

## Superstructures in calcite

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### ABSTRACT

Calcite cement ( $\text{CaCO}_3$ , space group  $R\bar{3}c$ ) occurring in Jurassic/Lower Cretaceous sandstones from the North Sea, precipitated from pore fluids at temperatures below 60 °C, has been investigated by TEM. The crystals contain minor amounts of Fe, Mg, and Mn. Calcite crystals vary from defect-rich to nearly defect-free. Irrespective of defect density, SAED patterns commonly reveal weak superstructure reflections that are not compatible with the structure of calcite. Dark field (DF) images of these reflections reveal small local domains within the host calcite. The reflections appear midway between the origin and  $11\bar{2}0$ ,  $10\bar{1}4$ , and  $01\bar{1}8$  fundamental reflections and symmetry equivalents. The reflections are interpreted in terms of cation ordering, and the experimental diffraction patterns are compared with calculated ones. A superstructure model is suggested in which (0001) layers within which cations are ordered are stacked systematically. Within each layer alternate rows of atoms parallel to the  $a$  axes consist of  $\text{Ca}, (\text{Fe}, \text{Mg}, \text{Mn}), \text{Ca} \dots$  and pure Ca. The space group of this model structure is  $R\bar{3}c$ .

### INTRODUCTION

Carbonates are among the most common rock-forming minerals, occurring in magmatic, hydrothermal, metamorphic, and sedimentary rocks, and they have been the subject of extensive investigations. Nevertheless, many details remain to be clarified, particularly regarding low-temperature phases. The common occurrence of metastable nonstoichiometric carbonates in sediments serves to illustrate the complexities. For a comprehensive review of the carbonate minerals, see, e.g., Reeder (1983).

During the last decade several studies relating to superstructures in low-temperature rhombohedral carbonates have appeared. Reeder and Wenk (1979) first documented weak extra reflections in diffraction patterns from sedimentary calcian dolomites and referred to them as  $c$  reflections. Subsequently there have been several descriptions of  $c$ -type superstructure reflections displayed by dolomite (Reeder, 1981; Barber et al., 1985; Van Tendeloo et al., 1985; Wenk and Zhang, 1985; Miser et al., 1987). The occurrence of  $c$  reflections in diffraction patterns of calcite has been reported less extensively (Gunderson and Wenk, 1981; Frisia Bruni and Wenk, 1985; Barber and Khan, 1987).

Reports of  $c$  superstructures in both calcite and dolomite have been associated with a kind of modulated microstructure. The crystallographic origins of both modulations and superstructures have been a matter of debate. Van Tendeloo et al. (1985) argued that  $c$  reflections were due to ordering of cations of calcian dolomite that are restricted to small domains. Gunderson and Wenk (1981), however, claimed that for pure calcite the  $c$  reflections were most likely caused by periodic rotational disorder of  $\text{CO}_3$  groups.

In the present paper, transmission electron microscopy (TEM) evidence of ordered phases in impure low-temperature sedimentary calcites is reported. The superstructures are present in crystals with a variety of microstructures and do not seem to be closely related to a modulated microstructure.

The interpretation of the TEM results is supported by calculated diffraction patterns, which are based on models incorporating cations other than  $\text{Ca}^{2+}$  in an ordered manner. Such cations, e.g.,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ , are commonly assumed to substitute randomly in calcite. The existence of ordered phases would have implications for the topology of low-temperature phase diagrams of carbonates.

### MATERIALS STUDIED

Carbonate cements in Jurassic/Lower Cretaceous sandstones from several localities in the North Sea were investigated by TEM. The samples have previously been studied by Saigal and Bjørlykke (1987). According to their isotopic studies, the calcite cements have grown at  $T = 15\text{--}60$  °C and at near surface to approximately 2-km depths. The cements have not been exposed to temperatures exceeding 120 °C. The size of the cement crystals, as determined by optical microscopy, ranges from a few  $\mu\text{m}$  to ca. 3 mm.

