

MICROSTRUCTURES IN SIDERITE

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ABSTRACT

Transmission Electron Microscopy (TEM) is a new technique in the study of internal structure of minerals. Siderite minerals from two localities are selected for investigation with TEM, coupled with EDX microanalysis and optical methods. The microstructures present are similar to those observed in other carbonates. The major microstructural features are the curving and branching ribbons in siderite regions and lath-like defects in calcitic grains present in Erzberg siderite. These laths are found dolomitic in structure. Similar microstructures have already been reported in saddle dolomites (Barber et al., 1985). Small calcite structured precipitates were encountered in the calcite grains, where iron concentration exceeds the already reported solubility limit. The occurrence of "c" type spots in the calcitic structure and their presence in more than one equivalent directions is also reported in this paper.

INTRODUCTION

Calcite and dolomite are the major carbonate-rock forming minerals. In the past much attention has been paid to study the microstructures in these minerals (Reeder and Prosky, 1986; Van Tendeloo *et al.*, 1985; Barber *et al.*, 1984; Wenk *et al.*, 1983; Reeder, 1982; Gunderson and Wenk, 1981; Reeder and Wenk, 1979a, b). Except the recent work of Barber and Khan (1987), not much work is done to study the other rhombohedral carbonates including smithsonite, siderite rhodochrosite, ankerite, kutnahorite and minrecordite for their microstructures. The study of these minerals seems necessary, in order to make a basic understanding of the microstructures, their relation to composition, their stability field and ultimately the solution of dolomite problem.

The modulated microstructure although has a compositional origin as the consensus of the authors shows, still "how it is formed" is a mystery. Although the dolomite-type compound of manganese, which has a larger ionic radius than iron cation radius, exist, the non-availability of Fe-dolomite in nature is not understood. The work of Peacor *et al.*, (1987) on kutnahorite shows that the $\text{CaMn}(\text{CO}_3)_2$ exist in nature both as an ordered compound and a disordered solid solution. The studies on the high temperature, high pressure synthesis of this compound also showed that the ordered dolomite-type compound of manganese

can not be synthesised at temperature greater than 400°C, though its composition approximates to a Ca/Mn ratio of 1. Weak "b" type diffraction spots, which are characteristic of dolomite-type structure, appeared when the synthesised specimen was annealed for longer time (90 days). This shows that the ordering temperature of kutnahorite lies somewhere between 200° and 400°C. More work is needed for its confirmation. For detail see Khan (1987).

The TEM studies of the samples of siderite show that the Fe-dolomite does not exist in nature. In the calcite regions of siderite, where the iron concentration increases beyond 40 wt%, precipitates are observed, but the information from diffraction patterns shows that these precipitates are not dolomite-like. Different types of microstructures and their relation to composition is reported in this paper. Although the study of these minerals under present investigation apparently does not show much economic importance, however understanding the relationship between composition and temperature, may ultimately lead to use the carbonate minerals as geothermometers.

MATERIALS AND METHODS

Siderite samples from two different localities, Erzberg, Styria, Austria (No. 4372) and Cornwall Districts England were investigated. The Erzberg sample is a bulk rock from which thin slices were cut with diamond saw and polished. The Cornwall siderite consists of small crystals grown on a substrate mineral which is not itself a carbonate. The crystals were selected for the microstructural studies. The cut slices and the selected crystals were stuck on to a glass slide with Crystal Bond and polished from both sides using carbide papers of varying grades. They were thinned down to about 50 micron and '7-HEX' TEM copper grids were stuck to the area of interest, selected by petrographic microscope, with Epoxy resin (Araldite). The specimen were left overnight for drying, removed from the glass slide by melting the crystal bond and rinsed in acetone. In order to avoid over heating of the specimen and making its surface amorphous, the selected samples were thinned for TEM studies in argon ion-beam thinner at an angle of 12-15 degree and low ion-beam current. Before the introduction of ion-beam thinners the thinning of minerals for TEM studies had been a problem in the past. This problem has delayed the use of TEM in mineral and ceramic studies, compared to its use in alloys and metals which can be thinned by other techniques. To avoid charging in TEM, the ion-beam thinned specimens were carbon coated.

JEOL 200-CX, transmission electron microscope, which was linked with a low angle (zero tilt) EDX (Energy Dispersive X-ray analysis) detector (Link Systems Ltd.) was used for microstructural studies and chemical analysis respectively.

