing a typical modulated structure with wavelength roughly 150 Å and **b** the coarsened structure after annealing at 800° C for 168 h. Wavelength is roughly 300 Å. Bar scale 0.1 μm for both micrographs

tic data (cf. Barber et al. 1981). Thus a comparison of observed and calculated orientations, a fundamental criterion demonstrating spinodal decomposition, cannot be made in the present situation.

A second aspect of spinodal decomposition which receives attention is in regard to experimental coarsening of the modulated structure. Several workers (Owen and McConnell 1974; Yund et al. 1974) have monitored the kinetics of coarsening as evidence of spinodal decomposition. In the present study several samples were heated to see if coarsening would occur. Annealing was done by two different methods. Exploratory runs were made in an oven at 1 atm for ~170 h at 440° and 510° C. Examination of the heated samples in the TEM revealed no change in the modulated structure, although the sample from 510° C had begun to decompose. In order to prevent decomposition the two subsequent runs were made at 10 kb confining pressure in a piston cylinder apparatus. A description of the technique is given by Goldsmith (1980). In a run at 900° C for 312 h complete exsolution occurred. Observations of products in the TEM showed dominantly homogeneous dolomite with small magnesian calcite grains (identified by EDX).

A final lower temperature run was done at 800° C for 168 hours. Examination in the TEM showed a conspiquous increase in lamellar wavelength throughout the sample. Figure 12 compares micrographs of the original and coarsened samples where average wavelength has increased from roughly 150 Å to 300 Å. Coherency is apparently still maintained as indicated by single reciprocal lattices in SAD patterns.

The coarsening of the modulated structure is consistent with the behavior of a composition fluctuation within the spinodal. However, APB structures may also coarsen and lattice imaging has not been undertaken yet to resolve this matter. Thus despite the likelihood that a slight fluctuation in composition and/or degree of order exists, there is no absolute proof of this, or that the spinodal mechanism operated. This ambiguity is further compounded by the uncertainty of the 'c' superstructure.

Future work must rely on structural imaging using high-resolution electron microscopy to learn the nature of the defects present. Such efforts are presently underway in conjunction with single-crystal x-ray structure refinements in order to better understand the structure and origin of non-ideal dolomites.

## Summary and Conclusions

The microstructural distinctions demonstrated in this study between calcian and stoichiometric dolomites reflect different processes operating during their evolution. The modulated structure characteristic of ancient calcian dolomites reflects processes affecting the phase following precipitation. In addition it is now clear that traditional concepts of substitutional cation disorder in sedimentary dolomites must be modified. Lamellar domains represent local differences in composition or degree of ordering, and discontinuous APB-like faults occur frequently in the structure. A "c" superstructure, doubling the unit cell, is associated with the modulated structure and is probably due to small structural distortions.

In contrast stoichiometric dolomites have homogeneous microstructures and Recent calcium-rich dolomites lack modulated structures, but show other heterogeneities.

The observations lead to several conclusions regarding the formation of dolomites:

1. Ancient calcian dolomites appear to have originally formed as phases more homogeneous than at present, and disordered or largely so; ordering and possibly incipient exsolution occurred subsequently.

2. Such reactions helped to stabilize the calcian dolomites somewhat, since they persist for long periods of geologic time (although metastably).

3. The homogeneous microstructures of stoichiometric dolomites indicate either that they formed by different processes (i.e., different chemical environments) or that having once been calcian they "recovered" via solution-reprecipitation processes. Most likely examples of both occur. In either case, the lack of domain microstructures indicates that stoichiometric dolomites formed as ordered phases rather than disordered phases which subsequently ordered.

4. Recent calcium-rich dolomites are structurally distinct from ancient calcian dolomites and have not (yet?) undergone the same reactions.

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