

## Modulated microstructures in calcian ankerite

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### ABSTRACT

Modulated microstructures have been frequently observed in dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] and occasionally in other rhombohedral carbonates. The modulations are often accompanied by a crosscutting banding that has been interpreted as growth banding, but whose crystallographic and genetic origins remain enigmatic.

In the present investigation calcian ankerites [ $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$ ] with a modulated microstructure have been characterized with TEM, revealing some new aspects of the modulation geometry. The modulations appear to be finger- or rodlike features oriented parallel to the growth direction of the crystals. This configuration may be the result of a microcellular growth mechanism with an accumulation of impurities between the cells.

### INTRODUCTION

Since the first documentation by Reeder and Wenk (1979), a number of workers have reported a modulated microstructure in transmission electron microscope (TEM) images of carbonates with space group  $R\bar{3}$  (dolomite type) (Reeder, 1981; Van Tendeloo et al., 1985; Wenk and Zhang, 1985; Reeder and Prosky, 1986; Barber and Khan, 1987; Miser et al., 1987), and occasionally carbonates with space group  $R\bar{3}c$  (calcite type) (Gunderson and Wenk, 1981; Frisia Bruni and Wenk, 1985). Most reports of modulated structures in  $R\bar{3}$ -type carbonates have been for dolomite. Reports of modulations in ankerite are scarce (e.g., Barber and Khan, 1987). Ankerite and dolomite are isostructural phases and form a solid solution in which up to approximately two-thirds of the Mg in dolomite can be replaced by  $\text{Fe}^{2+}$ . Because of the close relationship between these phases, it seems reasonable to assume that the crystallographic and genetic origins of characteristic microstructures are analogous in ankerite and dolomite.

The present paper is a documentation of modulated structures in calcian ankerite cement in a Jurassic sandstone from the North Sea. According to previous investigations of these samples by Saigal and Bjørlykke (1987), the ankerites formed at temperatures between 60 and 120 °C.

The modulated microstructures produce a wavelike contrast in TEM images, with alternating dark and bright regions. The modulations are often crosscut by a coarser banding, which has been interpreted as growth banding (e.g., Reeder and Prosky, 1986). Both modulations and banding have previously been interpreted as lamellar features, each approximately parallel to a plane of the form  $\{10\bar{1}4\}$ , although Reeder and Prosky (1986) emphasized that the trace of the modulations is always closely parallel to the growth normal of the respective sectors in the crystals.

Two types of weak superstructure reflections, one termed *c*-type reflections by Reeder and Wenk (1979) and the other termed *d*-type reflections by Van Tendeloo et al. (1985), have been recognized in carbonates with a modulated microstructure (Gunderson and Wenk, 1981; Wenk and Zhang, 1985; Barber and Khan, 1987; Miser et al., 1987). Both are observed for small local domains, as demonstrated through high-resolution electron microscopy (HREM) and dark-field (DF) imaging of dolomites by Van Tendeloo et al. (1985) and Wenk and Zhang (1985), and both display a superstructure that is incompatible with the ideal symmetry of the host carbonate. The *d*-type reflections have been observed in carbonates only with space group  $R\bar{3}$ , whereas *c* reflections occur in structures with both space groups  $R\bar{3}$  and  $R\bar{3}c$ . The superstructures most probably relate to ordering of the cations (Van Tendeloo et al., 1985; Wenk and Zhang, 1985; Reksten, 1990). An intimate association between *c*-type superstructures and the modulated microstructures has been described (Gunderson and Wenk, 1981; Reeder, 1981; Van Tendeloo et al., 1985; Miser et al., 1987). However, there are reports of dolomite with a modulated microstructure for which *c*-type reflections have not been detected (Wenk and Zenger, 1983). Also, recent observations by Reksten (1990) of *c*-type reflections in calcites with a whole range of microstructures, including nearly defect-free crystals, suggest that *c* reflections and modulated microstructures occur independently.

