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Surface structures of trigonal bipyramidal faces of natural quartz crystals

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Abstract

Microtopographical studies of about fifty $s(11\bar{2}1)$ faces of natural low temperature quartz crystals are reported. Growth hillocks and striations oriented parallel to *s–x*, *s–r*, *s–z*, or *s–m* edges are illustrated and their origin discussed. The probability that edge nucleation is three times that of central nucleation is explained. Natural etch pits on *s* faces and pits produced by laboratory etch methods are illustrated and interpreted.

Introduction

Previous investigators have obtained information about the mechanism and history of growth and dissolution of many crystals by studying their surface structures (*e.g.,* Sunagawa, 1964, 1968; Augustine and Hale, 1960; Joshi and Kotru, 1968). Study of the surface structures of the rhombohedral faces (Joshi and Vagh, 1966) and prism faces (Van Praagh and Willis, 1952) of natural low-temperature quartz crystals has given evidence of growth by a two-dimensional nucleation mechanism. In order to understand the mechanism of growth and development of trigonal bipyramidal faces of quartz crystals, a detailed investigation of the surface structures of about fifty *s* faces of natural quartz crystals was carried out. As far as is known to the authors, this is the first report about *s* faces of quartz.

Experimental

The crystal faces were thoroughly cleaned with concentrated HNO_3, distilled water, and hydrogen peroxide. They were examined using optical and interferometric methods, after coating them with a thin silver film to enhance the contrast. Occasionally electron microscopy was used. Hydrothermal etching (Joshi and Kotru, 1969; and Joshi *et al.,* 1970), etching with fused KOH (6 g of KOH + 3 cc of distilled water) at 250°C, and etching with dilute HF (20% HF) at 30°C were employed.

Observations and discussion

The *s* faces generally appear as small faces truncating the corners between rhombohedral and prism faces. On a right-handed crystal (Fig. 1a) the *s* face lies to the right of the *m* face which is below the predominating positive rhombohedron, *r*. On a left-handed crystal (Fig. 1b) the *s* face lies to the left of *m* below *r*. Almost all the *s* faces examined were smooth and lustrous. They were characterized by oriented growth pyramids and striations. Figures 2a and 2b are photomicrographs of *s* faces of left-handed and right-handed quartz crystals respectively. Both the growth pyramids and striations were parallel either to the *s–x*, *s–r*, *s–z*, or *s–m* edges. Interferometric studies were carried out to find the nature of these hillocks and the surfaces between them. Figure 3a represents a portion of an *s* face showing the growth pyramids starting from the *s–m* edge. Figure 3b is a multiple

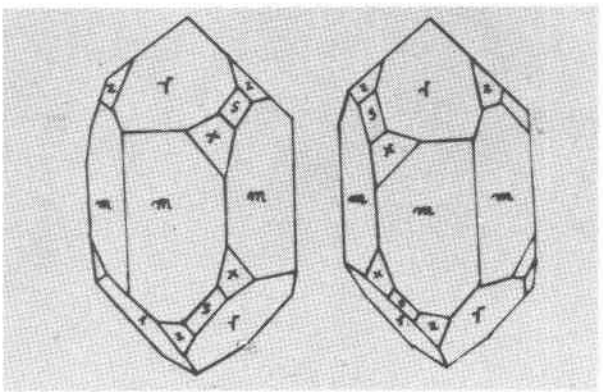

Fig. 1. Positions of *s, x, m, r,* and *z* faces on right and left-handed quartz crystals, respectively.