### METHODS

TEM samples were prepared from conventional petrographic thin sections. They were mounted on copper grids and further thinned in an Edwards ion mill. JEM 2000 FX and 200 CX transmission electron microscopes at the Department of Physics, University of Oslo, were used. Both are equipped with Tracor Northern energy-dispersive X-ray analyzers. In this study hexagonal indices [ $hkl$ ,

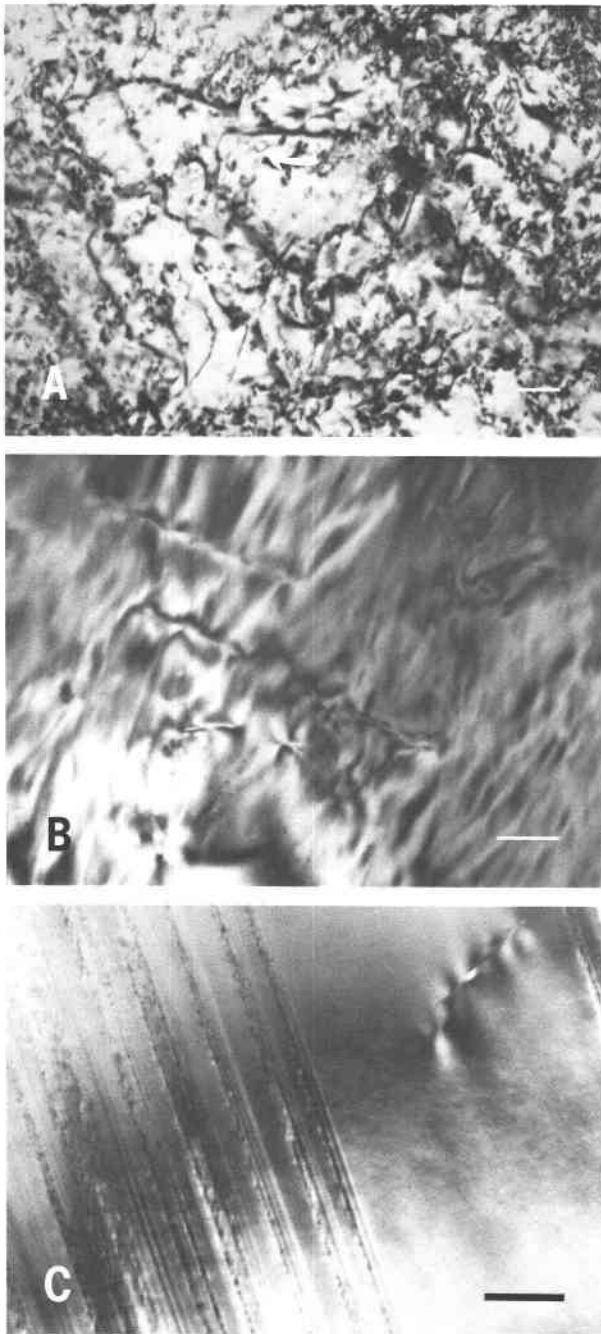


Fig. 1. TEM images of different types of microstructures observed in the calcite cement. (A) Defect-rich crystal region with a heterogeneous, irregular contrast. Most of the defects are dislocations. Small loops (indicated by arrow) are beam damage. Scale bar is 100 nm. (B) Scattered dislocations with a modulated background contrast. Scale bar 200 nm. (C) Crystal region with a few planar faults and a dislocation and large areas without linear or planar defects. Scale bar 200 nm.

$i = -(h + k)$ ] are used, for which the cleavage plane is  $(10\bar{1}4)$ .

### OBSERVATIONS

The TEM investigations revealed a wide range of microstructures in the calcite cements, with defect-rich to almost defect-free regions. Figure 1A shows the irregular heterogeneous contrast typical of defect-rich regions, with many dislocations and other defects. Some regions with a high defect density produce a more regular modulated contrast as a sort of pervasive background (Fig. 1B), with more recognizable features like dislocations and twins superimposed on it. In crystals with fewer defects there are large regions of uniform contrast between individual dislocations and planar faults (Fig. 1C). The uniform contrast is not disturbed even when the specimen is tilted through a large angle, indicating that these are crystal regions without linear or planar defects.