RESULTS

Siderite mineral from Erzberg, showed much interesting features in its study by TEM methods, coupled with EDX analysis system. The observations by petrographic microscope, showed the presence of regions which do not show any birefringence, a characteristic of carbonate minerals. These regions when observed on the TEM screen, are found to be quartz (SiO_2), leucite ($\text{KA1Si}_2\text{O}_6$) and hematite (Fe_2O_3). Such interpretations were confirmed by EDX. analysis, electron diffraction patterns, microstructural study and the stability under the electron beam. Since this study is related to carbonates only, it was tried to select the carbonate regions showing strong birefringence. No other separate grains were detected in the selected crystal of the mineral from Cornwall Districts.

TEM/EDX analyses on the selected sample of siderite show that the siderite region of rock have a composition with 87.5 wt% FeCO_3 , 8.0 wt% MgCO_3 , 3.8 wt% MnCO_3 and 0.7 wt% CaCO_3 . The specimen is also impure in the sense that it contained separate grains of quartz, leucite, hematite and calcite.

Siderite grains mostly exhibit a moderate to high density of curved dislocations and dislocation loops. Some features of this sample have already been reported (Barber and Khan, 1987). Unlike impure calcite which suffers beam damage, siderite is stable under the electron beam. The diffraction spots are sharp and hence they can assist in interpreting the structural defects. Mostly the bright field (BF) images show the siderite to be single phase but dark field (DF) images revealed the presence of faint fringes, defining ribbon-like defects, which suggest that very small coherent thin-laths of second phase exist. Siderite grains which are contiguous with calcite, are the most interesting. Twisting and curving ribbon-like defects were encountered which branch repeatedly as they get nearer to the calcite grains, (Fig. 1a). The fringes displayed by these ribbons in BF and DF are complementary and their behaviour is similar to those shown by calcite-ribbons of second phase in dolomite (King *et al.*, 1984; Barber *et al.*, 1985).

The diffraction patterns from such ribbon regions gave weak "b" type spots which are the characteristic spots of dolomite-type compound. Such a diffraction pattern from the ribbon region is shown in figure (1b). Using the average composition methods of analysis, it was further found that the Ca concentration increases with the increase in density of ribbons. The concentration of Mg is reduced in the ribbon regions compared to non-ribbon areas, which shows that Fe and Mg replace each other. This is a common type of replacement in Mg-Fe bearing minerals (Deer *et al.*, 1962). The concentration of Mn also increases in the ribbon regions of siderite, indicating the interdependence of Fe and Mn. The diffraction information supported by chemical analysis, indicates that the ribbons consist of second phase which has $\bar{R}3$ symmetry. Thus it is concluded that they are dolomite-like in structure, probably ankerite.

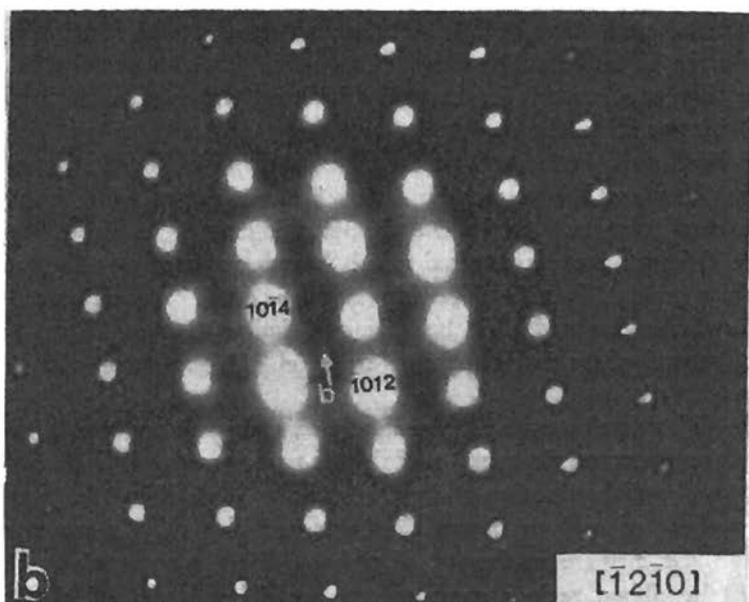
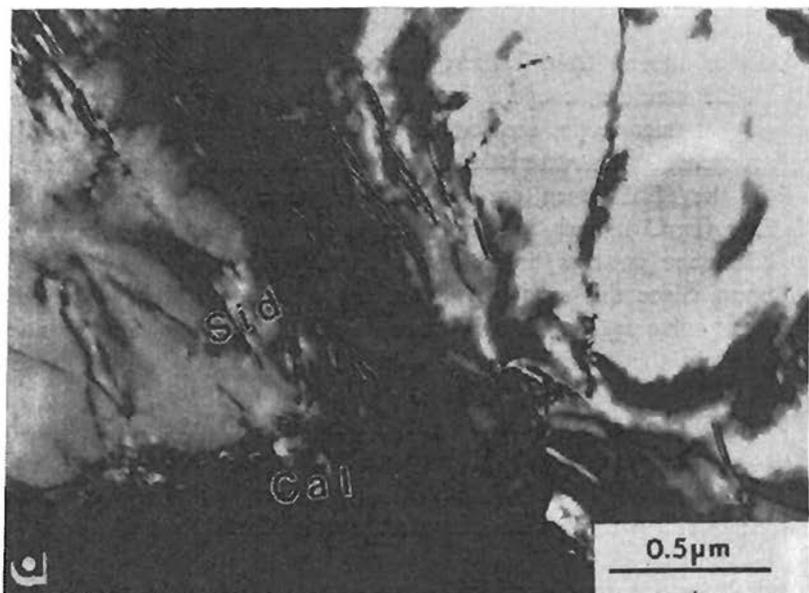