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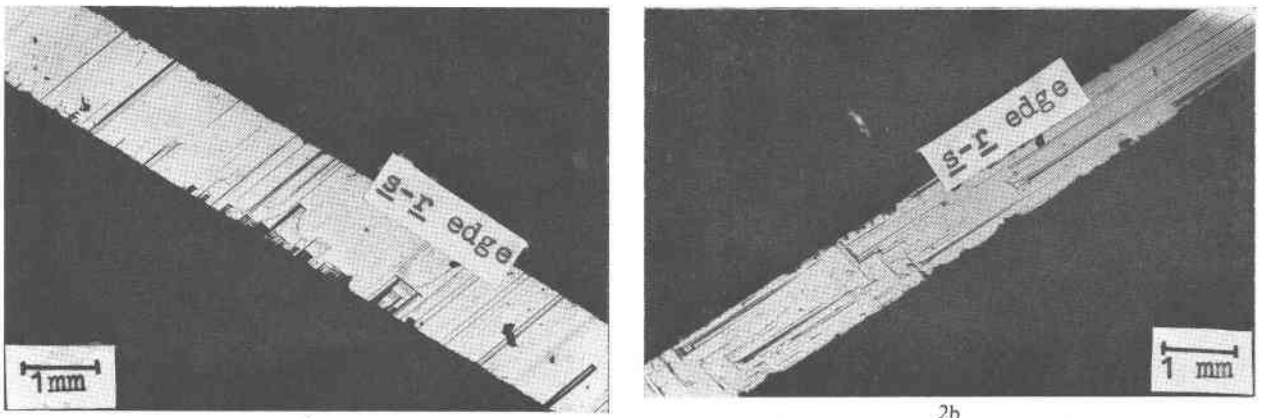


2a 2b

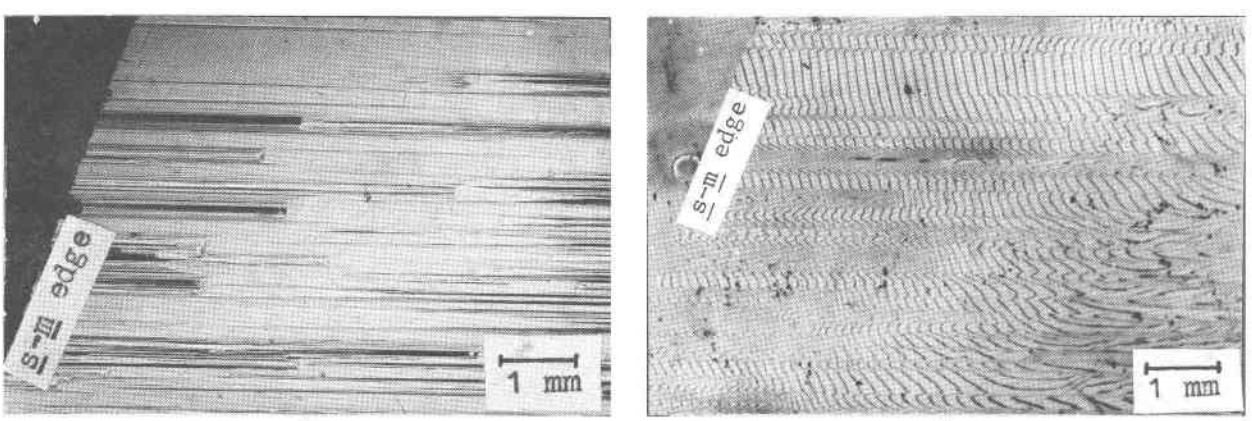
Fig. 2. Photomicrographs of typical *s* faces showing the growth hillocks and striations running parallel to the *s–r*, *s–z*, or *s–m* edges.

beam interferogram over this region. It reveals the flat tops and varying heights of some of the hillocks. Moreover the presence of small ridges on the top surfaces of some of the pyramids and the nature of the valleys between the neighbouring pyramids are also revealed by the interferogram.

Two growth pyramids at higher magnifications are illustrated in Figures 4a and 4b. Close examination of these photographs reveals the different layers stacked on one another to constitute the growth hillocks. This layered nature of the growth patterns leads one to suggest that these faces grow layer-by-layer. In order to get further evidence for the lamellar growth of the *s* faces, etching experiments were also carried out (Joshi and Paul, in preparation). The striations oriented parallel to the growth pyramids are interpreted as constituted by the longer (which are steeper) sides of such growth pyramids.

