CHAPTER - 3

MICROTOPOGRAPHICAL STUDIES OF (010) FACES OF NATURAL SCOLECITE CRYSTALS

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Captions of the figures
CHAPTER - 3

MICROTOPOGRAPHICAL STUDIES OF (010) FACES OF NATURAL SCOLECITE CRYSTALS

3.1 Introduction

By studying surface features of crystal faces, it is possible to deduce information about mechanism and history of crystal growth and dissolution. From such studies it is also possible to infer about the behaviour of internal imperfections such as dislocations, stacking faults, etc., since their existence affects, to a great extent, surface patterns formed by growth or dissolution process. Consequently studies of surface structures on habit faces of crystals are very helpful in understanding the development of crystal faces and mechanism of growth of crystals. Such studies have been reported by several investigators.1-5)

In the present work surface microtopography of about 300 natural scolecite crystals was studied. This chapter includes a brief description of theories of growth mechanism of ideally perfect crystals. It
also deals with dislocations and their role in crystal growth phenomenon. Surface features observed on (010) faces of natural scolecite crystals are illustrated and described. Microtopographical studies revealed isolated as well as densely populated oriented rectangular growth hillocks, feather like striations, vertical striations, hexagonal growth hillocks. Transparency and mechanism of growth of these crystals are explained, in light of observations reported here.

3.2 Growth of Ideally Perfect and Real Crystals

History of crystal growth can be classified broadly into two categories (i) growth of perfect (ideal) crystals and (ii) growth of imperfect (real) crystals. By a perfect crystal is meant a crystal in which each atom is symmetrically surrounded by neighbouring atoms in a regular geometrical configuration. As against this, an imperfect crystal is the one in which relative positions of atoms differ from those characteristic of an ideal lattice by amounts comparable to an interatomic spacing.

Growth of a crystal either from melt, vapour or solution must start from small beginnings.
Gibbs made use of the analogy of liquid drops and applied the conditions governing growth of water droplets in a mist to growth of a crystal. He argued that those faces would develop which lead to a minimum total surface energy for a given volume. In a drop of a liquid the atoms or molecules are randomly arranged whereas in a crystal the structural units are arranged in a regular way in three dimensions, according to certain symmetries. Curie calculated the shape and end forms of crystals in equilibrium with solutions or vapour, consistent with the conditions that the free energy was minimum for a given volume. Wulff extended his theory, and deduced a simple relation between velocities of growth of different faces in the directions of their normals and the appropriate specific surface free energies.

Essential ideas regarding mechanism of growth of a perfect crystal were summed up by Kossel. For the illustration of the growth of an ideal crystal, simple working model of a Kossel crystal, a simple cubic structure with first neighbour interaction will be considered. The boundary line, which divides the surface of the crystal into two regions, differing
in level by the height of monomolecular layer is called a step. Potential energy considerations show that at $0^\circ$K, the step will tend to be as straight as possible. As temperature increases, the component molecules tend to vibrate and as soon as the energy of vibration exceeds the binding energy, they will fly off. There is a greater probability for the molecules in the straight step flying off than for the molecules in any other positions. The vacant sites thus created are called kinks. Simultaneously with the transport of molecules from the crystal surface to the vapour, there is an incoming flow of molecules from the vapour to the crystal surface, the rate of which depends upon the degree of supersaturation. In the equilibrium stage at $T > 0^\circ$K the crystal face can, in general be represented by Fig. 3.1 in which A represents a site of a positive kink, C a surface vacancy and B an adsorbed molecule. The binding energies of molecules in these sites are different, as for example, the molecules at C, A and B are held by five, three and one of the neighbours respectively. According to Kossel, in view of various binding forces; growth of a crystal is essentially linked
with the filling up of kinks in the existing steps and, consequent advance of the steps. There are three processes which are responsible for the advance of steps on crystal surfaces, viz., (i) exchange of molecules between the vapour and the adsorption layer on the crystal surface, (ii) migration of adsorbed molecules on the crystal surface towards the step, and, (iii) migration of molecules along the step to the position of kinks in the step. All these conclusions were verified by Volmer, who studied growth of thin plates of mercury crystals grown from vapour.