Fig. 1. (a) BF image showing branching ribbons in the regions of siderite adjacent to a grain of calcite.
 (b) Zone-axis diffraction pattern from ribbon regions exhibiting weak "b" type dolomite spots.

Since this study was concentrated on carbonate regions, calcite grains in siderite were also investigated. The calcite grains were found to be ferroan

($\text{FeCO}_3 = 4 \text{ wt}\%$). Under the electron beam they are damaged rapidly and numerous dislocation loops appear. In diffraction patterns, diffuse scattering and more surprisingly diffuse "c" type spots were detected. Such reflections ("c" type) were previously noted only with $\overline{\text{R3}}$ carbonates, apart from the case of oolitic calcite where Gunderson and Wenk (1981) observed such affects. A very unusual finding is that the "c" type spots sometimes occur in all three possible reciprocal directions for a given zone. Previously, Reeder and Wenk (1979a, b) and Gunderson and Wenk (1981) have pointed out that the "c" type reflections occur between only one of the three possible directions in a particular zone. (For detail of "c" type spots see Khan and Ishaq, 1988). Strong striations were observed in those regions of calcite in siderite, where abnormally high concentration of Mg, Fe and Mn occur. Diffraction patterns from such regions also show weak "c" type spots but no "b" type spots have been noticed. Thus such regions are calcitic with "c" type superstructure.

In some other regions of calcite in siderite, EDX analysis shows that the concentration of Fe is close to the limit of solid solubility ($\text{FeCO}_3 = 40 \text{ wt}\%$). This idea seems to be born out by finding the fringed lath-like defects (see Fig. 2a, b) in some of the calcite grains. These lath-like defects are different in appearance from the ribbons in siderite. The latter are less twisted and less curved comparatively. The detailed observations show that their properties, like termination, fringed behaviour and coherency are similar to the lath-like defects occurring in other rhombohedral carbonates (Barber *et al.*, 1985). The diffraction patterns from such regions show both the ordering "b" type and superstructure "c" type spots as shown in figure 2c, in addition to "a" type spots. When these "b" and "c" type spots were used for imaging in DF, the laths brightened up, revealing that the laths are the regions of origin of these spots. When "c" type spots were used for imaging, other fine lamellae were also weakly observed in the calcite background. The "c" type spots were sometimes streaked and the streaking of all the spots was noticed to be in the same direction. Such a feature rules out the possibility that the "c" type reflections in two equivalent directions are because of different orientations of modulation lamellae which contribute the "c" type spots in the similar but different reciprocal directions. Such a situation can occur, if the selected area aperture is over a growth sector boundary across which the modulations change orientation. Imaging any of the "c" type spots reveal the same modulated area, which again rules out the possibility that the "c" types spots are due to the change in the orientation of the modulations. (see Fig. 3a, b)

X-ray microanalysis (EDX) shows that in addition to high Fe concentration, the concentration of Mg in the ribbon regions of calcite is increased comparative to clear calcite. On the other hand, Mn tends to have low concentration in ribbon region compared to clear ones. These relationships are shown in data scatter diagram (Fig. 4a-d).

