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AN ATEM MICROSTRUCTURAL STUDY OF KUTNAHORITE

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ABSTRACT

The mineral kutnahorite, from Kutna Hora, Bohemia, is selected for investigations by means of analytical transmission electron microscopy. Major microstructural features observed are revealed as fringed ribbon-like defects and fine modulations in diffraction contrast images. The microstructures observed are clearly impurity related as determined by energy dispersive X-ray microanalysis. The ribbon-like defects are thin layers of second phase. They are coherent with the host phase. Diffraction patterns obtained from the modulated regions clearly show the elongation of the diffraction spots and in addition the "c" type spots are also observed on strongly exposed films. Such spots ("c" type) were previously observed in electron diffraction patterns from non-stoichiometric dolomites.

INTRODUCTION

In carbonate group of minerals, calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] have been widely investigated by means of optical petrography, X-ray methods and recently by Analytical Transmission Electron Microscopy (ATEM). These investigations are reviewed by Wenk, *et al.,* (1983) which includes a discussion of the modulated microstructures found in calcian dolomites (Reeder and Wenk, 1979a, b). (For definition see Cowley *et al.,* 1979). Recent investigations on the mineral dolomite (calcium rich) revealed the occurrence of a second phase in the form of thin, curving and branching sheets, which appears as ribbons when seen in very thin sections used for ATEM methods (Barber and Wenk, 1984; Barber *et al.,* 1985). The second phase is crystallographically coherent with the host phase. This is confirmed both by the diffraction methods and the calculation of model images (King *et al.,* 1984). Since most of these samples have a low temperature origin, the precipitation of such a phase after crystallization is ruled out because of the low mobility of cation at such a low temperature ($T < 100°C$). Therefore, it is thought to be a growth feature. Dolomite accepts very low impurities and when the impurity concentration increases in the crystallizing fluid, a second phase appears readily.

The investigations of Reeder and Wenk (1979a, b) revealed that the modulated microstructures in calcian dolomites are the result of non-stoichiometry of the host. The questions which need to be answered are: (a) is there any relationship between the ribbon-like structures and the modulations, and (b) is the ribbon-like structure a manifestation of modulation ? Barber and Khan (1987) reported such microstructures in ankerites, kutnahorite and synthetic cadmium-dolomite [$CdMg(CO_3)_2$]. Their observations revealed that in calcium bearing samples, the regions with high population of second phase ribbons showed higher calcium concentrations compared to ribbon-free areas. The ribbons are calcitic ($R\bar{3}c$) in dolomitic ($R\bar{3}$) host.

The modulated microstructures observed in calcite-type carbonates, siderite and smithsonite are necessarily impurity related (Khan, 1987; Barber and Khan, 1987; Khan and Barber, 1988). It was also found by these authors that ribbon-like microstructures with similar morphology and diffraction properties, as observed in calcian dolomites, occur in these minerals. The second phases which occur here, are found to be dolomitic ($R\bar{3}$) in calcitic (R3c) host. A very clear proof of their dolomitic nature is observed in the siderite from Erzberg (Austria), where the regions showing ribbon-like structure exhibit ordering dolomite-type ($h\bar{h}01$, with $l=2n+1$) spots in diffraction patterns (Khan, 1987). Calcite grains, which occur in the siderite from this locality also contained dolomite-structured ribbons.

The diffraction patterns obtained from dolomite with modulated microstructures have shown that diffuse superstructure reflections, which are called "c" reflections, first reported by Reeder and Wenk (1979a b,) occur. The occurrence of these extra reflections have been correlated with an excess of calcium cations which substitute for magnesium cations in the basal plane. Van Tendeloo *et al.,* (1985) proposed a model for calcium and magnesium arrangements in dolomite which could explain these "c" type reflections. However, it is now observed that "c" type reflections also arise from the ribbon regions of calcite grains in siderite from Erzberg (Khan, 1987), in synthetic calcium-manganese carbonate (Barber and Khan, 1987) and in calcitic and dolomitic regions of zincian dolomite (Khan and Barber, in prep.). Dark field (DF) imaging using "c" type spots has shown that the extra reflections originate from the ribbons or from materials immediately adjacent to them in siderite. The model proposed by Van Tendeloo *et al.,* (1985) when applied to these minerals does not agree as the concentration of impurities is too low but the spots observed are comparatively stronger. Also the occurrence of these spots in more than one equivalent reciprocal directions of a zone cannot be explained on the basis of this model. Bearing these ideas in mind, another mineral, kutnahorite, ideally [$MaMn(CO_3)_2$], is selected for investigation by ATEM methods. The observations of Peacor *et al.,* (1987) on

natural kutnahorite mineral from different localities revealed that this mineral exists in nature both as an ordered dolomite-type compound and a disordered solid solution, although the composition is ideal for the ordering to occur. The mineral kutnahorite is never synthesised in laboratory at temperatures exceeding 400°C. The observations of this author show that although the composition of the synthetic material is ideal for the ordering to occur (Ca:Mn=1:1), the resultant material is a disordered solid solution (Khan, 1987). A full report about the synthesis of this mineral will be published soon (Khan and Barber, in prep.).