Detailed calculations by Burton, Cabrera and Frank showed that the steps would not be created by thermodynamic fluctuations on a low indexed face, unless the temperature was above a certain value. According to their surface nucleation theory, it is necessary to nucleate additional layers for growth to proceed. Moreover, before a new layer can grow, a two-dimensional nucleus or an island monolayer of probably 100 molecular diameters has to be formed, on the edges of which growth can proceed. The first experimental evidence of growth by
deposition and spreading of monolayers on crystal faces was reported by Marcelin\textsuperscript{13} Kowarski extended Marcelin's work further and found that layers were in general initiated at the edge of the face, and in particular at the point of intersection of the edge with a neighbouring crystal. The layers were found to be circular near the center of initiation but became more and more irregular as they proceeded across the face. Bunn and Emmett\textsuperscript{14} ascribed this to an increase of energy with decrease of step height. According to Frank\textsuperscript{15,16} the initial bunching of monomolecular layers is due to fluctuations in concentration at the initiation point. Bunn and Emmett\textsuperscript{14} have carried out an extensive study of growth by layer deposition and spreading in the case of many different crystalline substances, both ionic and non-polar. Main conclusions of their experiments are:

1. The centres of initiation of growth layers are, in general, at points on a face away from corners and edges, rather than at corners or edges.

2. As the layers proceed away from the growth centre they become thicker and thicker.
3. If the rate of growth is rapid, growth fronts become more irregular but as the rate of growth decreases they tend to become more regular confirming the symmetry of the face.

4. Growth sheets are visible only in the case of ionic crystals.

Seager\textsuperscript{17}) studied surface structures of many minerals and came to somewhat similar conclusions. His main study was centred on mechanism of layer spreading and formation of growth hillocks on habit faces of crystals. Several hypothetical cases were considered, in which layers were initiated on different parts of a face at either a constant or a variable rate, and spread with either a constant or a variable velocity. Combinations of these variables give rise to several possible structures and types of habits. From his studies on growth patterns on hematite crystals, Sunagawa\textsuperscript{18}) concluded that growth took place by two dimensional spreading of growth layers parallel to (0001) and that other faces were formed mainly by the edges of these layers, although growth layers parallel to these or other faces could
develop when they become large. By studying growth patterns on (111) and (111) faces, he showed the difference in the growth patterns on different faces. Wentrof studied synthesis of diamond by hydrothermal process. He found that in the case of octahedral faces, the layer apparently nucleated afresh before growth could spread out across the face, and the conditions necessary for steady growth were very similar to those required for central nucleation.

The nucleation theory had to be re-examined because of the discrepancy between the experimentally observed rate as the theoretical rate. At this stage, in 1849, Frank suggested that in crystal growth we might recognize that real crystals are not ideally perfect as had been assumed. Ideally perfect crystals would consist of a periodic array of atoms whose arrangement would confirm with the symmetry of one of the 230 space groups. All real crystals will have various types of imperfections in their structure. Main imperfections are Schottky defects, Frenke defects, dislocations, lineage boundaries, grain boundaries and stacking faults. Out of these, dislocations play an important role in the growth of real
crystals. According to Frank (loc. cit.) growth of a crystal can be catalysed by the presence of screw dislocations. During growth building units are attached to a step at the emergence point of such a dislocation (Fig. 3.2.1) and this tends, consequently, to be displaced parallel to itself. However, since it is anchored at the emergence point, it will wind up into a spiral (Fig. 3.2) as growth proceeds. During further growth each part of the spiral moves outward and, as a result, the spiral apparently rotates around its centre (Fig. 3.2). Whether the resulting spiral will be circularly symmetric or polygonal, is determined by the mean distance (displacement) of adsorbed molecules on the crystal surface. If it is greater than the mean distance between the kinks, the spiral will be circularly symmetric, if not, polygonal.