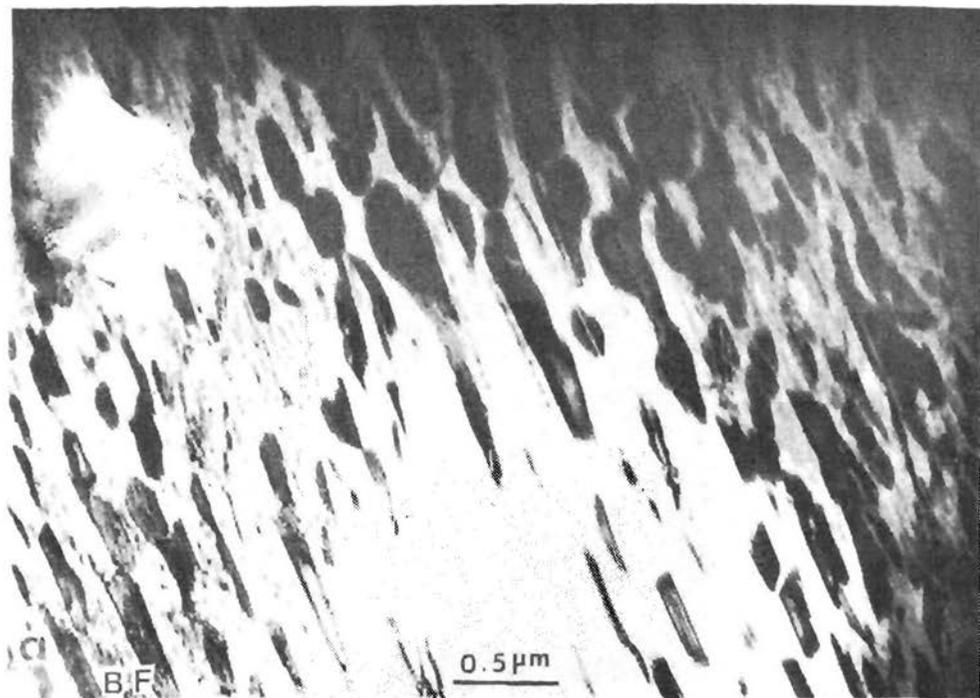


Fig. 2. (a) BF and (b) DF images of lath-like defects in calcite grain in siderite from Erzberg.

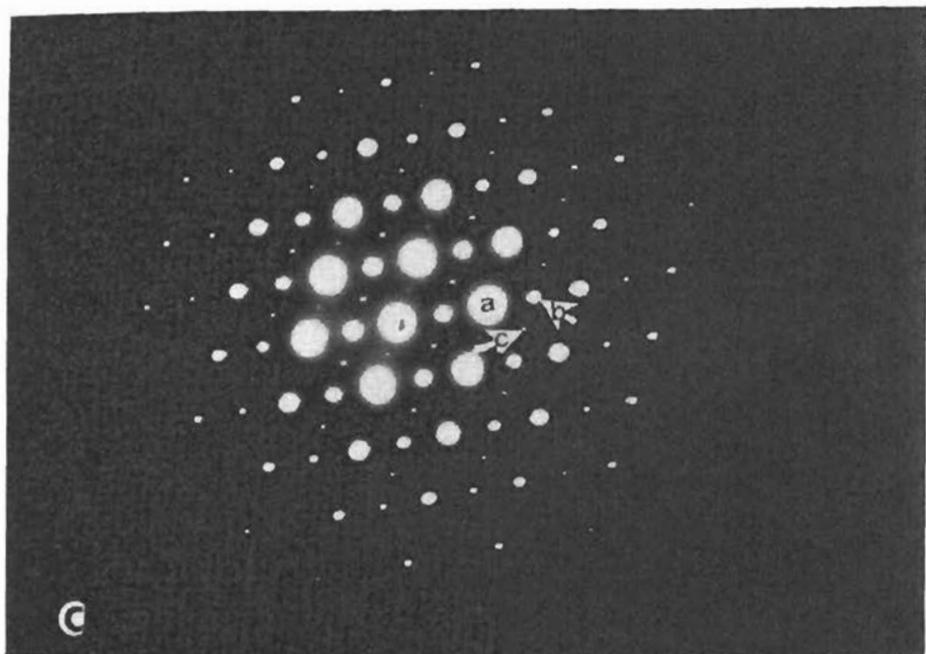


Fig. 2. (c) $[12\bar{1}0]$ zone-axis diffraction pattern from (a) revealing strong "a", weak "b" and still weak "c" type diffraction spots.

The observation of microstructures coupled with deduction from the diffraction patterns, show that the lath-like defects are coherent with the host phase but have slightly different lattice parameters because of the impurities whose nature is indicated by EDX analysis. The occurrence of "b" type spots shows that laths have $R\bar{3}$ symmetry. These lath-like defects are dolomitic in nature, probably ankerite with "c" superstructure.

