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Etching of Calcite Cleavages

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Study of the progressive development of etch pits on clacite shows that the growth is asymmetric. Oppositely matched cleavage faces have been etched with an acid, with an alkali and with an acidic salt and one-to-one correspondence has been established in the number and positioning of the pits. The implications are discussed. The structures of matched etch pits on matched faces have been studied; the fact that they differ is explained, by postulating inclined linear dislocations in the crystal. By etching small cleaved-out blocks, a striking stratigraphy is revealed, the stratigraphical sheets going right through the whole crystal. The etch strata have therefore revealed the growth history of the calcite.

Introduction

It is now recognized that etch pits can nucleate on dislocations and other surface defects and that etch-pit formation, especially in the early stages of etch, can be a powerful technique for revealing the history of growth of crystals. The etch patterns are intimately related to the growth phenomena provided that the etch is not carried so far that general surface destruction sets in.

Experiments on etching of calcite have been carried out in the past by a number of workers (e.g. Pandya & Pandya, 1959). In the present investigation we have used the technique developed by Patel & Tolansky (1957) of etching matched cleavage faces. They reported that matched faces of mica and diamond etched under similar conditions show a remarkable degree of coincidence of the two patterns. In this paper similar studies are reported on calcite cleavages, first on the progressive development of the etch pits, second on the etch pattern produced on the matched faces by different etchants, third on the structures of the pits formed on the matched faces by a given etchant, and fourth on etched faces of a small cleaved-out block of calcite. These studies reveal the growth history of calcite and the nature of some of the dislocation content.

Experimental

Large samples of transparent calcite obtained from Panchmahal District in Gujarat State, India, were cleaved and the two freshly separated faces etched by immersing in the etchant at room temperature. The etchants used were sulphuric, nitric, hydrochloric, citric, acetic and tartaric acids, potassium hydroxide and potassium dihydrogen phosphate. The time of etch was adjusted to each etchant. Immediately after the etch the crystals were washed in water. The etched surfaces were then silvered and studied under the microscope, with phase contrast (Bennet, Osterberg, Jupnik, 1951), multiple-beam interference fringes (Tolansky, 1948), and light-profile microscopy (Tolansky, 1952).

Progressive development of etch pits

Patel & Tolansky (1957) have shown that for mica and diamond a pit initiates at a dislocation, gradually expanding around such an origin with increasing time of etch. For diamond the centre of each triangular pit is the original source of the pit. The experiment described here shows that this is not quite so in calcite.

Figs. 1(*a*), (*b*) and (*c*), taken with a cine camera, show the progressive growth of a pit formed by etching a calcite cleavage with citric acid. The pit is point-bottomed. The development of the pit can be studied using the corner of the frame as a reference. The rate of development of the pit in the direction of the 'tail' appears to be more rapid than in the direction

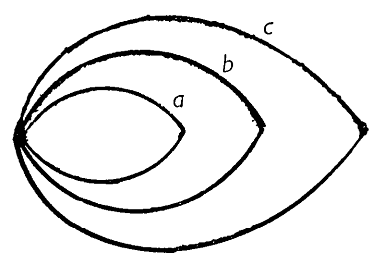


Fig. 2. Schematic diagram illustrating the development of etch pits.

of the 'nose'. The pit nucleates and develops around the point where the 'diagonals' cross over. This point is clearly fixed relative to the frame edges. The pit expands round this in a regular fashion, but the rate of growth is faster towards the 'tail' than towards the 'nose'. This is illustrated schematically by Fig. 2 which shows the three successive stages of etch.

Etch patterns on matched faces

It has been established by Patel & Tolansky (1957) that matched cleavage faces etched with the same etchant produce virtually identical etch patterns. Pandya & Pandya (1959) have shown that with matched cleavage faces of mica, one etched with sodium hydroxide and the other with potassium hydroxide, produce similar etch patterns. We have extended such investigation to the matched faces of calcite cleavages, etching in accordance with the following scheme:

(1) One surface attacked with one acid and the other with a different acid.
(2) One surface attacked with acid and the other with alkali.
(3) One surface attacked with acid and the other with acid-salt.