According to X-ray microanalyses in the TEM, the cement crystals have from 2–7 mol%  $(\text{Fe}, \text{Mg}, \text{Mn})\text{CO}_3$ . There is a slight tendency for cations other than  $\text{Ca}^{2+}$  to occur in defect-rich regions. However, this variation is within error of analysis and may not be meaningful. The relative estimated error is about 5% for Ca and 10% for Fe and Mn, whereas for Mg it is about 15%. The relative proportions of Fe, Mg, and Mn vary, but Fe is usually the dominant substituting element. One or two of the substituting elements are sometimes below detection limits.

Irrespective of the type of microstructure encountered in the calcite crystals, SAED patterns commonly reveal weak extra reflections (*c* type) that do not conform to the calcite structure and that cannot be the result of multiple diffraction. The extra reflections have been observed to occur midway between the central beam and fundamental reflections of indices  $11\bar{2}0$ ,  $10\bar{1}4$ , and  $01\bar{1}8$  in all symmetrically equivalent directions (Figs. 2a, 2b). No significant difference in intensity between symmetrically equivalent *c* reflections has been noted. The superstructure reflections are sometimes sharp and sometimes merely diffuse streaks running from the central beam, with intensity maxima positioned halfway to the respective fundamental reflections.

Occasionally very weak extra reflections appear midway between the central beam and  $01\bar{1}2$  fundamental reflections. However, such superstructure reflections have not been observed in zones where they cannot be produced by double diffraction (Fig. 3a). On close inspection the weak reflections in the reciprocal lattice row, including both the origin and a  $01\bar{1}2$ -type reflection (i.e.,  $1\bar{1}02$  in Fig. 3b), are seen to be distinctly weaker than those in parallel rows, from which double diffraction could take place. Hence, it is concluded that the apparent doubling of the periodicity along  $\langle 01\bar{1}2 \rangle^*$  is purely a dynamical effect.

DF imaging of *c*-type reflections strongly suggests that the reflections arise in small local domains (Fig. 4). The size of the domains is on the order of 10 nm. The domains are located randomly or in linear arrays, some-