MATERIALS AND METHODS

Kutnahorite samples from Kutnahora, Bohemia were selected for investigations using optical perography and ATEM methods. The mineral was provided in very small quantity and hence these could be the only possible means of investigation. Small crystals were picked up and stuck on to the glass slide with crystal-bond resin and ground to a thickness of about 30–50 micron working from both sides, using abrasive papers of progressively finer grade. Diamond pastes were used for polishing one side of each piece so that a petrographic microscope could be employed for the selection of suitable area for ATEM investigation. Single-hole or type "7–HEX" copper TEM grids were stuck on to the area of interest using epoxy resin (Araldite). The specimens were left overnight for drying and were removed from the glass slides by melting the crystal-bond and rinsed in aceton. The final thinning of the specimen to electron transparency was carried out with argon ion-beam thinners using small angles of incidence (12–15°) at 5.5kV and low ion-beam current. These precautions were necessary in order to minimize overheating and to avoid amorphization of the specimen surface. In order to avoid the charging by the electron beam, the ion-beam thinned specimen were carbon-coated before their use in TEM.

The sample (BM, 1969, 283) for which the results are being reported here, was provided by Dr. A.M. Clark, British Museum (Natural History) London. The electron microscope used was a JEOL 200–CX which was operated at 200kV for imaging and diffraction analysis and at 120kV for X-ray microanalyses. The microanalyses were carried out by means of a high take-off angle detector linked to a quantitative spectrum processing system. Most of the analyses were carried out in TEM mole on untilted specimens utilizing the reduced electron probe diameters that are possible with free control of electron-lenses. K–factors (Cliff and Lorimer, 1975; Wood *et al,* 1984) used in processing the X-ray spectrum were experimentally determined using thin section standards of known composition.

RESULTS

The microstructures in a sample of kutnahorite were investigated by ATEM. Some of the preliminary results obtained on this sample have already

been reported along with the microstructural investigations on other carbonates (Baber and Khan, 1987). At the time of that report this sample was in the process of study by ATEM methods and a full report is presented here.

The major microstructural features noted in kutnahorite are: (1) the modulated microstructures, and (2) the ribbon-like defects. Generally, the ribbons observed are widespread in occurrence but the modulations are comparatively restricted. The fringed ribbons, as shown in Figure 1a, b, have complementary contrast in bright field (BF) and DF images. Their usual orientation is nearly parallel to the traces of $(10\bar{1}4)$ planes. It is similar to the orientation of already reported ribbons in dolomite (Barber *et al.*, 1985) and siderite and smithsonite (Barber and Khan, 1987; Khan, 1987). A model for interpretation of these ribbons in dolomite was proposed by King *et al.*, (1984) and they were described as the thin-laths of second phase which is coherent with the host. The observations show that the ribbons are more susceptible to damage under the electron beam compared to the homogeneous areas between the ribbons. This is apparent by the comparasions of Figures 2a, b, c which are taken after each other with a gap of few seconds in between. Numerous small rounded voids or bubbles form on or close to the ribbons, probably at the matrix-ribbon interface or transition zone.

Diffraction patterns from such ribbon regions show the "a" and also the "b" type spots which are the characteristics of dolomite-like structures. Distinct spot splitting of high order spots was noted and is shown in Figure 1c with a magnified inset of the split spot. It is also observed that if high order spots are used for imaging, the ribbons brighten up relative to the surrounding matrix. This shows that the ribbons consist of a different phase to the matrix.

Microanalyses show excess calcium over manganese in the ribbon regions. Small traces of magnesium and iron were also detected. Since no perfectly clear (*i.e.* structure-free) regions are ever observed in this sample, it is not possible to establish a relation whether there is a preference for iron and magnsium in the ribbons or for the host kutnahorite by microanalysis, but the damaging behaviour of ribbons coupled with the excess concentration of calcium in such regions suggests that the ribbons are similar in nature to impure calcite. The splitting of the high order diffraction spots further supports this idea.

The modulated microstructures occur only in certain regions and are observed especialy in healed cracks between two ribbon regions. This is shown in Figure 3. The modulations are very strong with a typical orientation roughly parallel to the traces of $(10\bar{1}4)$ planes, as these structures were observed in calcium-rich dolomites (Reeder and Wenk, 1979a, b) and in other calcite-type carbonates, siderite (Khan, 1987) and smithsonite (Khan and Barber, 1988). The diffraction patterns from such regions show "a", "b" and "c" type spots.