The modulations were initially interpreted as an exsolution product in metastable nonstoichiometric carbonates, but it is now evident that they are related to growth of the crystal (Reeder and Prosky, 1986), even though a proper model for the growth mechanism is still lacking. Different theories for the cause of the modulations have been put forward. Most authors seem to support the idea of a slight variation in the concentrations of different cations, since most modulated structures are observed in

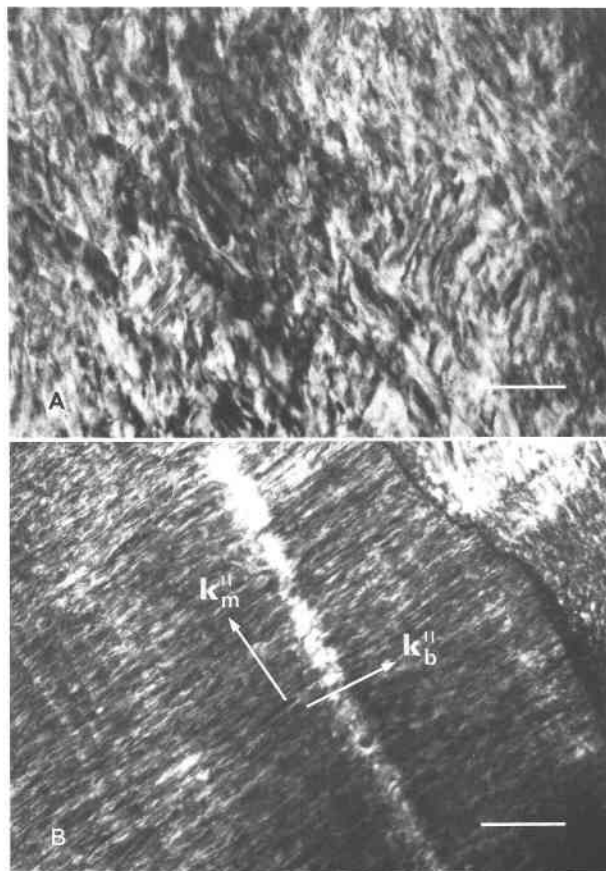


Fig. 1. Typical microstructures in the ankerite cement. (A) Heterogeneous irregular type of contrast. Scale bar is 200 nm. (B) Modulated microstructure with crosscutting banding. The vectors  $k_m^{\parallel}$  and  $k_b^{\parallel}$  are normal to the traces of modulations and banding, respectively, and are used for analyses of the traces. Scale bar is 300 nm.

nonstoichiometric carbonates (Reeder, 1981; Van Tendeloo et al., 1985; Wenk and Zhang, 1985; Barber and Khan, 1987). Efforts to verify this correlation by direct chemical analyses of dark and bright regions of the modulations have not been successful, owing to their fine scale. Alternative theories are based on observations of modulated structures in stoichiometric carbonates. Gunderison and Wenk (1981), reporting on modulated structures in pure calcite, favor the idea of rotational disorder of  $\text{CO}_3$  groups giving rise to the modulations. Miser et al. (1987) suggest that volumetrically insignificant  $c$  domains cause a modulated strain effect in the structure of a stoichiometric dolomite. There is, of course, a possibility that there are different origins of the modulated contrast in different cases.

The present investigations have revealed some new characteristics of the modulated microstructures. The modulations appear not to have the lamellar configuration indicated by previous workers. The modulated microstructure is a signature of the processes leading to its