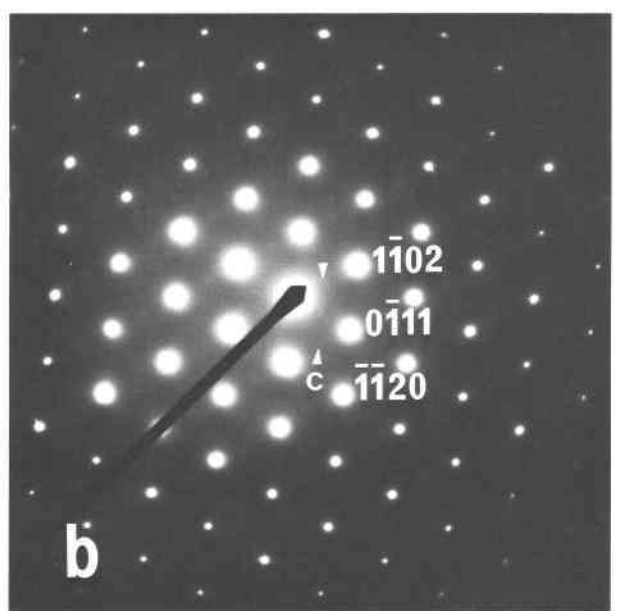
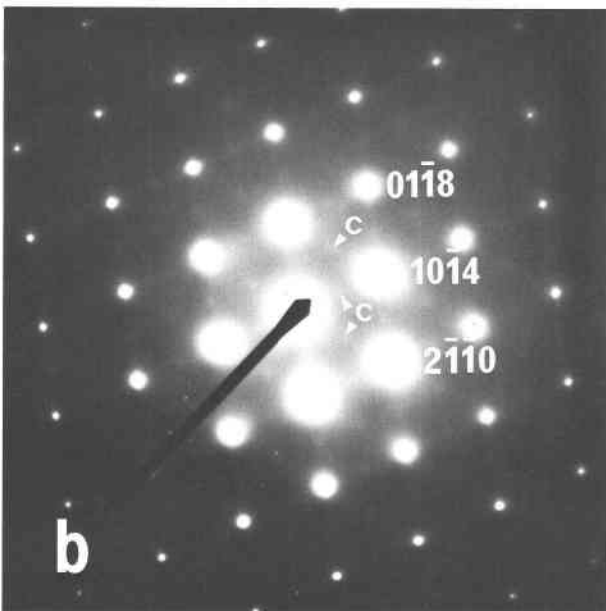
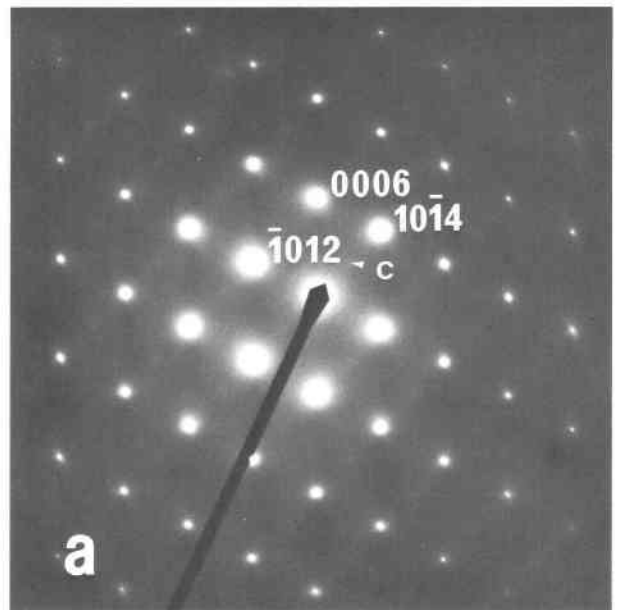
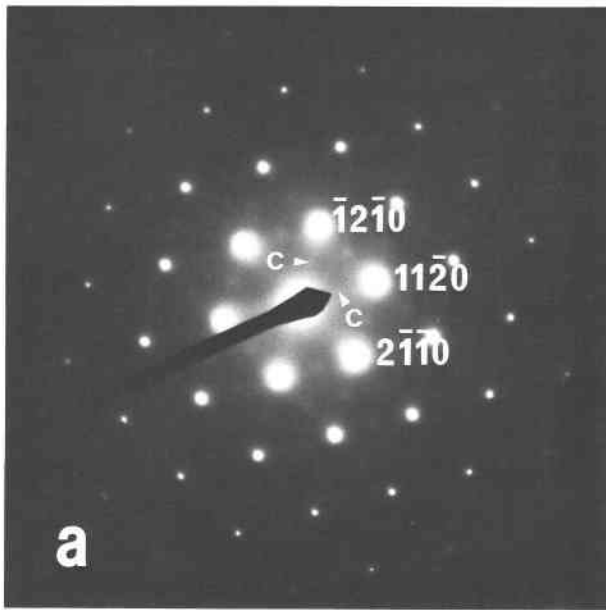


Fig. 2. SAED patterns of calcite showing weak  $c$  reflections. (a) [0001] projection with superstructure reflections midway to  $11\bar{2}0$  and symmetrically equivalent positions. Note that the rhombohedral symmetry has not been violated. (b) Projection showing  $c$  reflections in positions midway to  $11\bar{2}0$ ,  $10\bar{1}4$ , and  $01\bar{1}8$  fundamental reflections.

Fig. 3. SAED patterns from calcite illustrating that  $c$  reflections present midway toward  $01\bar{1}2$  occur only when permitted by double diffraction. (a) Projection along one of the  $a$  axes, with  $c$  reflections along  $[10\bar{1}4]^*$ . Note absence of  $c$  reflections in the  $[\bar{1}012]^*$  direction. (b) Projection showing weak  $c$  reflections midway toward  $1\bar{1}02$  (arrow) produced by double diffraction from  $c$  reflections midway toward  $1\bar{1}20$ .

times parallel to planar defects, and their distribution seems to be nonuniform.

#### DISCUSSION

In their study of calcian dolomite, Reeder and Wenk (1979) found the  $c$  reflections to be positioned halfway to fundamental reflections of the type  $11\bar{2}0$ ,  $01\bar{1}2$  and  $10\bar{1}4$ , in only one of the three symmetrically equivalent direc-

tions. Later reports by other workers have generally been in accordance with these observations on  $c$  reflections in dolomite.