Figs. 3(*a*) and (*b*) (×200) show the results obtained, by etching respectively with citric acid and nitric acid and Figs. 4(*a*) and (*b*) (×100) with citric and hydrochloric acids. Figs. 5(*a*) and (*b*) (×100) were obtained by etching in citric acid and acid salt (sodium dihydrogen phosphate) and Figs. 6(*a*) and (*b*) (×200) were obtained by etching with citric acid and sodium hydroxide. For comparison we have selected the regions where pits are randomly distributed. In these figures attention is drawn to the following features:

(1) The shapes and structures of the pits depend on the etchant.
(2) The pits can form both with point-bottom and flat-bottom, the majority having point-bottom.
(3) If we ignore the shape and structure there is a mirror-image correspondence in the number and positioning of the pits on any pair of matched faces.
(4) Occasionally a point-bottom pit on one face corresponds to a flat-bottom pit on its counterpart.
(5) The cleavage lines are displaced relative to the pit patterns.

The shapes and structures of the pits produced by different etchants suggest that the rate of dissolution for the same etchant varies with direction in the crystal and it also varies in the same direction with different etchants. The correspondence of a point-bottom pit on one face with the point-bottom pit on the other face and a flat-bottom pit on one face with a point-bottom pit on the other face can be explained by Fig. 7(*a*). The vertical lines *AA*, *bb*, *CC*, *DD* illustrate defects and the horizontal dotted line *PQ*, the trace of the cleavage plane. If in the act of cleavage a large portion of defect remains in both the parts, as with the defects *AA* and *DD*, the pits nucleated at these defects will be point-bottom and a point-bottom pit on one face will correspond to a point-bottom pit on the other, while a point-bottom pit on one face will correspond to a flat-bottom pit on the other if the large portion of the defect remains in one part while a very small portion in the other as with *bb* and *CC*. The correspondence of the etch pits

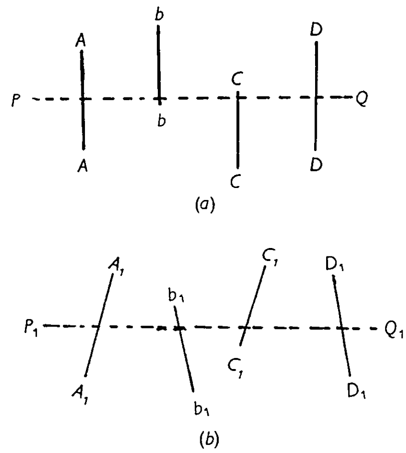


Fig. 7. Schematic diagram illustrating the vertical and inclined linear defects.

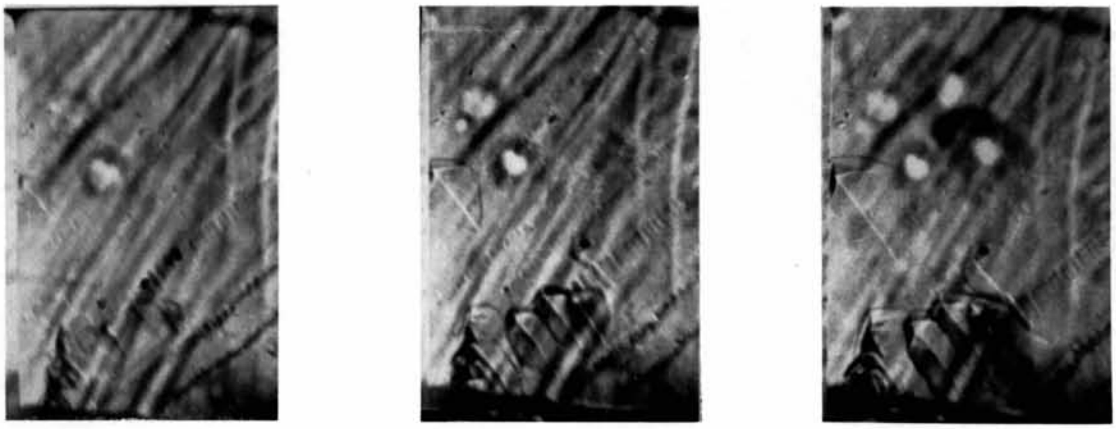
on the matched faces produced with different etchants suggest that during the growth of the crystal some foreign element might precipitate or some structure defect might occur which produces the defect which is attacked preferentially whatever may be the etchant.