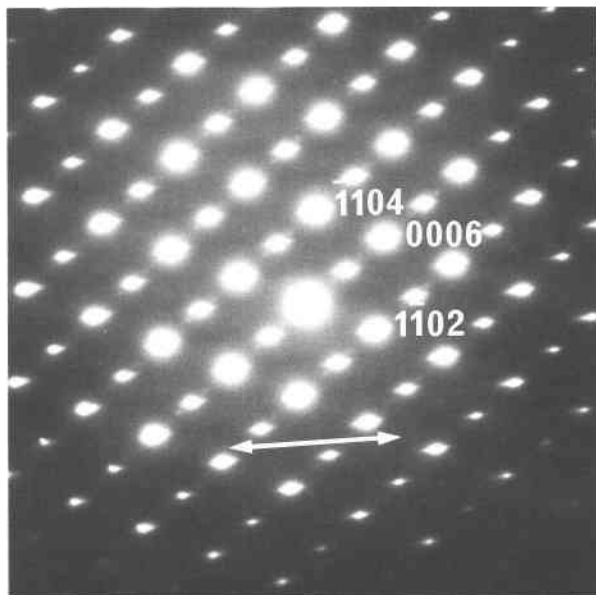


Fig. 2. SAD pattern from calcian ankerite with a modulated structure. Weak streaks invariably occur for all reflections, even when crystals are tilted up to  $50^\circ$  about an axis nearly parallel to  $[\bar{1}104]^*$ . The direction of streaking is indicated by an arrow on the photograph.

formation, and an interpretation of this microstructure must be based on a correct description of the modulation geometry.

## METHODS

Areas of interest were selected in petrographic thin sections and mounted on copper grids. The samples were further thinned in an Edwards argon ion mill and then coated with a thin layer of carbon to avoid charging.

Two JEOL instruments, a 200 CX and a 2000 FX at the Department of Physics, University of Oslo, were used in this study. Both were equipped with Tracor Northern X-ray microanalyzers using energy dispersive Si(Li) detectors.

## EXPERIMENTAL RESULTS

The chemical composition of the ankerite as determined by X-ray microanalyses in the TEM,  $\text{Ca}_{1.12}\text{Fe}_{0.44}\text{Mg}_{0.40}\text{Mn}_{0.04}(\text{CO}_3)_2$ , deviates from ideal cation stoichiometry. Estimated errors for Ca and Fe are about  $\pm 5\%$ . For Mg it is probably as much as 15% and for Mn about  $\pm 10\%$ .

TEM images of the ankerite reveal a pervasive heterogeneous contrast. The microstructure is either quite irregular, as in Figure 1A, or is a more regular modulated microstructure (Fig. 1B). The modulations have a wavelength of approximately 100–300 Å and are commonly accompanied by a straight crosscutting banding with a more variable wavelength.

There seem to be several degrees of development of the modulated microstructure. The boundaries between dark

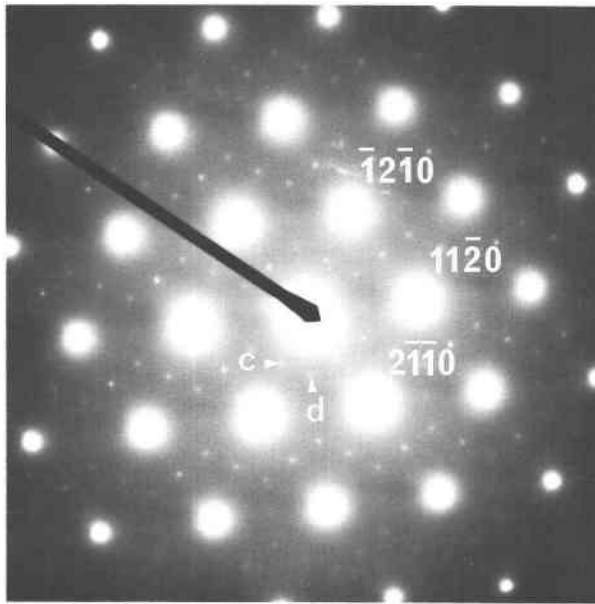


Fig. 3. SAD pattern of ankerite with *c*- and *d*-type superstructure reflections indicated by arrows.

and bright regions are sometimes diffuse and sometimes rather sharp. It is difficult to diminish the contrast in both modulations and banding in some crystals, whereas in others it is difficult to obtain the contrast.