There are still other regions where the concentration of FeCO_3 increases ($\text{FeCO}_3 = 46 \text{ wt}\%$) which is close to the concentration of CaCO_3 ($\text{CaCO}_3 = 45 \text{ wt}\%$). In such regions, small coherent precipitates, with larger dimensions at dislocations showing Moiré fringes were observed. Such sites (dislocations) are preferable for exsolution to occur. No "b" or "c" type spots were observed from these regions but slight elongation of the "a" type spots is noted. This shows the difference between the lattice parameters of the matrix and the precipitates. Such precipitates can be seen in a DF image (Fig. 5). Similar precipitates have been also observed occasionally in the clear regions between the ribbons. When both the ribbons and precipitates are present, both the "b" and the "c" type spots can be observed, whereas only precipitate regions do not give any "b" or "c" type spots. This clearly shows that precipitates are calcitic in nature, probably siderite itself.

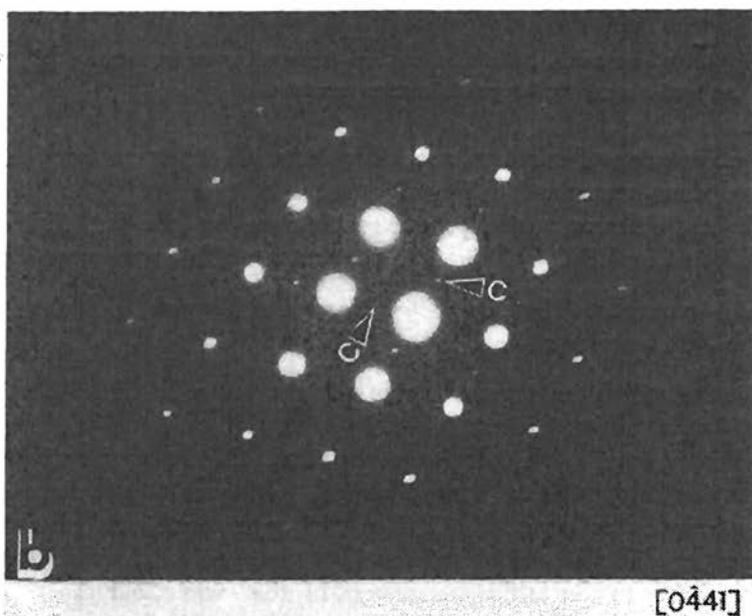
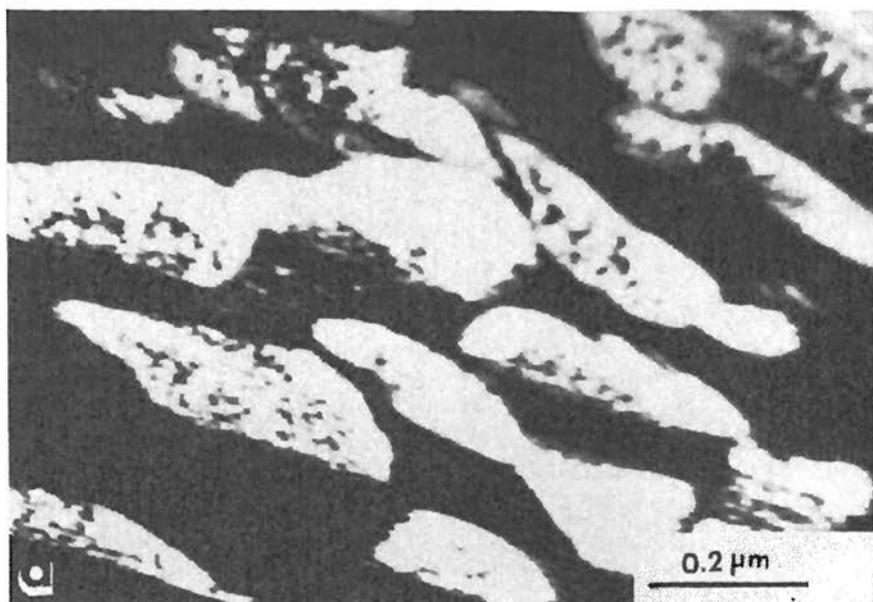


Fig. 3. (a) DF image using weak "c" type spot, revealing lath-like structure as the source of these spots in the calcitic grain in Erzberg siderite.
 (b) Zone-axis diffraction pattern from (a) showing weak "c" type spots in more than one equivalent directions.