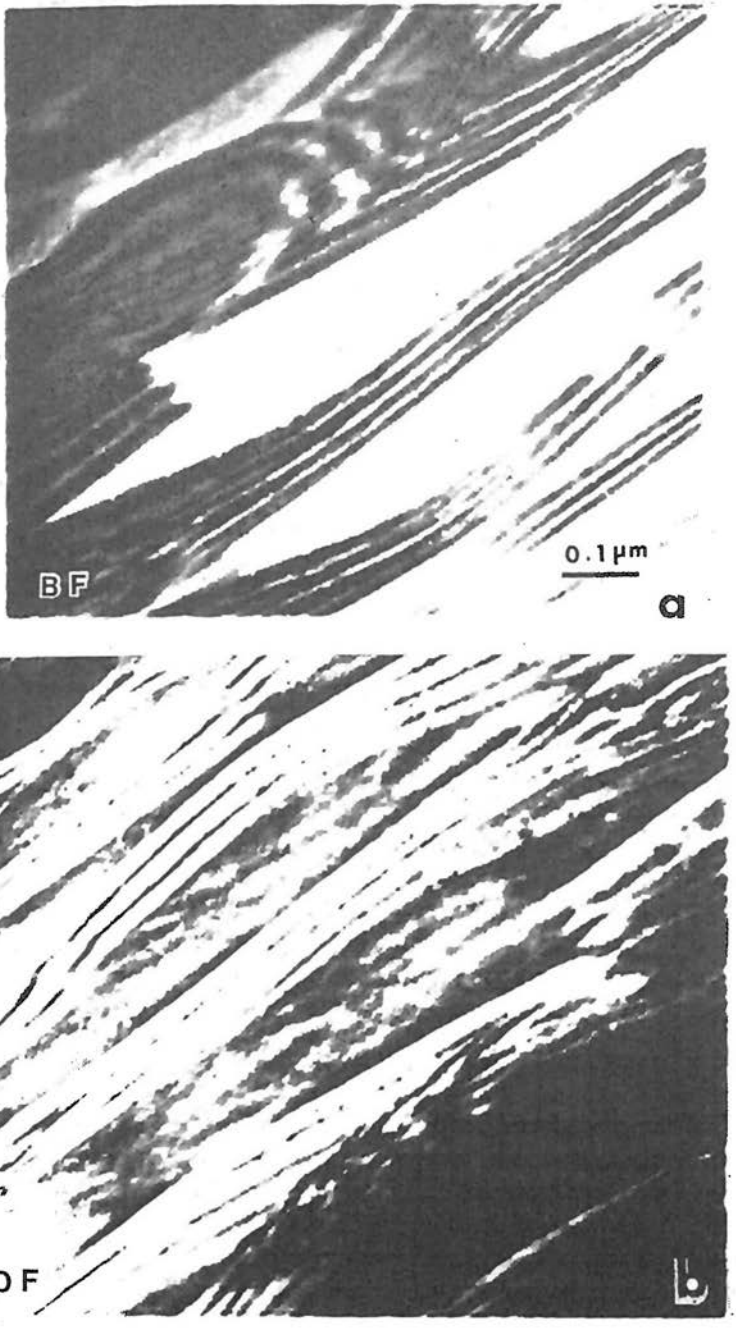


Fig. 1. (a) BF and (b) DF images of ribbon-like defects in kutnahorite from Kutna Hora, Bohemia.