In selected-area diffraction (SAD) patterns of regions having a modulated microstructure, the reflections are somewhat broadened or streaked in a direction perpendicular to the trace of the modulations (Fig. 2). The streaking is present even when the specimen is tilted through a large angle about an axis normal to the streaking. The streaking seems to be more distinct when the modulations are more pronounced.

Weak *c*- and *d*-type superstructure reflections have been noted in the diffraction patterns (Fig. 3). The *c*-type reflections occur halfway to fundamental reflections such as  $11\bar{2}0$ ,  $10\bar{1}4$  and  $\bar{1}018$ , whereas *d* reflections appear at the positions of  $01\bar{1}0$  (which is extinct in  $R\bar{3}$  structures) and as satellites around  $000l$  reflections parallel to  $c^*$ . The intensity and sharpness of the superstructure reflections from different crystals or crystal regions are variable. The *c*-type reflections are slightly more intense than the *d*-type reflections. DF images of *c*-type reflections reveal small localized domains, a few tens of nm in size, sometimes elongated parallel to the trace of the modulations (Fig. 4). The volume fraction of such domains seems to vary from region to region within a crystal, as also implied by the variable intensities of the superstructure reflections.

#### Tilting experiments

The TEM image is a two-dimensional projection parallel to the optic axis of the microscope. The three-dimensional crystallographic orientation of individual micro-

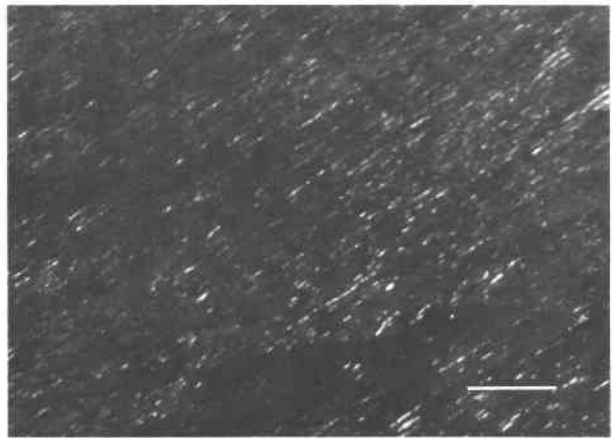


Fig. 4. DF image of *c*-type superstructure reflection revealing small domains within the host ankerite. Note elongation of domains parallel to the trace of the modulations. Scale bar is 200 nm.

structural features can be found through tilting experiments. It is important to note, however, that the traces of modulations and banding not only depend on the orientation of the crystal relative to the incident electron beam, but also on how the specimen has been cut. Thus it is necessary to carry out tilting experiments on several crystals that have been cut differently with respect to the orientation of the microstructures to find the true orientation of modulations and banding.

The ankerite crystals used for tilting experiments were cut in three distinctly different directions. This should provide reliable results from the analyses of the traces, which have been carried out through the application of stereographic projections (see e.g., Johari and Thomas, 1969).

Let the vector  $\mathbf{k}_m$  denote the direction parallel to the shortest period associated with the modulations, whereas the corresponding vector  $\mathbf{k}_b$  serves for the banding. For every TEM image of modulations and banding there are corresponding vectors, denoted  $\mathbf{k}_m''$  and  $\mathbf{k}_b''$ , measured along the normals to the traces of modulations and banding, respectively (Fig. 1B). The vectors  $\mathbf{k}_m''$  and  $\mathbf{k}_b''$  are fixed by the direction of incidence of the electron beam and the orientation relations between microstructures and foil surface. Tilting experiments of one single crystal provide a range of  $\mathbf{k}_m''$  and  $\mathbf{k}_b''$  vectors, which are marked as points in the stereoplot (Fig. 5A).