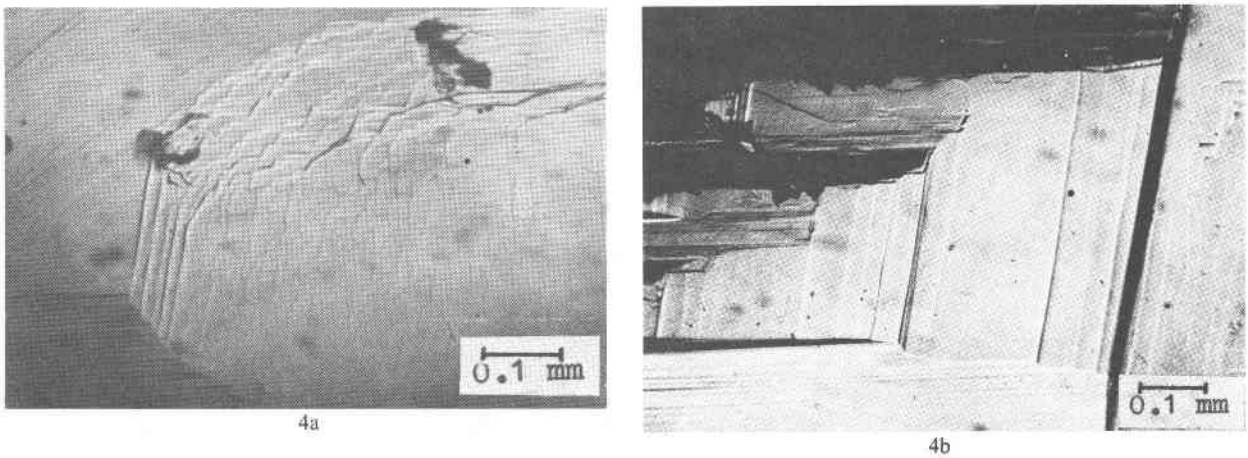
Edge nucleation was observed on almost all faces. About 25 percent of the growth hillocks initiate approximately at the center of the *s* faces, while the remaining ones have their growth centers on the *s–m*, *s–r*, *s–z*, or *s–x* edge. This suggests that the probability of edge nucleation is several times greater than that of central nucleation at least for the *s* faces examined in the present study. According to Kossel (1928) the energy of formation of a two-dimensional nucleus is least at the center of the face. If this is the only mechanism of growth, one would expect the majority of the growth centers to originate at the central regions of the face.

Since only about 25 percent of the growth hillocks have their initiation centers at the central regions of the *s* faces, one should consider some alternative growth mechanism. A majority of the growth centers are on the *s–m* or *s–r* edges. This type of edge nucle-



3a 3b

Fig. 3. Portion of an *s* face and its multiple beam interferogram.



4a 4b

Fig. 4. Examples of growth hillocks on *s* faces showing their lamellar structure.

ation cannot be explained by two-dimensional nucleation theory, but can be explained by considering the influence of adsorbed impurities on the process of growth. Such impurities may either be pushed along the face by the advancing growth layers, or grown over by the layers and incorporated in the body of the crystal as impurities. In the former case, the impurity molecules may be pushed to the edge of the face where they become trapped by growth layers spreading from adjacent face. But even in this trapped region they can still behave as nuclei for further growth. These observations suggest that a compound nucleation mechanism, including two-dimensional nucleation, plays a significant role in the growth and development of the *s* faces.

Figure 5 shows one of the several pieces of evidence to support our conclusion that edge nucelation has a greater probability than nucleation at the central region. Here the growth hillocks have their centers of initiation on the *s*–*m* edge. In addition to these hillocks, a large number of similar hillocks are observed nucleating from an incidental crack labelled ABC. The crack may provide centers for selective adsorption of impurities, so that the impurities may act as centers of nucleation for further growth. One should expect, therefore, a large number of growth pyramids originating from such cracks. This observation also accounts for greater probability of impurity (edge) nucleation.