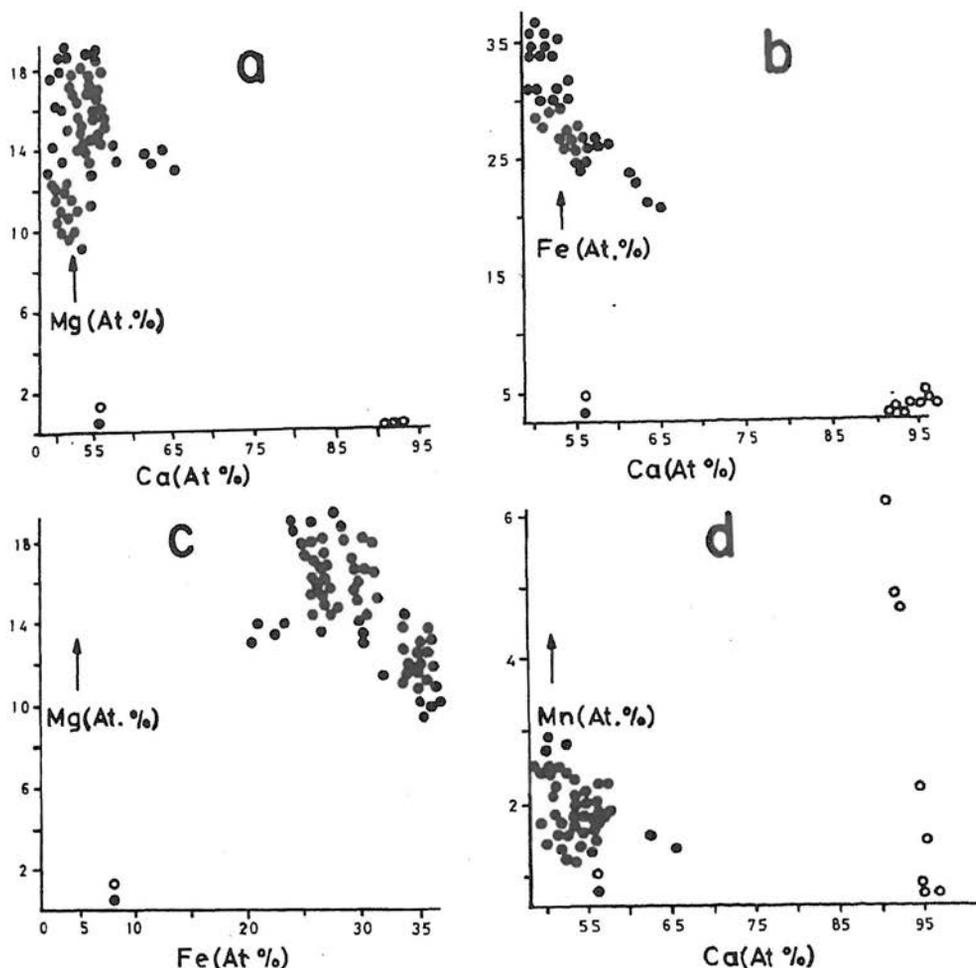


Fig. 4. Graphs showing the results of TEM/EDX microanalyses on the ribbon regions of calcite in Erzberg siderite. Open circle = clear CAL; Filled circle = Ribbon CAL
 (a) MgCO_3 versus CaCO_3 (b) FeCO_3 versus CaCO_3
 (c) MgCO_3 versus FeCO_3 (d) MnCO_3 versus CaCO_3

DISCUSSION

The results described for the calcite-type (R3c) carbonate, siderite show that particular forms of impurity related microstructures occur in this mineral, like the previously described microstructures in calcite (Gunderson and Wenk, 1981), smithsonite (Barber and Khan, 1987, Khan and Barber, 1988) and dolomites (Reeder and Wenk, 1979 a, b; Reeder, 1981; Barber and Wenk, 1984; Barber