3.3 Dislocations and Crystal Growth

Dislocations were first postulated to explain the great discrepancy between theoretically calculated and experimentally observed yield strength. A dislocation has been defined in terms of (i) a line imperfection and (ii) a slip vector. In edge
dislocations\textsuperscript{20}, dislocation line and slip vector are mutually perpendicular, whereas in screw dislocations, dislocation line and slip vector are parallel.\textsuperscript{21} One of the ways of forming an edge dislocation is to insert, in imagination, an extra half plane of atoms above the slip plane or remove half plane from below the slip plane. The former is called positive dislocation and the latter negative dislocation. In a screw dislocation atomic planes, parallel to the top face, are not actually discrete planes, one on top of the other, but they are parts of one continuous spiral ramp, helicoid or screw, the axis of which is parallel to the dislocation line, and hence it is named screw dislocation. Like an edge dislocation, screw dislocations are of two types, right-handed and left-handed.

When a screw dislocation emerges on a face of a crystal, it provides the face with a step. This step is self-perpetuating. When one or more layers of atoms have been laid down on the crystal surface, the step still remains. Hence the steps needed for the growth of a crystal can be provided by the screw dislocation, in which case two-
dimensional nucleation is not needed for further growth. This offers a mechanism for the growth of crystals at low supersaturations. So, the perpetual step of screw dislocations partially smoothened the difficulty experienced by Kossel and others in the explanation of crystal growth under low supersaturations.

The first published experimental observations supporting the theory of growth by spiral mechanism was given by Griffin\(^2\) who observed one or two turns of a spiral markings and other growth patterns on beryl crystals. He explained these patterns on the basis of Frank's theory. Dawson and Vand\(^2\) observed growth spirals on the basal planes of paraffin crystals. Verma\(^2\) observed spirals on SiC crystals. Bhide and Nafde\(^2\) reported that triangular, hexagonal and circular growth spirals were sometimes observed on the (111) faces of crystals of silver grown by electrolysis an aqueous solution of AgNO\(_3\). Joshi\(^2\) has summarised literature reported in this direction during the decade 1949-1959. Joshi and Tolansky\(^2\) observed spirals on synthetic quartz crystals.
3.4 Scolecite Crystals

Scolecite belongs to zeolite family of crystals. It belongs to monoclinic system and has chemical formula \( \text{Ca(Al}_2\text{Si}_3\text{O}_{10})_3\text{H}_2\text{O} \). It has nearly perfect cleavage along m(110). The crystal faces are fairly lustrous. Most parts of crystals protruding out of the geode were found quite transparent, while their other ends towards the geode were transluscent. Crystals were of different sizes ranging from 3 mm to 60 mm in length, 0.5 mm to 14 mm in width and 0.1 mm (thin flakes) to 6 mm in thickness. One geode of natural scolecite crystals is shown in Fig. 3.3.

Recently structural studies on these crystals have been reported by Falth and Hansen28. However, there is no report so far on microtopographical studies of habit faces of natural scolecite crystals. A schematic diagram of habit faces of a natural scolecite crystal is shown in Fig. 4.1 (Chapter 4).

3.5 Experimental

Scolecite crystals were characterized by X-ray powder data, IR spectral studies, electron microprobe analysis and thermogravimetric analysis.
These results are discussed in subsequent sections and chapters.

The crystal faces were cleaned with usual reagents and were coated with silver films to enhance reflectivity. They were examined under a metallurgical microscope.

3.6 Observations and Discussion

3.6.1 Striations

(010) faces of scolecite crystals are characterized by feather like striations. One such case is shown in a photomicrograph, Fig. 3.4. The axis of the feather is very nearly parallel to the c-axis of the crystal. Its branches diverge away from the axis. Another striking feature of (010) faces of natural scolecite crystals is presence of vertical striations parallel to C-axis of the crystal, as shown in Fig. 3.5(a). Here striations are remarkably straight and smooth. Some are very closely spaced. Their narrow spacing is attributed to bunching of growth fronts. Bunching is due to relatively faster rate of advance of later
growth fronts which tend to catch up their predecessors. Further, it is interesting to note that the region between neighbouring some widely spaced striations is devoid of any growth forms. This means no growth has taken place on such areas after the spreading of these layers from growth centres. That some striations are quite smooth is indicative of practically no fluctuations in growth conditions. It also shows absence of interactions of growth fronts extending from other initiation centres. Smooth nature of striations is also indicative of absence of obstacles, like impurities, in the path of advancing growth fronts, which constitute these striations. Such observations are indicative of comparatively small number of growth nuclei on the face. These striations are the longer edges of growth layers composing growth pyramids (almost rectangular) observed on these faces. These vertical striations are also helpful in orienting the crystal and hence in the study of crystal morphology.