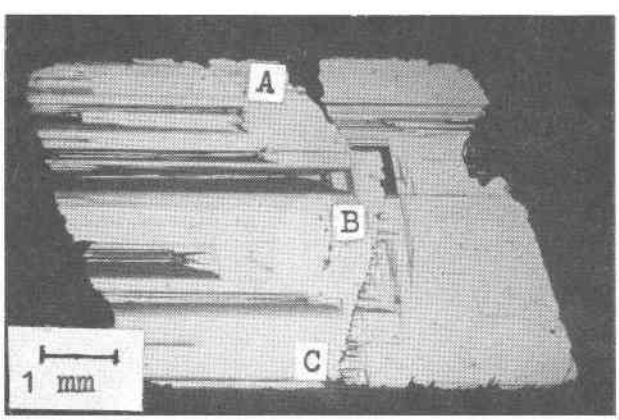


Fig. 5. Photomicrograph of an *s* face showing the growth hillocks originating from an *s*–*m* edge and from a crack (ABC).

A few *s* faces show pits due to natural etching. These oriented pits are four sided, as illustrated in Figure 6a. The four sides are approximately parallel to the edges of the faces on which they occur. The density of such pits varies from face to face and from site to site on the same face. In addition to the etch patterns just mentioned, the *s* faces are often covered with hexagonal depressions (with a smaller one inside each bigger one). An electron micrograph (Fig. 6b) reveals these patterns as depressions. They are randomly oriented and have different depths. The outlines of the inner and outer hexagonal patterns are parallel to each other.

Chemical and hydrothermal methods were used to etch the *s* faces. The etch patterns produced after etching in 20 percent HF for 6 hours, fused KOH at 250°C for 1 hour and by steam (280°C, 100 bars) for 10 hours are illustrated in Figures 7a, 7b, and 7c, respectively. The shapes of the pits depend upon the nature of the etchant and etching behaviour. With continued etching the pits grow deeper and wider without any change in shape and orientation. This suggests that all of the pits represent the points of emergence of dislocations.

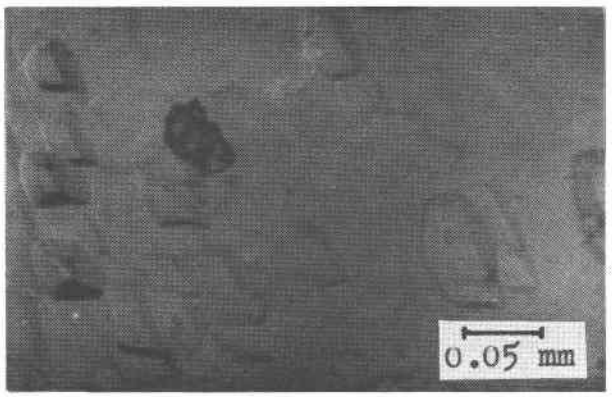


Fig. 6a. Etch pits observed on *s* faces due to natural etching.

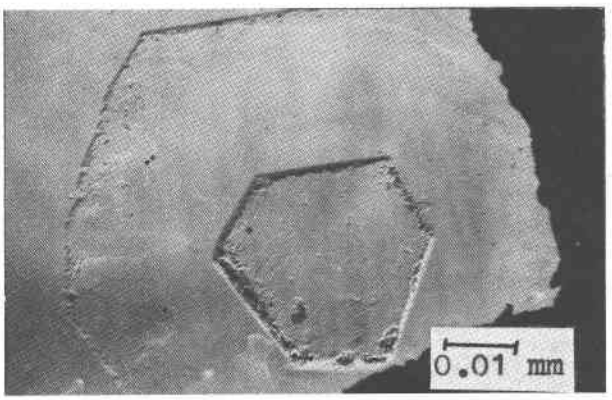


Fig. 6b. Electron micrograph of hexagonal cavities.