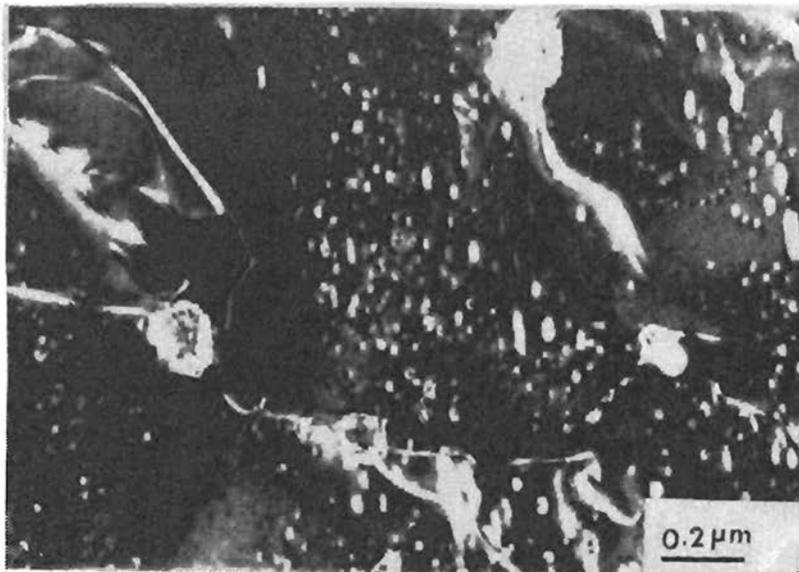


Fig. 5. DF image showing small precipitates in calcite grain with high iron concentration ($\text{FeCO}_3 > 40 \text{ wt}\%$) in Erzberg siderite. The larger size of precipitates at dislocations is apparent.

et al., 1985). The microstructures occurring in this mineral can be categorised as, (a) modulated microstructures (b) lath-like defects and (c) small precipitates. The modulated microstructures, first reported by Reeder and Wenk (1979 a, b) for non-stoichiometric dolomites are now seen to occur more widely. They are often observed in close proximity to the lath-like defects. Here the calcite regions in siderite show modulations and it is observed that they are related to the impurities in the crystal. Because of the low temperature of formation of this mineral, the origin of these modulations could be the growth process as the diffusion of cations after the formation of crystal is negligible at such a low temperature ($T < 100^\circ\text{C}$).

Although other impurities, like magnesium and manganese do exist in siderite, the concentration of calcium, a cation with larger radius, is very small. Even then weak fringed defects are seen in DF images. The presence of lath-like defects is strongly dependent on the concentration of calcium. EDX microanalysis show that it is only the calcium which increases in the ribbon regions, where as magnesium and manganese have scattered values. The presence of "b" type spots in the diffraction patterns show the dolomitic nature of the ribbons, perhaps the ankerite itself as the iron dolomite $[\text{CaFe}(\text{CO}_3)_2]$ is neither found in nature nor synthesised (Goldsmith *et al.*, 1962; Rosenberg, 1963a). However there is one exception where Kucha and Weizorek (1984) suggested that iron dolomite does exist in the ankerites of Erzberg and Buchegg mines, Austria.

This is in the form of small grains of 20–40 micron size. The existence of separate calcite grains within the siderite sample further support the view that larger cations are opposed to enter crystals having smaller octahedral sites and will tend to grow as separate grains.

The concentration of iron in calcite grains from Erzberg siderite is sometimes close to or higher than the solid solubility limit. The change of microstructures with the composition is apparent. Goldsmith *et al.*, (1962) provided data on the occurrence of iron in calcite and claimed that 45 wt% FeCO_3 could exist as solid solution. Rosenberg (1963a), however, showed that only 20 at% FeCO_3 can exist as solid solution in calcite. The extreme unstability of ferroan calcite noted here under the electron beam and the evidence that the small, apparently pre-existing plate-like precipitates in such calcites grow during irradiation (Barber and Wenk, 1984), casts doubts about the solubility limit previously determined by the low resolution methods, Goldsmith *et al.*, (1962). The existence of lath-like defects in calcite grains with higher iron concentration supported by the presence of "b" and the "c" type spots in the diffraction patterns show that the laths have dolomitic nature. The trend of the increase of magnesium and reduction in manganese concentrations with the increase in iron concentration show that the laths are ankeritic. Splitting of the diffraction spots is a further proof of the difference in the lattice parameters of the laths and the host phase.

The occurrence of the "c" type spots in more than one equivalent directions in the diffraction patterns can not be explained on the model proposed by Van Tendeloo *et al.*, (1985). The streaking of the "c" type spots could be the result of the difference in the lattice parameters of the "c" ordered lamellae in calcite and ankerite ribbons. The existence of such ordered lamellae both in calcitic and ankeritic ribbons is apparent when the streaked "c" type spots are imaged in DF.

The presence of plate-like precipitates, with larger size at dislocations resulting Moire fringes on them and the absence of both the "b" and the "c" type spots in the diffraction patterns from such regions show that the precipitates are of calcitic structure. Since much higher concentration is noted ($\text{FeCO}_3 = 46$ wt%), in such regions, the precipitates could be siderite itself. This further supports that $\text{CaFe}(\text{CO}_3)_2$ does not exist in nature and when the concentration of iron exceeds the solubility limit, it will precipitate out locally as a separate phase. The splitting of high order spots in the diffraction patterns from such regions is the result of the differences in the lattice parameters of calcite and the precipitated phase. The measurements of the splitting is not useful as the interplanar distances changes with the composition and the exact composition of either phase is not known. Imaging of the "b" type spots, when ribbons and precipitates are both present, reveal that only the ribbons brighten up and not the small precipitates. This leads us to make a conclusion that precipitates are not dolomitic but are calcitic, an $\bar{R}3c$ in $\bar{R}3c$.