Structure of matched etch pits

We have studied in detail the structure of matched etch pits on matched cleavage faces produced by citric acid using fairly high magnification. Fig. 8 (×500) shows such a pair of matched pits. The pits are point-bottom. Their structures, shapes, and sizes appear superficially to be the same. If however these pits are superposed in such a way that their boundaries coincide, the point-bottom of one pit does not coincide with the point-bottom of the other. This is revealed in every matched pair we have studied. If, however, the defects are linear and perpendicular to the cleavage face as shown in Fig. 7(*a*) the point-bottom of a pit will not move with progressive etching and at every stage if the pits on matched faces are superposed such that the boundaries coincide then the point-bottoms should also coincide. In the present case when the boundaries coincide the bottoms of the pits do not, and the separation increases progressively as the pits grow. This suggests that the linear dislocations might be inclined to the cleavage surfaces as shown in Fig. 7(*b*).

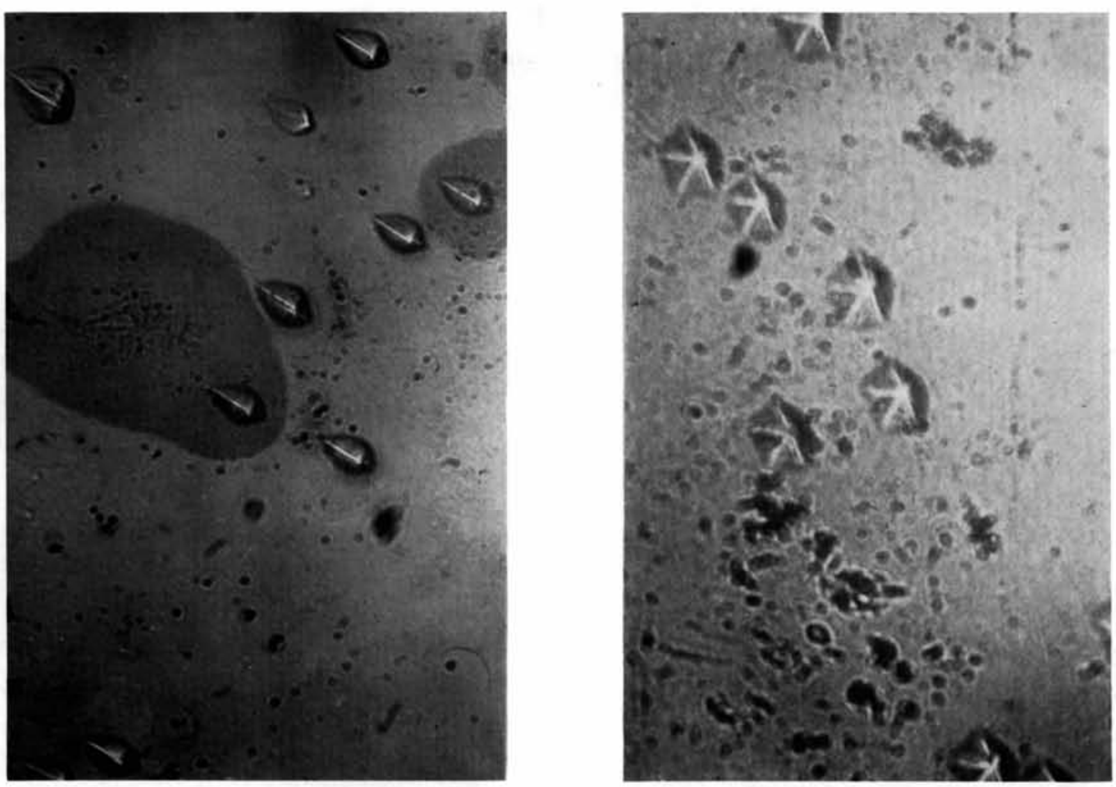
Etching of cleaved out blocks

In addition to separate etch pits, striking linear etch patterns are formed as happend with diamond (Patel & Tolansky, 1957). Such linear patterns are oriented strictly crystallographically, parallel to one of the pairs of the edges of the crystal. An example is shown in Fig. 9 (×33). These linear etch patterns when crossing a large cleavage step displace in one direction. This displacement suggests that, as for diamond, the



(a) (b) (c)

Fig. 1. Progressive development of etch pits produced by citric acid.



(a) ×200 (b) ×200

Fig. 3. Etch patterns produced on matched cleavage faces, by etching one with citric acid and other with nitric acid.