Another set of vectors,  $\mathbf{k}_m'$  and  $\mathbf{k}_b'$ , are functions only of the foil surface orientation relative to the crystallographic axes and the microstructure. These vectors are normal to every single  $\mathbf{k}_m''$  and  $\mathbf{k}_b''$  vector, respectively. Hence,  $\mathbf{k}_m'$  and  $\mathbf{k}_b'$  are represented by the intersections of great circles drawn around each  $\mathbf{k}_m''$  and  $\mathbf{k}_b''$  point in the stereoplot. Note that the  $\mathbf{k}'$  vectors are parallel to the line of intersection between the foil surface and the respective microstructure in a crystal. Experiments on one single

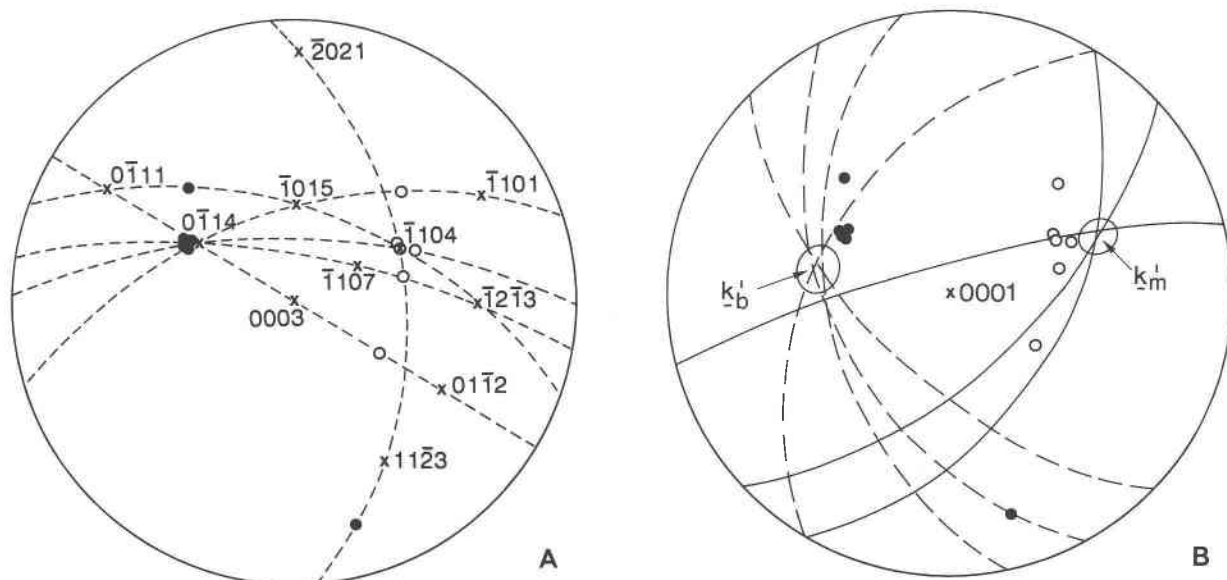


Fig. 5. (A) Stereographic plot of data for different orientations of a single specimen. Each great circle (indicated by a dashed line) corresponds to a diffraction pattern. The orientation of  $k_m''$  and  $k_b''$  vectors relative to their corresponding diffraction patterns are marked with solid dots and open dots, respectively. (B) Stereographic plot showing orientation of  $k_m'$  (solid dot) and  $k_b'$

(open dot) vectors as in Figure 5A. Great circles indicated by solid lines are drawn  $90^\circ$  from the individual  $k_m''$  vectors, and great circles indicated by dashed lines are drawn  $90^\circ$  from the  $k_b''$  vectors. Approximate orientations of  $k_m'$  and  $k_b'$  at intersections of great circles, indicated by both solid and dashed lines, are shown.

crystal result in one  $k_m'$  vector related to the modulations and one  $k_b'$  related to the banding (Fig. 5B).