The new findings in this study on siderite are the existence of $\overline{R3}$ in $\overline{R3c}$ carbonates, which is the inverse of the previous findings, where $\overline{R3c}$ occurs in $\overline{R3}$ carbonates (Barber and Wenk, 1985). Also the occurrence of "c" type spots in more than one equivalent positions in the diffraction patterns is not reported before for other carbonates, both calcite and dolomite.

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REFERENCES

- Barber, D.J. & Khan, M.R. 1987. Composition induced microstructures in rhombohedral carbonates. *Min. Mag.* 51, 71—86.
- Barber, D.J., Reeder, R.J. & Smith, D.J. 1985. A TEM. microstructural study of dolomite with curved crystal faces (saddle dolomite). *Contrib. Mineral. Petrol.* 91, 82—92.
- Barber, D.J. & Wenk, H.R. 1984. Microstructures in carbonates from Alno and Fen carbonatites. *Contrib. Mineral. Petrol.* 88, 233—245.
- Deer, W.A., Howie, R.A. and Zussman, J. 1962. *Rock forming minerals*, Vol. 5: non silicates. Longmans: London.
- Goldsmith, J.R., Graf, D.L., Witters, J. & Northrup, D.A. 1962. Studies in the system CaCO_3 - MgCO_3 - FeCO_3 : (1) Phase relation; (2) a method for major element spectrochemical analysis; (3) composition of some ferroan dolomites. *J. Geology*, 70, 659—688.
- Khan, M.R. & Ishaq, M. 1988. Crystallography of carbonates and the occurrence of "c" and "d" type superstructures in calcite and dolomite-type compounds. *J. Sci. and Tech. Peshawar University* (in press).
- Khan, M.R. & Barber, D.J. 1988. A TEM Microstructural Study of Smithsonite. *J. of Engin. and Applied Sci. N.W.F.P. Univ. of Engineering and Technology, Peshawar* (in press).
- Khan, M.R. 1987. A TEM Microstructural study of natural and synthetic rhombohedral carbonates. Thesis, Ph.D. (unpubl.), Univ. Essex, U.K.
- King, A.H., Fu, Rong Chen, Reeder, R.J. & Barber, D.J. 1984. Calculated images of dolomite-calcite interfaces features identification in saddle dolomite. *Proc. of the 42nd. Annual Meeting of the Electron Microscopy Soc. Am.* 586—587.
- Kucha, H. & Weizorek, A. 1984. Evidence of Superstructuring in Ankerites. *T.M.P.M. Tschermaks Min. Petr. Mitt.* 32 247—258.

- Gunderson, S.H. & Wenk, H.R. 1981. Heterogeneous microstructures in oolitic carbonates. *Am. Mineral.* 66, 789—800.
- Peacor, D.R., Essene, E.J. & Gains, A.M. 1987. Petrological and crystal chemical implications of cation order/disorder in kutnahorite [CaMn(CO₃)₂]. *Am. Mineral.* 72, 319—328.
- Reeder, R.J. & Prosky, J.L. 1986. Composition sector zoning in dolomite. *J. Sed. Petrol.* 56, 237—247.
- Reeder, R.J. 1982. Crystal growth defects in sedimentary carbonate minerals. *Estudios. Geol.* 38, 179—183.
- Reeder, R.J. & Wenk, H.R. 1979a. Microstructures in low temperature dolomites. *Geophy. Res. Lett.* 6, 77—80.
- Reeder, R.J. & Wenk, H.R. 1979b. Modulated structures in sedimentary dolomites. In: (Cowly, J.M. et al. Eds.) *Modulated structures*, Am. Inst. Phys. New York. 330—332.
- Rosenberg, P.E. 1963a. Subsolidus relations in the system CaCO₃-FeCO₃. *Am. J. Sci.* 261, 683—690.
- Van Tendeloo, G., Wenk, H.R. & Gronsky, R. 1985. Modulated structures in calcian dolomite: A study by Electron Microscopy. *Phy. Chem. Minerals.* 12, 333—341.
- Wenk, H.R., Barber, D.J. & Reeder, R.J. 1983. Microstructures in carbonates. In: (R.J. Reeder, Ed.) *Carbonates: Mineralogy and Chemistry. Reviews in Mineralogy.* 11, 301—367. *Min. Soc. Am.*