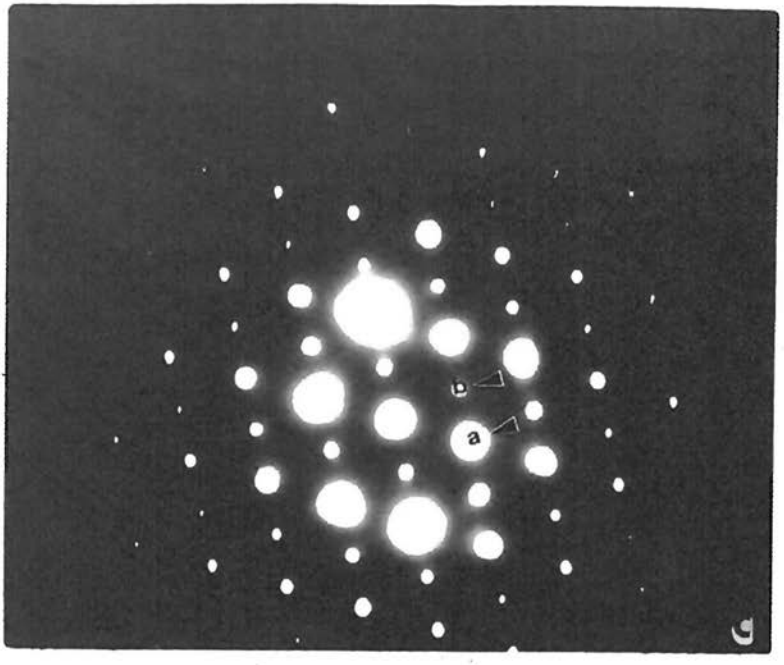
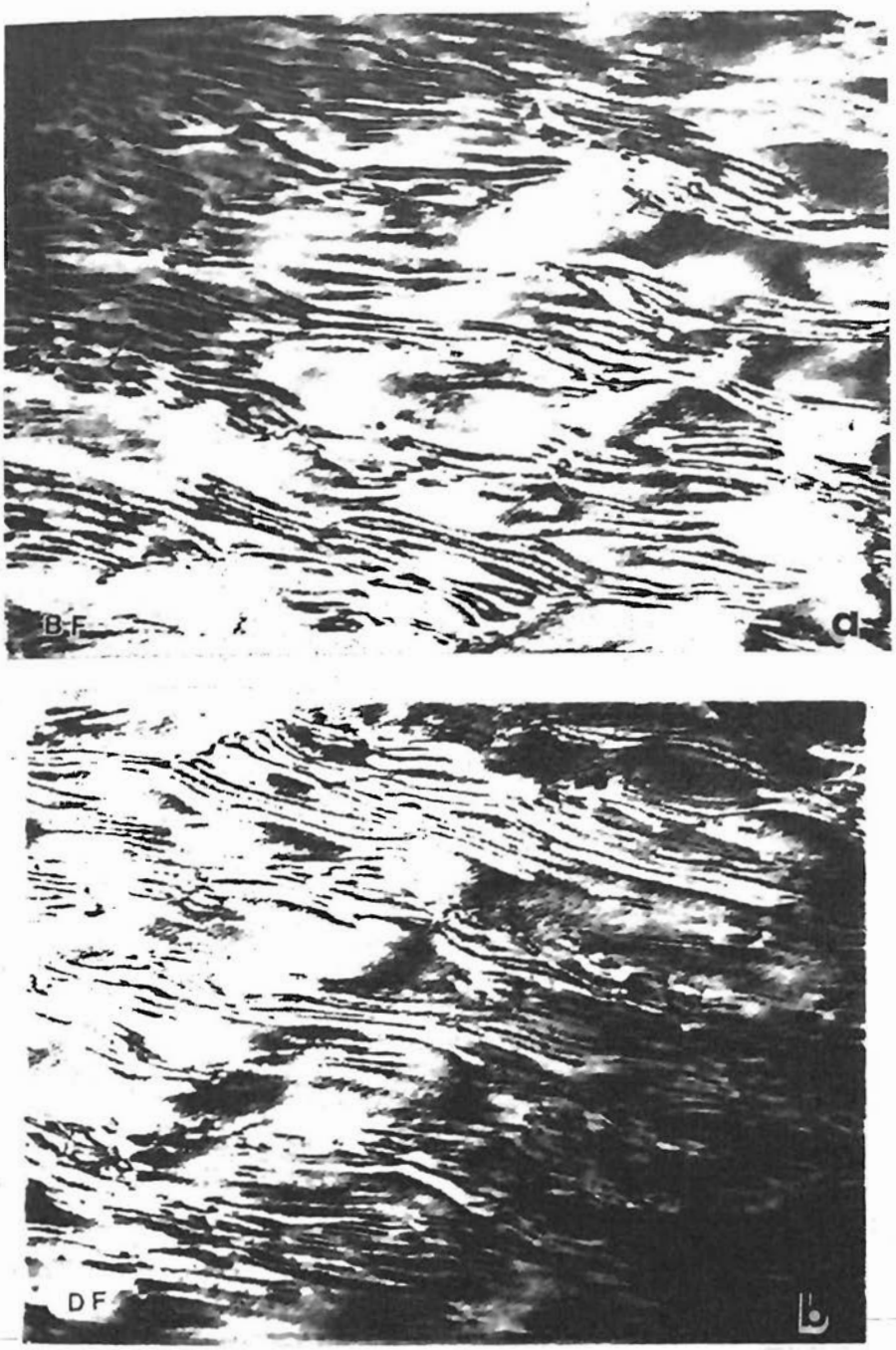


Fig. 1. (c) Zone-axis diffraction pattern from (a) showing "a" and "b" type diffraction spots with a magnified inset of a split spot.

The "c" type spots are always very weak and are only detected on strongly exposed films. The "a" and the "b" type spots are clearly elongated, and are perpendicular to the traces of the modulations. A diffraction pattern exhibiting these spots ("a", "b" and "c" types) and the corresponding modulated areas in BF and DF are shown in Figure 4a–c, respectively. The "c" type spots are also streaked and the direction of streaking is parallel to the elongation of the "a" and the "b" type spots. Although the "c" type spots were not visible on the microscope screen, their approximate positions were tried for imaging in DF but nothing prominent was detected. The "c" type spots as shown in Figure 4a occur in preferred directions *i.e.* $10\bar{1}4$, $01\bar{1}2$ and $11\bar{2}0$ of the reciprocal lattice.