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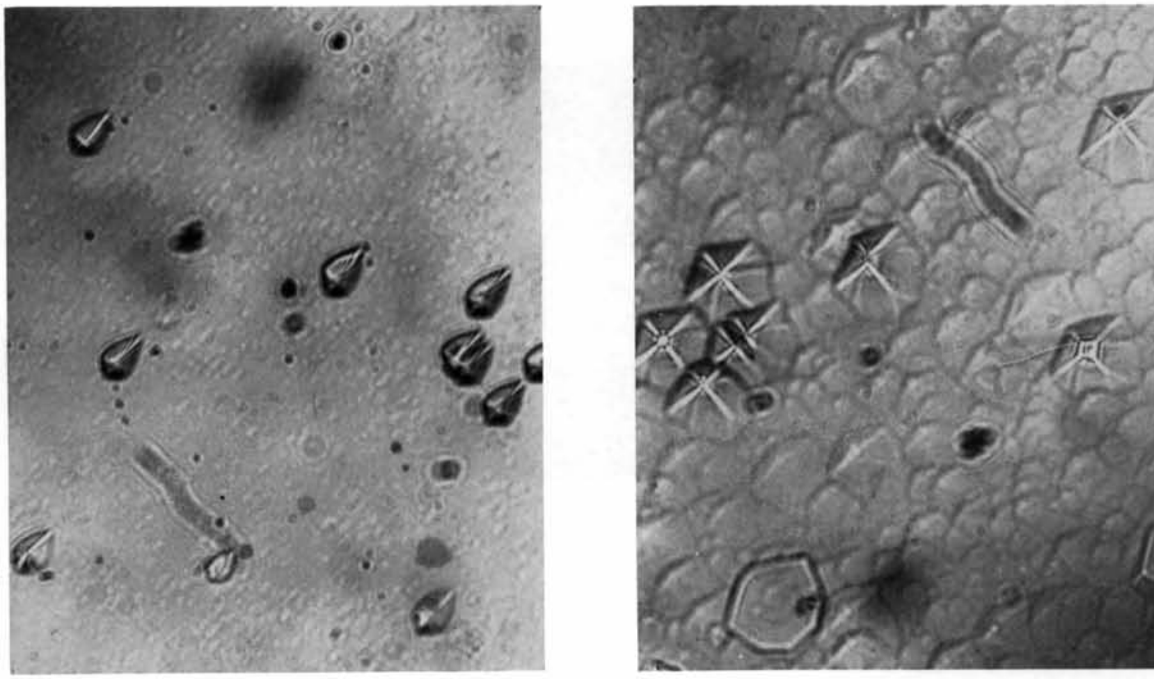
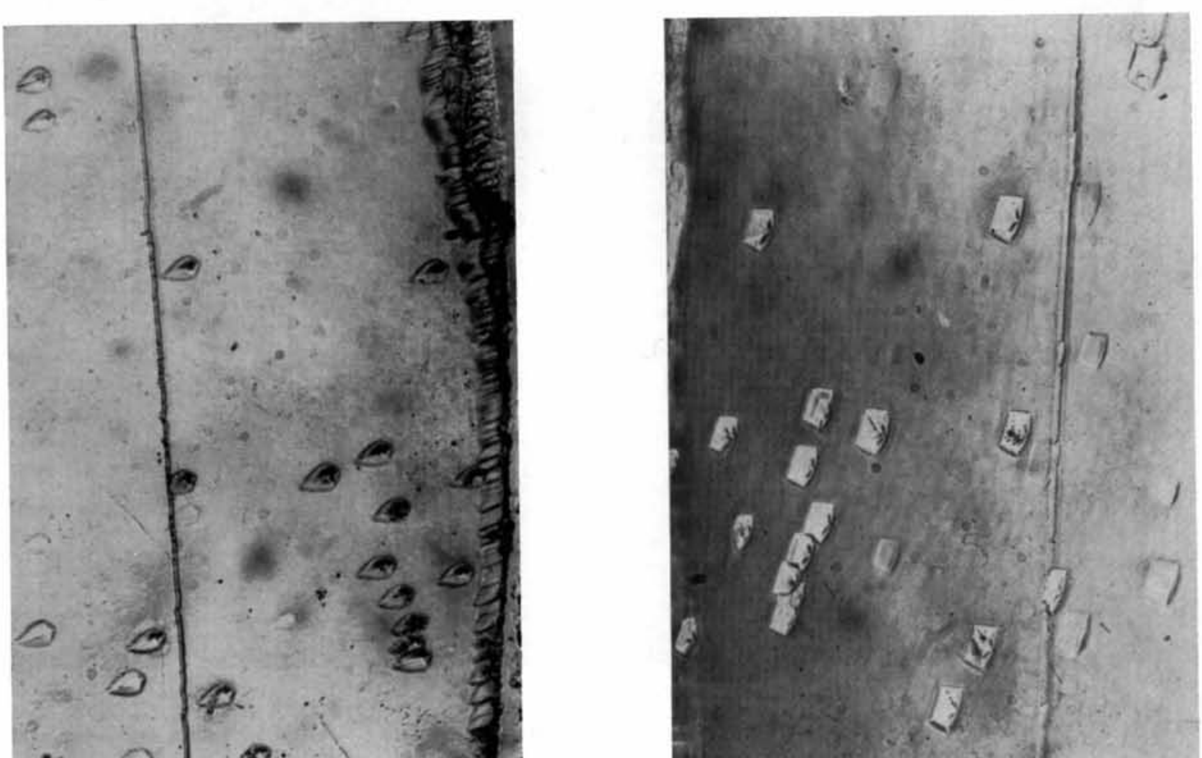