Reports of  $c$  reflections in calcite are scarce and appear more or less as a documentation of their presence, referring to previous work on dolomite for details. Gunderson and Wenk (1981) observed  $c$  reflections from calcite in

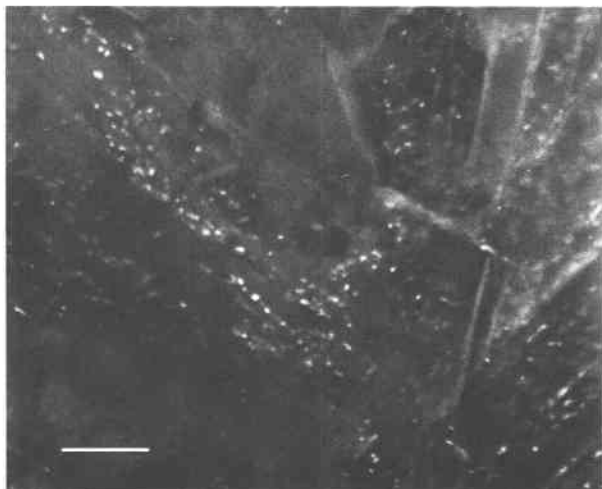


Fig. 4. DF image of  $c$  reflection showing domains occurring randomly or in association with planar defects. Scale bar is 250 nm.

one of the three symmetrically equivalent directions  $[11\bar{2}0]^*$ ,  $[01\bar{1}2]^*$ , and  $[10\bar{1}4]^*$ , analogous to the observations by Reeder and Wenk (1979). Barber and Khan (1987) reported on  $c$  reflections from calcite inclusions in siderite, the calcite being ferroan ( $\text{FeO} \approx 4 \text{ wt\%}$ ). In the latter case the  $c$  reflections occurred in all three equivalent directions. Frisia Bruni and Wenk (1985) also reported  $c$  reflections from calcite.

The results presented here deviate from most previous reports—with the exception of Barber and Khan (1987)—in that  $c$  reflections occur in all three symmetrically equivalent orientations, as consistent with the rhombohedral symmetry. In addition,  $c$  reflections do not occur midway toward  $01\bar{1}2$  reflections, except by double diffraction. Instead, superstructure reflections are clearly present midway toward  $01\bar{1}8$  and symmetrical equivalents.

Van Tendeloo et al. (1985) and Wenk and Zhang (1985) described evidence that the  $c$  reflections of dolomite arise from small, local domains in the host crystal, the domains being a few tens of nanometers in size. This was documented through DF and HREM (high resolution electron microscope) imaging. Miser et al. (1987) described  $c$  reflections from well-ordered stoichiometric dolomite and suggested that the superstructures were located in volumetrically insignificant domains. In the present work, DF imaging of  $c$ -type reflections reveals that  $c$  domains occur in calcite as well. The domains are commonly distributed randomly in the calcite, large regions being devoid of such domains. Occasionally the domains seem to be associated with planar defects in the crystals. This may be due to greater ease of diffusion, which is often encountered in faulted regions as compared with ideal ones, thus making the formation of superstructure domains kinetically more favorable. If this is so, it probably indicates that the domains formed by exsolution from

a disordered host calcite, as opposed to simultaneous precipitation of the  $c$  phase and the surrounding calcite from an aqueous solution.

The  $c$  superstructure of the present work does not seem to be associated with any particular kind of microstructure except the domain microstructure described above. In all the cases of  $c$  reflections reported earlier in both calcite and dolomite structures, an intimate association between  $c$  reflections and a specific modulated microstructure has been suggested.

The crystallographic periodicity giving rise to the  $c$  reflections has been under discussion. Gunderson and Wenk (1981) argued that cations in pure calcite couldn't form a superstructure and suggested an anion periodicity induced by rotational disorder of  $\text{CO}_3$ -groups. Van Tendeloo et al. (1985) however argued that the  $c$  reflections in dolomite arise from cation ordering. They suggested that the  $c$  superstructure in dolomite consists of cations ordered in (0001) layers with rows of Ca and Mg cations alternating parallel to one of the hexagonal  $a$  axes. The stacking of such basal layers implies a violation of the rhombohedral symmetry of dolomite. This violation is indicated by several reports of  $c$  reflections occurring in only one orientation variant of the rhombohedral host structure.