EDX microanalyses performed on the modulated regions show clear variations in the concentration of manganese, iron and magnesium compared to the ribbon or ribbon and modulation-free regions. This is clear from the data scatter diagrame of Figure 5a–d. It is noted that the concentration of manganese is reduced while that of iron and magnesium is increased in the modulated areas. Although there are no prominent variations in the concentration of calcium in going from the ribbons to the modulated regions, there is still a slight increase in calcium concentration in the modulated areas. All these increments are at the expense of manganese, which is decreased. Superimposed X-ray peaks from the



(b)

Fig. 2. (a) BF and DF images of ribbon region in kutnahorite, from Kutna Hora, Bohemia.

Fig. 2. (c) Same as (a), showing preferential damage at ribbons after a few seconds exposure to electron beam.

modulated and ribbon regions, as shown in Figure 6 also confirm the above analysis. Generally, it appears that major changes are occurring at the "B" sites of the dolomite-type structure which are mostly occupied by manganese, iron and magnesium, although some manganese can reside on the "A" sites even in nearly ideal kutnahorite (Lumsden and Lloyd, 1984; Lloyd *et al.*, 1985). The composition of these modulated regions is closed to ankerite than kutnahorite. The ATEM results obtained on other samples of this mineral from Broken Hill, New South Wales (BM, 1974, 288), Chavletice, Bohemia and Piz-Cam, Bergell Alps, Switzerland have already bene reported (Barber and Khan, 1987), where also the clear microstructural relations with the composition were noted.

DISCUSSION

The impurity related microstructures, which were reported previously in certain carbonate minerals (Reeder and Wenk, 1979a, b; Barber and Wenk, 1984; Barber *et al.*, 1985; Van Tendeloo *et al.*, 1985; Barber and Khan, 1987, and Khan, 1987) are now found to occur in a much wider variety of carbonates having diffeernt origins and chemistries. The principal types of microstructures observed are the fringed lath-like defects and the modulations.

Kutnahorite, which exists in nature both in ordered and disordered phases (Peacor *et al.*, 1987), is of the former category here. The ribbon microstructures

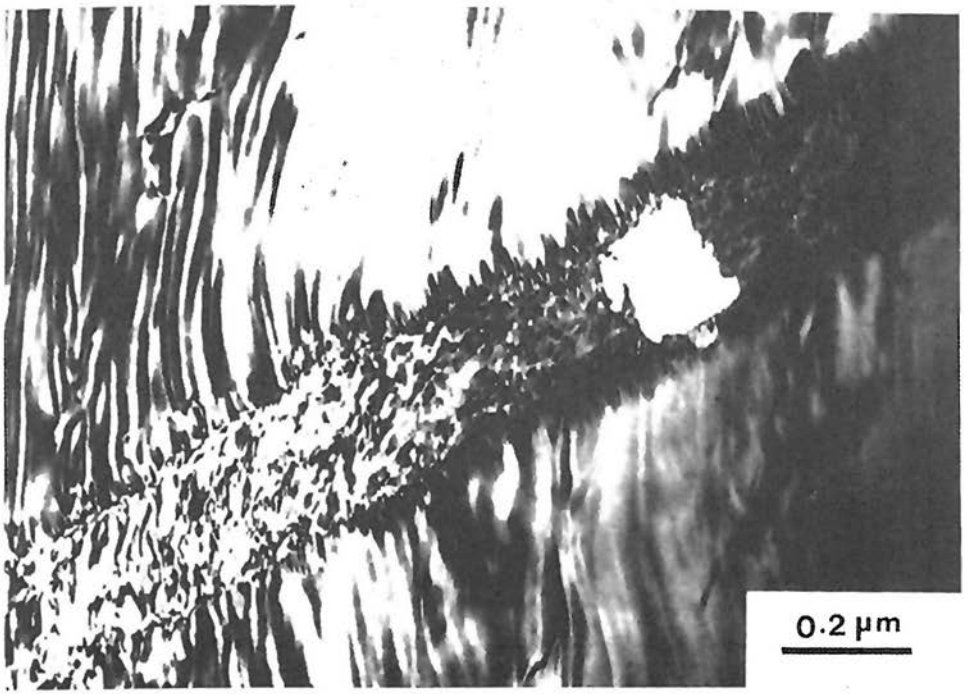


Fig. 3. Modulated microstructures in healed crack between two ribbon regions of kutnahorite, from Kutna Hora, Bohemia.