Fig. 3.5(b) is a multiple beam interferogram, in reflection, over some vertical striations. Kinks in these fringes reveal the profile and structure of vertical striations. These fringes endorse
the above given interpretation of characteristics of 
the vertical striations. The fringes are obtained by 
using collodion thin film multiple beam interfero-
metric technique.

3.6.2 Growth hillocks

Over fifty percent of the crystals 
examined exhibited on their (010) faces presence of 
oriented rectangular growth pyramids. These growth 
pyramids are found very crowded in some regions. 
However, isolated rectangular growth pyramids are not 
uncommon. In both the cases longer sides of these 
growth hillocks are oriented along C-axis of the 
crystal. Fig. 3.6(a) illustrates densely populated 
rectangular growth hillocks, while Fig. 3.6(b) 
shows isolated rectangular hillocks. Occasionaly, 
rectangular hillocks are found to align along 
directions which are parallel to the traces of pyramidal 
faces on the (010) face on which they occur. One such 
case is represented in photomicrograph

Existence of growth hillocks indicates 
independent growth on (010) faces. This growth takes 
place by spreading and piling up of rectangular growth
layers parallel to the face in question. Since density of growth hillocks is random we conclude that density of their growth nuclei or centres of initiation of growth varies from face to face and also is not the same in different regions of a given face. Morphology of these growth hillocks confirm the symmetry of (010) faces on which they occur. Development of pyramidal faces must have left on the (010) faces concerned (at their earlier stage of growth), some sort of discontinuity which would provide kinks or sites for further growth. Growth at such kinks along these directions accounts for the observed alignment of rectangular growth hillocks along directions parallel to the traces of the pyramidal faces.

Morphology of rectangular growth hillocks suggests that growth along c-directions is faster than that along the lateral directions. This is also supported by the fact that the lateral facets of rectangular growth hillocks are steeper than the other two (top and bottom).

Several (010) faces exhibit on them closely spaced, overlapping hexagonal oriented growth hillocks. One such case is illustrated in Fig. 3.8.
The outline of these structures is parallel to the outline of the (010) face on which they occur. It is noteworthy that growth fronts of such pyramids are not visible. Their surfaces are not very smooth and plane. Such pyramids are observed almost always near the transparent terminal ends of the crystals.

Another noteworthy observation is oriented, densely populated, parallelogram shaped growth hillocks as shown in Fig. 3.9(a). Their vertical sides are parallel to the c-axis. However, unlike the rectangular hillocks of Fig. 3.6, the lateral sides are not perpendicular to c-axis but are all inclined. These hillocks are found on those portions of the crystals which are near the geode. Fig. 3.9(b) is scanning electron micrograph of the surface near the lower edge of a parallelogram shaped hillock of Fig. 3.9(a). Although the surface of a parallelogram shaped hillock in Fig. 3.9(a) appears to have no structures on it, the scanning electron micrograph in Fig. 3.9(b) clearly shows that the surface is crossed over by vertical striations. They are uneven but are more or less parallel to the c-axis.
In Fig. 3.9(a) it is interesting to note a large number of closely packed, oriented, tiny needle like crystals. It is firmly believed that this is the very early stage of growth. This observation endorses the fibrous nature of scolecite crystals. Such fibrous zeolite crystals have been grown recently by Joshi and Bhoskar.29)

Many regions of several (010) faces exhibit on them presence of very shallow, elongated, almost needle like, rectangular growth hillocks, which are oriented along the c-direction of the crystal. One such case is shown in Fig. 3.10.

3.6.3 Transparency

The transparency of the terminal ends of scolecite crystals, far away from the geode, is attributed to almost complete absence of impurity, comparatively lower temperature of growth and a better controlled environment of growth. It is also due to comparatively smaller rate of nucleation.

Scolecite crystals diverge out from the geode. They are much more closely packed in and near geode. Non-transparency of these portions of the
crystals is attributed to comparatively higher temperature, comparatively higher density of nuclei, higher susceptibility of incorporation of impurities and comparatively less controlled growth conditions. Degree of transparency gradually increases for almost every crystal as one goes from the geode towards the remote end of the crystal away from the geode.