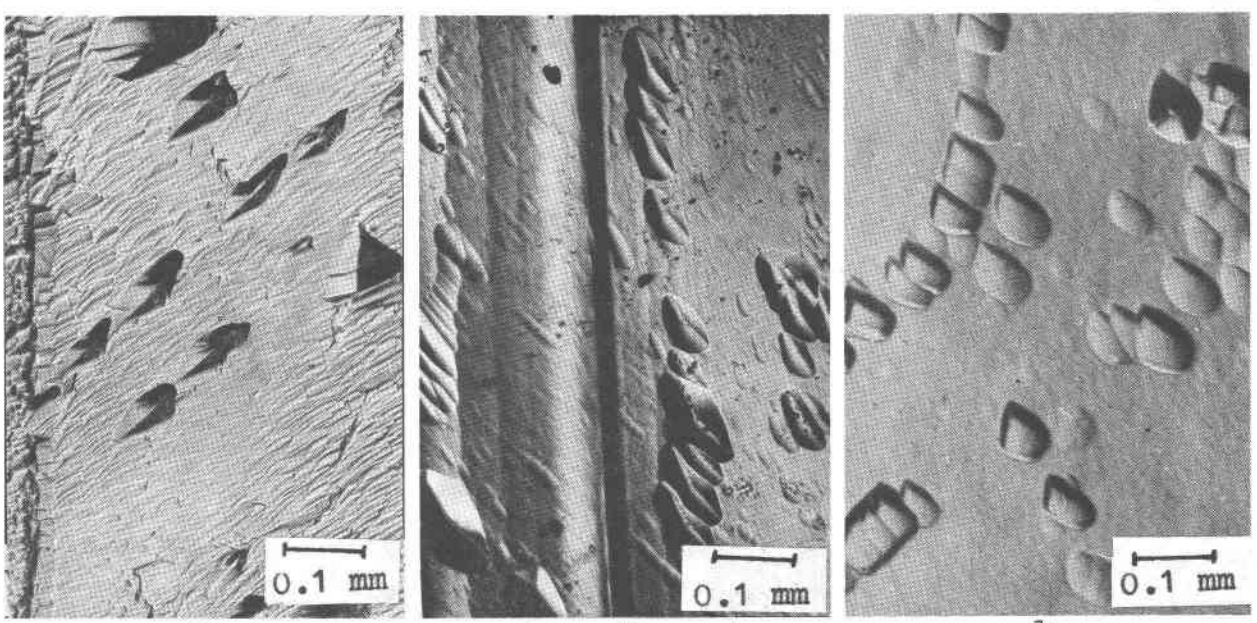
Summary and conclusions

Most of the *s* faces studied are neither rough nor mottled; this rules out the possibility of appreciable natural dissolution of these faces. It also, therefore, excludes the possibility of the formation of hillocks on these faces as a result of dissolution. The hillocks may be assumed to be truly growth hillocks. According to Buckley (1951) all natural hillocks should be treated as produced by growth when they show (as observed in this study) a symmetry corresponding to that of the faces. The absence of spirals on these faces also rules out their growth at screw dislocations.

The present study suggests that growth can be due either to two-dimensional nucleation or to impurity nucleation at the edges of the faces. The latter seems to be a dominant factor in controlling the growth of these faces. Growth layers starting at such nucleation sites spread two-dimensionally, and consequently the growth of these faces takes place by two-dimensional spreading and piling up of growth sheets.

Dislocation etching experiments carried out on the *s* faces show that dilute HF at room temperature (30°C), fused KOH at 250°C, and steam at a pressure of 100 bars and 280°C are effective etchants in revealing dislocations intersecting *s* faces.

Comparison of the laboratory-produced etch pat-



7a 7b 7c

Fig. 7. Etch patterns produced by HF, KOH, and steam etching.

terns with natural etch patterns shows close similarity between the hydrothermal etch pits and natural pits. The randomly oriented hexagonal depressions observed along with the natural etch patterns may be formed by tiny quartz crystals getting attached to this face, with their *c*-axes either perpendicular or slightly inclined to the face. Some of them may then drop off from the face at a later stage, and others remain attached to the face. In fact, a number of tiny quartz crystals have been detected in their attached positions.

Acknowledgment

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