observed are interpreted as calcitic second phases on both chemical and crystallographic grounds. These ribbons exist in the form of long, thin, coherent precipitates with a strong crystallographic control over their orientation. The splitting of the diffraction spots and the presence of excess calcium over Mn+Mg+Fe in the ribbon regions show that the ribbons are calcitic, probably impure calcite itself. The scintillation of some carbonate grains during electron irradiation has already been mentioned by Barber and Wenk (1984). They attributed this process to the formation of microvoids by the decomposition of calcite causing the emission of CO_2 gas. This behaviour is mostly noted in impure calcite. A review artical by Townsend (1983) states that non-stoichiometric compounds are more susceptible to sputtering by electrons than stoichiometric ones. Here, since the rate of beam damage under the electron beam is rapid for ribbons compared to its damage in clear areas between the ribbons, the ribbons with the support of diffraction and chemical analyses are recognised as impure calcite. The origin of these calcitic ribbons is, however, not perfectly clear but at least the low temperature of formation of kutnahorite in nature makes the exsolution of calcite unlikely from impure kutnahorite containing calcium, iron and magne-

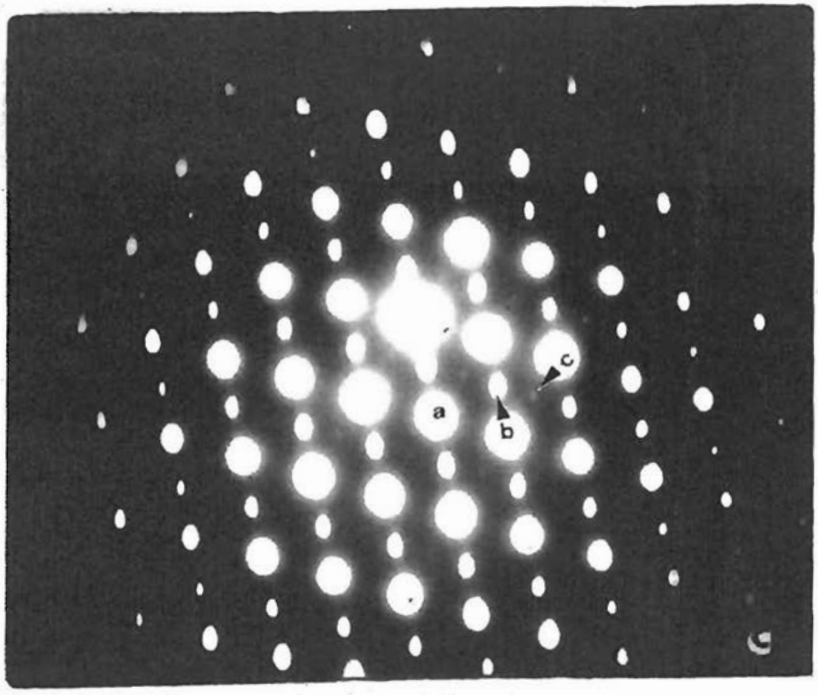


Fig. 4. (a) Selected area, zone axis diffraction pattern from the modulated area of (b) exhibiting "a", "b" and weak "c" type diffraction spots.

sium in concentration exceeding solid solubility limit. The slow diffusion rate . cations at such a low temperature ($T < 100^{\circ}C$) rules out the possibility exsolution and hence these ribbons are most likely of growth origin.

Clear differences in the compositions and the microstructures (ribbons and modulations) of different regions of the same specimen or between specimens of different origin (locality), show the dependance of microstructures on the composition of the crystal. The results obtained by this author on different regions of the specimen from one locality and those already published (Barber and Khan, 1987) on the specimens from different localities, support the idea of compositional variations being correlated with the microstructures. During the crystal growth, impurities tend to be rejected (depending upon the kind of impurity and the corresponding crystal). This results in an increase in the impurity concentration of the solution. If, during rapid growth (or otherwise), the impurities are introduced into the crystal, they will have effects on the microstructures of the crystal. Here, it is noted that the introduction of iron in place of manganese changes the microstructure from ribbon-like to that of strong modulations. Very clear compositional changes have been noted in going from ribbon to the modulated areas in this mineral.