In the present work,  $c$  reflections appear in all three symmetrically related orientations. As the  $c$  superstructures occur in domains of a few tens of nanometers in size, this may be the result of averaging effects across several domains with different orientations. However, it doesn't seem very likely that the different domain orientations would be represented by equal volumes within the small selected diffracting areas. Therefore, intensity differences between symmetrically equivalent  $c$  reflections should be expected. No such intensity differences have been encountered. This suggests that the ordering within basal planes is different from the model of Van Tendeloo et al. (1985), and that the rhombohedral symmetry is preserved. Insofar as this has not been documented by more direct means, it seems appropriate to put forward two superstructure models: Model 1 is based on the basal plane model of Van Tendeloo et al., doubling one of the  $a$  axes. In model 2 both  $a$  axes are doubled, and the rhombohedral symmetry is conserved. In both models the superstructure is assumed to involve only ordering of cations.

The degree of ordering is apparently variable. This is indicated by diffuse streaking through the  $c$  reflections and by the fact that the intensity of the  $c$  reflections varies considerably, sometimes being below levels of detection. The latter emphasizes that the development of superstructure domains does not occur pervasively throughout the crystals, as also observed in DF images of  $c$  reflections (Fig. 4).

#### Model 1: $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$ , 1:1 $c$ phase

Positions of substituting cations ( $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ) doubling the periods along  $[2\bar{1}0]^*$ ,  $[10\bar{1}4]^*$  and  $[\bar{1}018]^*$

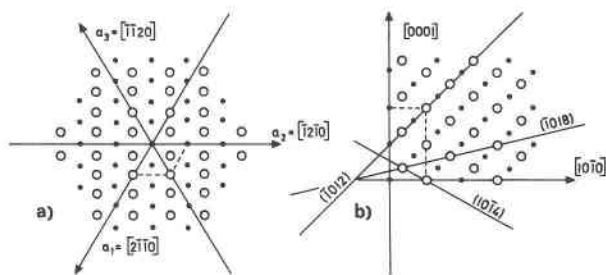


Fig. 5. Schematic illustration of model 1 cation positions. Substituting cations = ●,  $\text{Ca}^{2+}$  = ○. Traces of important crystallographic planes are indicated. (a) [0001] projection. The rhombohedral symmetry is violated. (b)  $[\bar{1}2\bar{1}0]$  projection showing stacking of identical (0001) layers.

can be deduced by inspection of the calcite structure. Figure 5a shows a projection along [0001], and Figure 5b is a  $[\bar{1}2\bar{1}0]$  projection of model 1. The space group of this model structure is  $P2/c$ . The substituting ion positions as shown in these figures satisfy the observed doubling of periods. All basal cation layers are identical. This is necessary in order to avoid changes in the periodicity parallel to [0001], which would produce superstructure reflections along  $c^*$ . Such reflections are not present in the experimental SAED patterns.

In model 1, ordered basal layers are stacked in a manner that optimizes the interlayer distance between identical types of ions. According to Burton (1987), this is an energetically favorable situation.

Model 1 has been tested by calculations based on kinematic diffraction theory. According to these calculations, model 1 will produce extra reflections in positions corresponding to the experimental results, but only in one of the symmetrically equivalent directions. Thus, model 1 seems to be an appropriate model for the  $c$  domains, provided the experimental diffraction patterns are averages across approximately equal volumes of domains with different orientations.

#### Model 2: $\text{Ca}_3(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_4$ , 3:1 $c$ phase

In model 2 all threefold symmetrical equivalents of the periods are doubled. Starting with a basal layer of model 1, both  $a$  axes are doubled by exchanging every second substituting cation in a row with a  $\text{Ca}^{2+}$  ion, as shown in Figure 6a. All relevant periods are doubled if these layers are stacked as suggested in Figure 6b. This has been tested by calculations, showing that superstructure reflections will occur in the same positions as the experimentally observed ones. Also note that in model 2, both inter- and intralayer distances between substituting cations are maximized.