Following this procedure for several crystals cut in different orientations, a range of great circle intersections is found, each consistent with a  $k_m'$ - or  $k_b'$ -type vector. This is indicated in Figure 6, which reveals that  $k_m'$  vectors from different crystals plot in a region around  $[\bar{1}104]^*$ , whereas  $k_b'$  vectors are spread out defining a great circle in the stereoplot that is very close to the trace of  $(\bar{1}104)$ . The vectors  $k_m$  and  $k_b$ , defining the real orientations of modulations and banding, are normal to all the  $k_m'$  and  $k_b'$  vectors respectively. Hence,  $k_b$  is normal to the plane spanned by  $k_b'$  vectors from different crystals, i.e., parallel to  $[\bar{1}104]^*$ . The modulation vector  $k_m$ , however, does not have a single direction, but rather may take any direction within the plane  $(\bar{1}104)$ . Because the  $k$  vectors are parallel to the shortest periods of their corresponding microstructures, the banding is a planar or lamellar structure parallel to  $(\bar{1}104)$ , whereas the modulations can be described as undulant fingers or rods pointing in a direction normal to the plane of banding (Fig. 7A).

## DISCUSSION

The results of the present investigation strongly suggest that the modulated contrast observed in calcian ankerites (and calcian dolomites) is caused by a rod-shaped variation within the crystal. This is primarily indicated by analyses of tilting experiments, but streaking of reflections in SAD patterns also supports the conclusion (Fig.

2). The streaking normal to the trace of the modulations was present even when the sample was tilted through a large angle about an axis parallel to the trace. This indicates that the streaks through the spots are merely projections of disk-shaped reflections, which are the expressions in reciprocal space of rodlike structures.

In agreement with previous observations on dolomites (Wenk et al., 1983; Van Tendeloo et al., 1985; Wenk and Zhang, 1985), the present investigation shows that weak  $c$ -type superstructure reflections arise in small local domains. The domains are present in variable amounts, as observed in DF images (Fig. 4) and as indicated by the variable intensities of the superstructure reflections. This limited occurrence is in contrast to the pervasive distribution of the modulated microstructure throughout the crystals. A direct correlation between the  $c$ -type superstructure reflections and the modulations seems unlikely. If the modulations were caused by strain bordering the  $c$  domains, one would expect the microstructure to be less pervasive, more or less varying with the proportions of domains present. In addition, Reksten (1990) reports that the occurrence of  $c$ -superstructure reflections for calcite bears no relation to modulated microstructures, supporting the lack of correlation observed in ankerite.

The observation that  $c$  domains are sometimes elongated parallel to the trace of the modulations may indicate an association, however. It has now become evident that the modulations are related to growth of the crystals (Reeder and Prosky, 1986) with the trace of the modu-