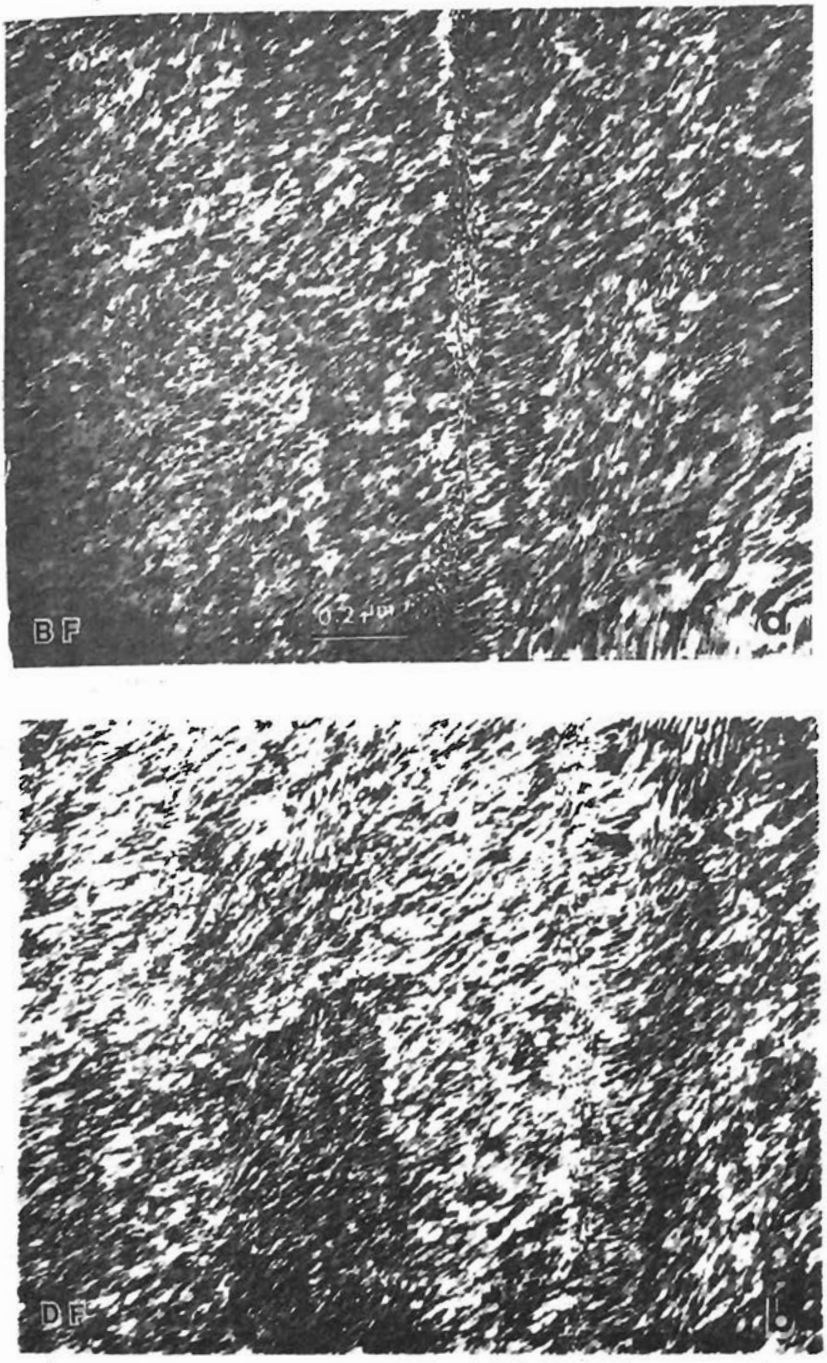


Fig. 4. (b) BF and (c) DF images showing modulated microstructures in kutnahorite from Kutna Hora, Bohemia.