Model 2 is identical to the  $R\bar{3}c$  3:1 model of Burton (1987). On the basis of theoretical analyses, Burton claimed that intralayer ordering is favored in calcite-type structures with less than 30 mol% of substituting cations

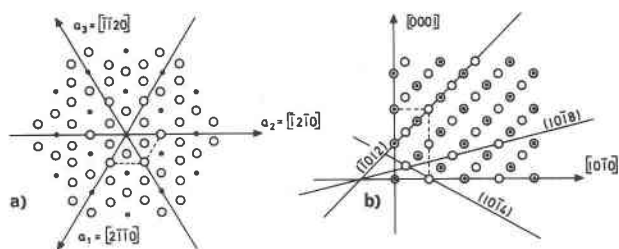


Fig. 6. Schematic illustration of cation positions in model 2. (a) [0001] projection. Note preservation of rhombohedral symmetry. Substituting cations = ●,  $\text{Ca}^{2+}$  = ○. (b)  $[\bar{1}2\bar{1}0]$  projection. Projections of rows with alternating  $\text{Ca}^{2+}$  and substituting cations are indicated by ⊙.

and that a 3:1 phase with composition  $\text{Ca}_3\text{Mg}(\text{CO}_3)_4$  is probably stable at low temperatures.

Another 3:1 model was suggested by Burton (1987) and Burton and Davidson (1988), wherein all cation basal layers are identical, with rows of Ca-Ca-Ca... alternating with rows of Ca-Mg-Ca... parallel to one of the hexagonal  $a$  axes. The model has space group  $C2/c$ . Both this model and the 3:1 model with space group  $R\bar{3}c$  have ordering patterns with a maximum inter- and intralayer separation between identical types of cations, and they should both be energetically more stable than model 1. However, calculated diffraction patterns based on the  $C2/c$  3:1 model do not conform with the experimental observations of this study, and hence this model has been rejected in this particular case.

From the present investigation alone, model 2 seems more plausible than model 1. Model 1 has 1:1 cation composition, which is the same as in ideal dolomite. Domains with a structure like model 1 would probably fit coherently with the surrounding calcite more easily than would dolomite-structured domains. It seems, nevertheless, somewhat unlikely that with the dolomite composition, a structure like model 1 would be preferred to the dolomite structure. In addition, there is no indication in the experimental diffraction patterns that the rhombohedral symmetry has been violated. Lastly, according to Burton's theoretical approach, model 2 should be energetically the more favorable of the two.

## CONCLUSIONS

SAED patterns of calcite cement formed at temperatures not exceeding 60 °C, with a few mol% (Fe,Mg,Mn) $\text{CO}_3$  substituting for  $\text{CaCO}_3$ , reveal weak superstructure reflections midway between  $11\bar{2}0$ ,  $10\bar{1}4$  and  $01\bar{1}8$  fundamental reflections and the origin. The  $c$  reflections arise from small local domains within the host calcite. The occurrence of  $c$  reflections bears no relation to any other particular kind of microstructure in the calcite crystals, since the  $c$  reflections are present in both defect-rich and nearly defect-free regions. A possible  $c$  superstructure is modeled by a regular stacking of ordered cation basal layers, in which  $\text{Ca},(\text{Fe},\text{Mg},\text{Mn}),\text{Ca}$ ... rows parallel to

the  $a$  axes alternate with rows of only Ca atoms. This arrangement effectively doubles the hexagonal  $a$  axes, and the  $R\bar{3}c$  symmetry is conserved. Both intra- and interlayer distances between substituting cations are at a maximum, giving rise to an energetically favorable configuration.

The results presented here, as well as other reports of equivalent phenomena in calcian dolomites, indicate that similar ordering occurs in both  $R\bar{3}c$ - and  $R\bar{3}$ -type carbonates with a nonideal cation composition. The development of superstructures may be the most favorable way to accommodate substituting ions and was anticipated on theoretical grounds by Burton (1987) for the system  $\text{CaCO}_3$ - $\text{MgCO}_3$ .

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