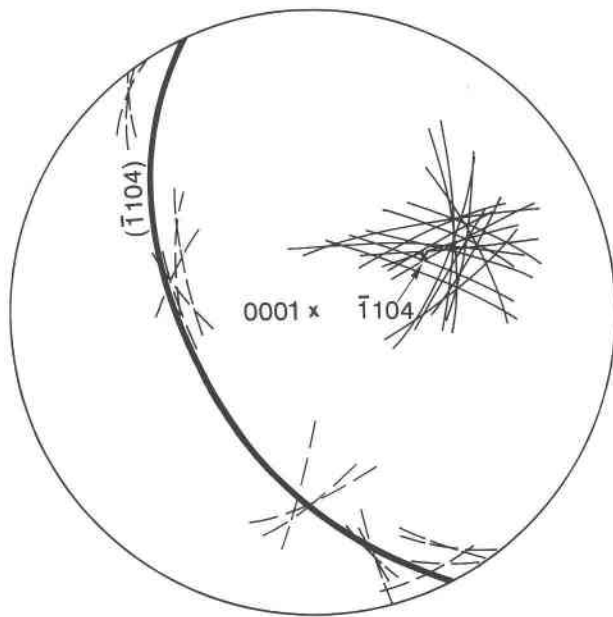
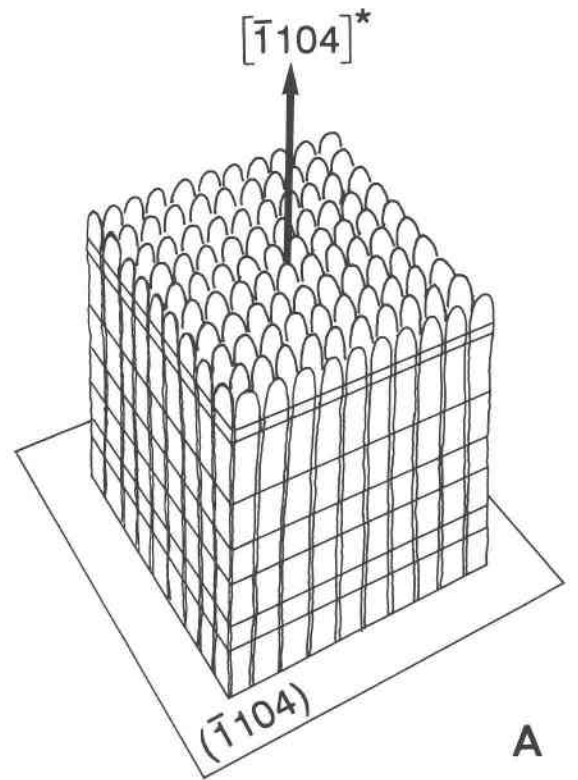


Fig. 6. Stereographic plot showing regions of intersection of great circles indicating  $k_m'$  and  $k_b'$  vectors for specimens cut in different orientations—as illustrated for one crystal in Figure 5B. The normal to all  $k_b'$  vectors, i.e.,  $k_b$ , is approximately parallel to  $[\bar{1}104]^*$ . The plane  $(\bar{1}104)$  is nearly normal to all  $k_m'$  vectors.

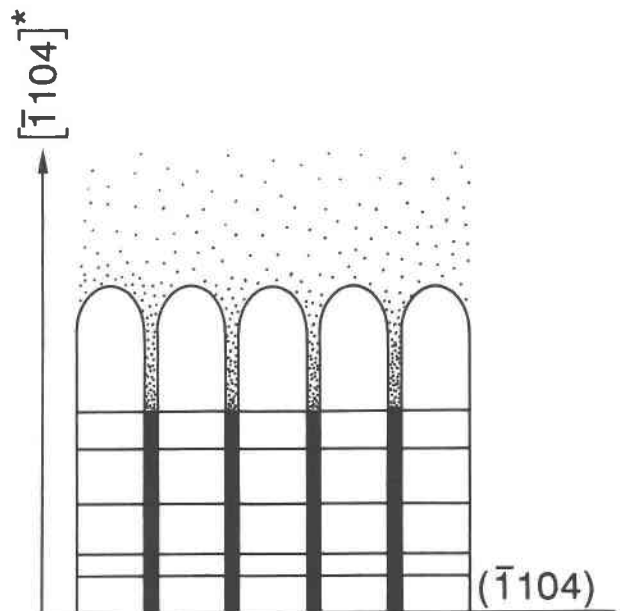


A

lations, as seen in TEM images, closely following the growth normal. Hence, it seems likely that the elongation of domains and the occurrence of modulated structures are both results of growth processes. Such an indirect relation seems more reasonable than the idea that one of the features is the direct result of the other.

Gunderson and Wenk (1981) considered rotational disorder of  $\text{CO}_3$  groups to be the most likely origin of the modulations and the  $c$ -type reflections in pure calcite. They believed a disordered arrangement of  $\text{CO}_3$  groups would be particularly likely to occur during rapid growth on  $\{10\bar{1}4\}$ . Although rotational disorder of  $\text{CO}_3$  groups cannot be ruled out completely, variation in cations seems to be a more plausible cause of the modulated structures.