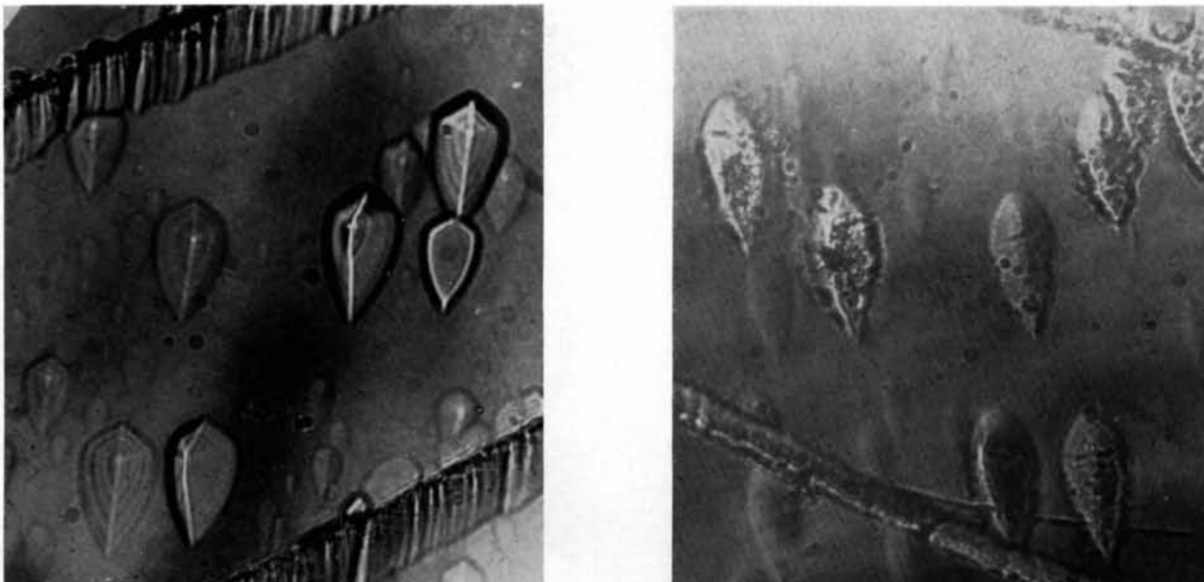
(a) ×100 (b) ×100

Fig. 4. Etch patterns produced on matched cleavage faces, by etching one with citric acid and other with hydrochloric acid.