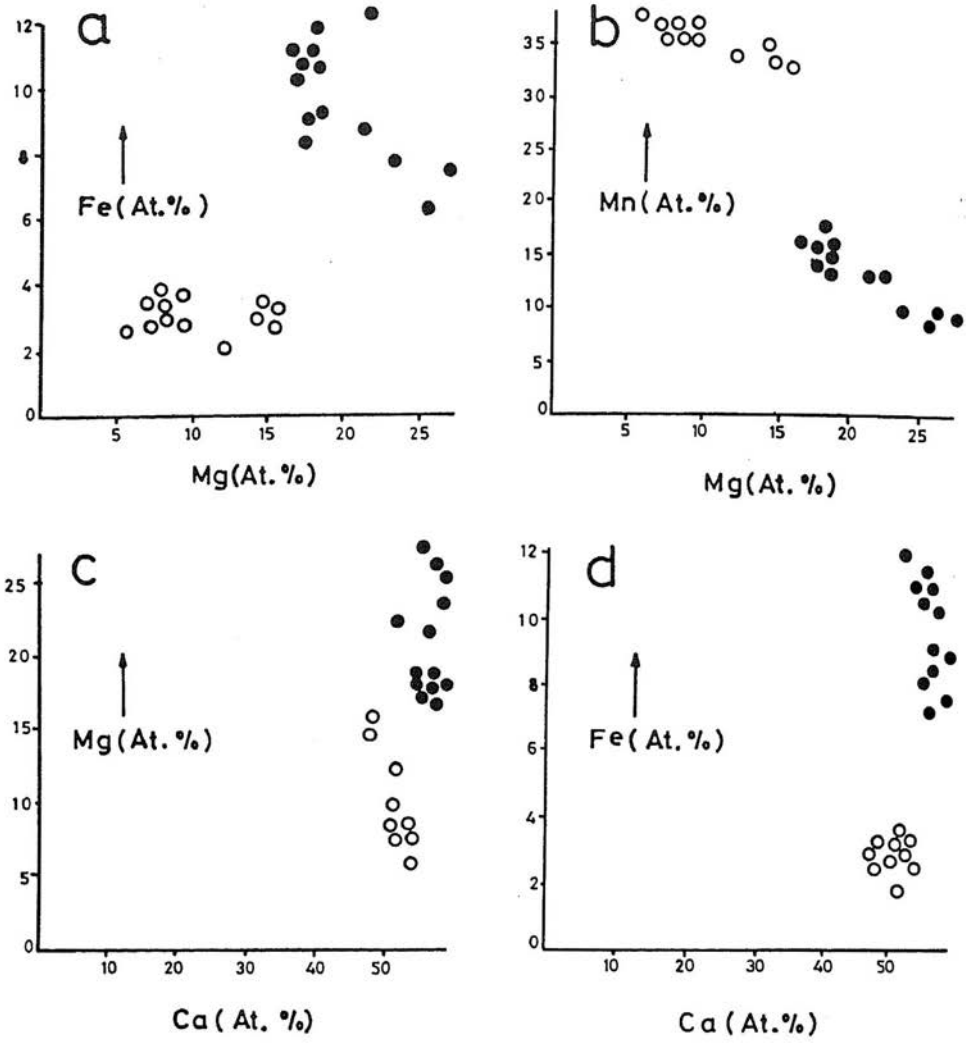


Fig. 5. Graphs showing the plots of (a) Fe versus Mg (b) Mn versus Mg (c) Mg versus Ca (d) Fe versus Ca. The data is obtained from TEM/EDX microanalyses of ribbon and

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	Ca	Mn	Fe	Mg
Ribbons	47.8	40.9	1.8	9.5
Modulations	48.2	2.4	41.1	8.5

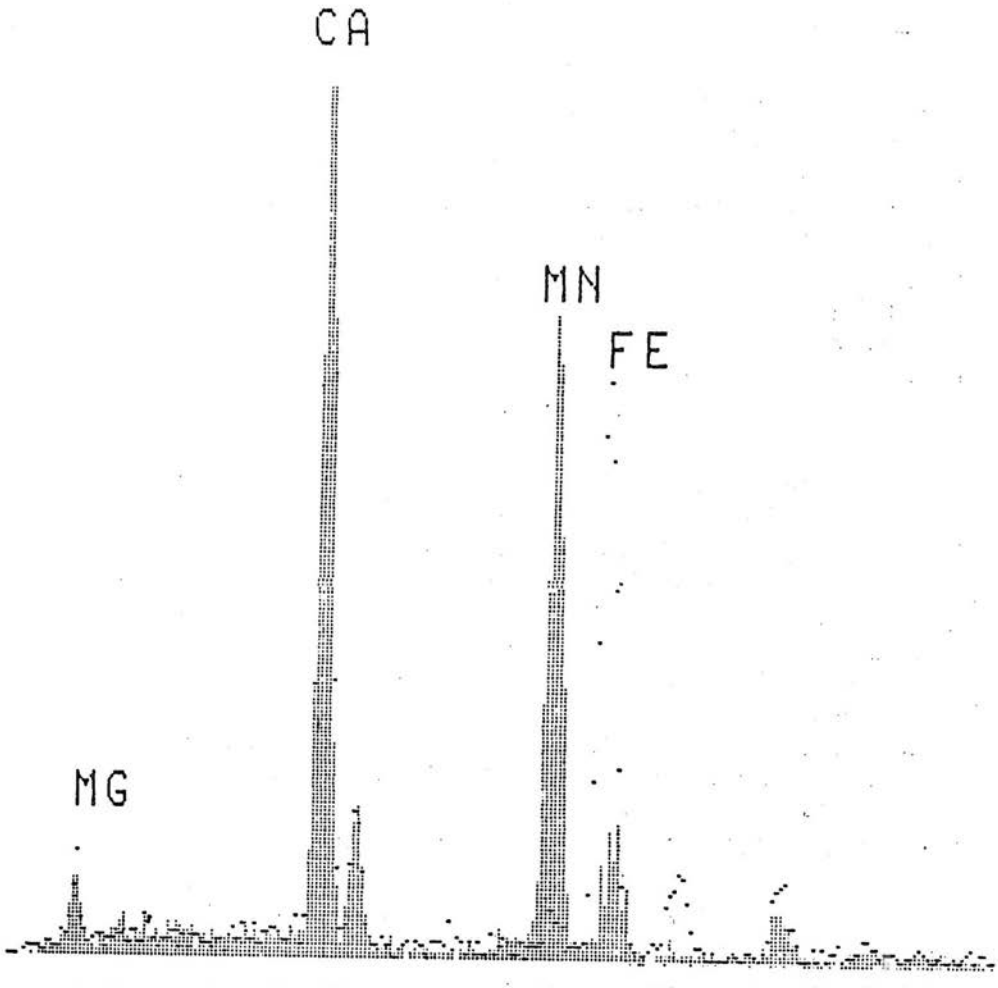

Fig. 6. Superposed TEM/EDX spectra corresponding to ribbon and modulated regions in Kutnahorite from Kutna Hora, Bohemia. Peaks are from the ribbon regions and dots are from modulated areas.

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