Both  $c$ - and  $d$ -type domains supposedly contain more Ca than the ideal ankerite structure, as proposed for the analogous case of dolomite by Van Tendeloo et al. (1985) and Wenk and Zhang (1985). The presence of these domains could account for much of the excess Ca encountered in the samples. Still, some of the excess Ca could be involved in the formation of a modulated microstructure, possibly supported by trace elements. Small variations in cation concentrations probably explain the banding that crosscuts the modulations, which according to Reeder and Prosky (1986) is clearly a growth banding. Growth banding most often reflects variable conditions or compositions of the pore fluids from which the crystal has grown. Such variables could be reflected in a modulated microstructure as well, if crystal growth is microcellular with impurities accumulating between rodlike cells



B

Fig. 7. (A) Perspective drawing of rodlike cells growing normal to a  $(\bar{1}104)$  face of ankerite. (B) Cross-section of Figure 7A, normal to the growth face, illustrating cellular growth with accumulation of impurity elements between the cells.

(Fig. 7B). Cellular growth of rhombohedral carbonates has not been documented, but it was, nevertheless, suggested by Barber et al. (1985) as a possible growth mechanism for saddle dolomites with a ribbon microstructure. Cellular growth generally requires a high degree of supersaturation (Sunagawa, 1981). The exact degree of supersaturation that is necessary varies with the phases and conditions involved, and data relevant to ankerite or dolomite growth are not available. The size of ankerite crystals with a pervasive modulated structure may be of the order of several  $\mu\text{m}$ , as observed in this study. Thus, if cellular growth is responsible for these microstructures, the degree of supersaturation must somehow have been kept at a rather high level for long periods of time. The variation in sharpness of contrast in images of the modulated microstructures in different crystals may be the expression of different degrees of supersaturation.

From a crystallographic point of view microcellular growth is a reasonable model. The rods or cells are normal to the  $\{\bar{1}104\}$  growth bands, which are really fossil growth surfaces, and which occur commonly on crystals of dolomite. The cells must be bounded by appropriate cell walls. The planes  $(11\bar{2}0)$ ,  $(10\bar{1}2)$ ,  $(2\bar{1}\bar{1}6)$ ,  $(1\bar{2}16)$  and  $(0\bar{1}12)$  are all nearly parallel to the cells, or  $[\bar{1}104]^*$ , whereas the planes  $(1\bar{1}02)$  and  $(1\bar{1}08)$  deviate from parallelism by only  $10\text{--}20^\circ$ . The forms  $\{11\bar{2}0\}$  and  $\{0\bar{1}\bar{1}2\}$  occur commonly on crystals of many rhombohedral carbonates, and  $\{1\bar{1}08\}$  is a common twin plane. All of these planes may plausibly constitute walls for the microcells.

### CONCLUSIONS

1. The modulated microstructure of calcian ankerite has a rodlike geometry, the rods being oriented parallel to one of the  $\langle\bar{1}104\rangle^*$  reciprocal directions.

2. The crosscutting banding is a lamellar structure parallel to  $\{\bar{1}104\}$ , i.e., normal to the rods.

3. The banding has previously been interpreted as growth banding, which, assuming this is a correct interpretation, implies that the rods are oriented normal to the growth surface.

The rod structure may be the result of a cellular growth process, during which minor elements (i.e., some of the excess Ca or, possibly, trace elements) accumulate in the reentrants between the cells. At least 6–8 crystallographic planes parallel or nearly parallel to  $[\bar{1}104]^*$  constitute plausible cell walls. The difference between intra- and intercell composition could be responsible for the modulated contrast observed by TEM.

Much of the excess Ca encountered in the ankerite samples can probably be accounted for through incor-

poration in *c*- or *d*-type superstructure domains. The domains occur in a nonpervasive manner, and there seems to be no direct correlation between superstructure domains and modulated microstructures.

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