3.6.4 Overgrowth

One very outstanding feature of (010) faces of scolecite crystals is abundance of overgrowth of apophyllite crystals on them. Fig. 3.11 is a photomicrograph showing such overgrowths. A detailed account of such overgrowths is given in Chapter 4.

3.7 Conclusions

These crystal faces develop mainly by independent growth on them in the form of rectangular growth hillocks. The faces are highly striated. Only some regions are plane and smooth. They owe their origin to growth by two dimensional nucleation mechanism. Overgrowth of apophyllite on scolecite is common, at least for the variety of crystals studied.
3.8 References

1. Sunagawa Ichiro  
   J. Crystal Growth, 1 (1967) 102

2. Joshi M.S.* and Ittyachen M.A.  

3. Joshi M. S., Kotru P.N. and Wagh A. S.  
   J. Crystal Growth, 2 (1968) 329

4. Enlo Yugi and Sunagawa Ichiro  
   Am. Miner., 58 (1973) 930

5. Joshi M. S. and Paul B.K.  
   Am. Minerg., 62 (1977) 122

6. Gibbs J.W.  
   Collected works, Longmans Green and Co. London (1878)

7. Curie P.  
   Bull. Soc. Franc. Miner., 8 (1885) 145

8. Wulff G.  
   Z. Krist., 34 (1901) 449.

9. Kossel W.  
   Nachr. Ges. Wiss, Gottingen, (1927)
10. Volmer M.
   Z. Phys. Chem., 102 (1922) 288

11. Burton W. K., Cabrera N. and
    Frank F. C.
    Nature, 163 (1949) 398

    Phil. Trans. Roy. Soc., A 234
    (1951), 299

13. Marcelin A.
    Ann. Phys., 10 (1918) 185

14. Bunn, C.W. and Emmett H.

15. Franck F. C.

16. Frank F. C.
    Acta Cryst., 4 (1951) 497

17. Seager A. F.
    Mineral. Mag., 30 (1953) 1

18. Sunagawa Ichiro
    Am. Mineral., 47 (1962) 1139

19. Wentrof R. H. (Jr.)
    Advances in Chemical Physics.,
    2 (1967) 365

20. Orwan E.
    Z. Physik., 89 (1934) 634
21. Burgers J. M.
42 (1939) 293

22. Griffin, L. J.
Phil. Mag., 41 (1950) 196

23. Dawson I. M. and Vand C. M.

24. Verma A. R.
Phil. Mag., 42 (1951) 1005

25. Bhide V. G. and Nafde W. G.
Curr. Sci., 27 (1958) 167

26. Joshi M. S.

27. Joshi M. S. and Tolansky S.

28. Faith L. and Hansen S.
Acta Crystallogr., Sect. B. B 35,
Pt. 8, (1979) 1877

29. Joshi M. S. and Bhoskar B. T.
J. Crystal Growth, 47 (1979) 654
Fig. 3.3

Fig. 3.4  X 280

Fig. 3.5(a)  X330

Fig. 3.5(b)  X 660
Captions of the figures

Fig. 3.1 Growth on \{100\} faces of a cubic crystal by repeatable step mechanism.

Fig. 3.2 Different stages of the formation of spiral at a screw dislocation.

Fig. 3.3 A geode of natural scolecite crystals.

Fig. 3.4 Feather-like striations.

Fig. 3.5(a) Vertical striations parallel to c-axis.

Fig. 3.5(b) Multiple beam interferogram over vertical striations.

Fig. 3.6(a) Densely populated rectangular hillocks.

Fig. 3.6(b) Isolated rectangular hillocks.

Fig. 3.7 Rectangular hillocks aligned along directions parallel to the traces of pyramidal faces.

Fig. 3.8 Densely populated, overlapping hexagonal oriented growth hillocks.

Fig. 3.9(a) Overlapping parallelogram shaped growth hillocks with lateral sides inclined to c-axis.

Fig. 3.9(b) Scanning electron micrograph of the surface near the lower edge of a parallelogram shaped hillock of Fig. 3.9(a).
Fig. 3.10  Shallow, elongated, needle like, rectangular growth hillocks.

Fig. 3.11  Overgrown apophyllite crystals on (010) faces of scolcite crystals.