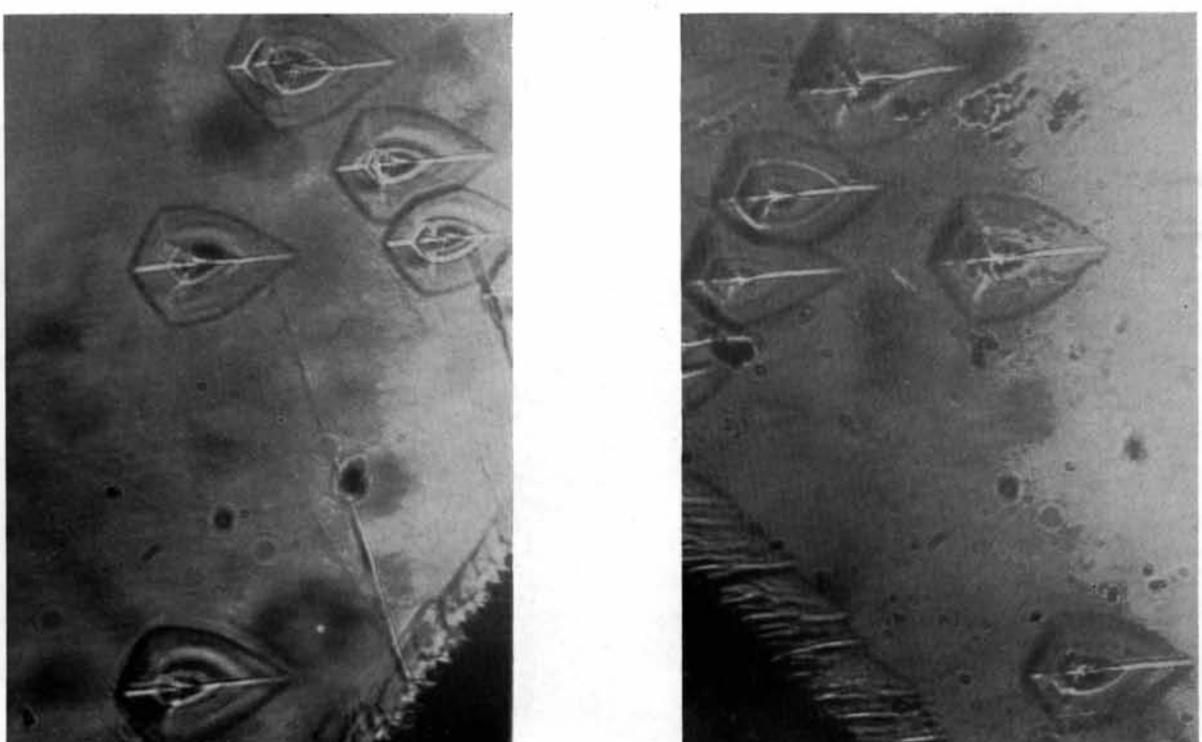
(a) ×100 (b) ×100

Fig. 5. Etch patterns produced on matched cleavage faces, by etching one with citric acid and other with sodium dihydrogen phosphate.



(a) ×200 (b) ×200

Fig. 6. Etch patterns produced on matched cleavage faces, by etching one with citric acid and other sodium hydroxide.



(a) ×500 (b) ×500

Fig. 8. Structure of pits on matched cleavage faces.

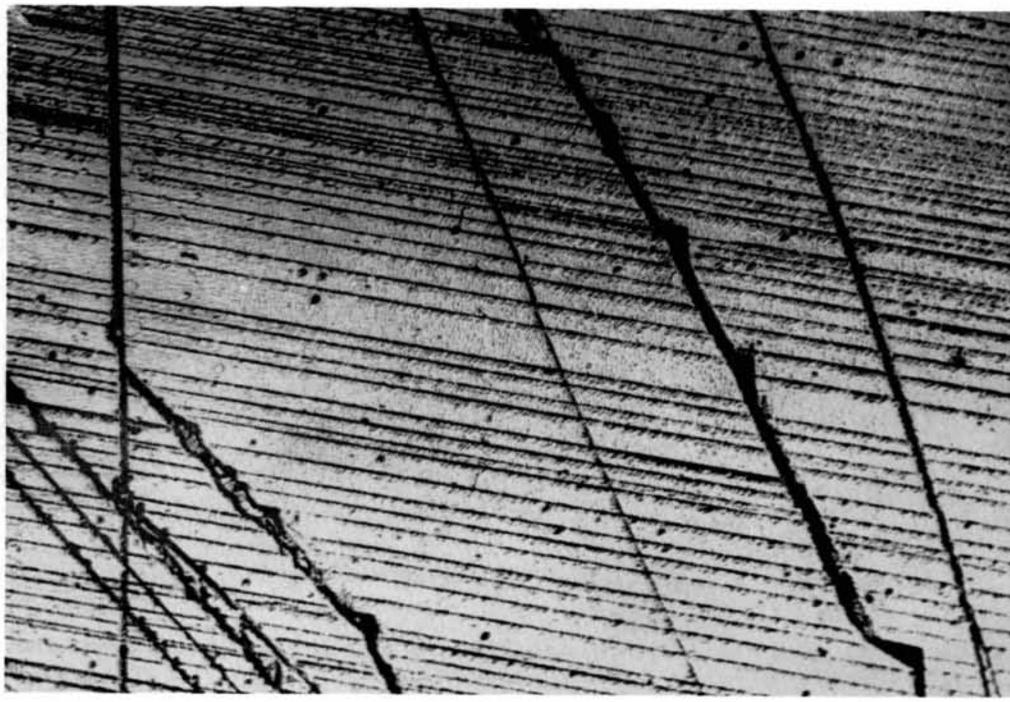
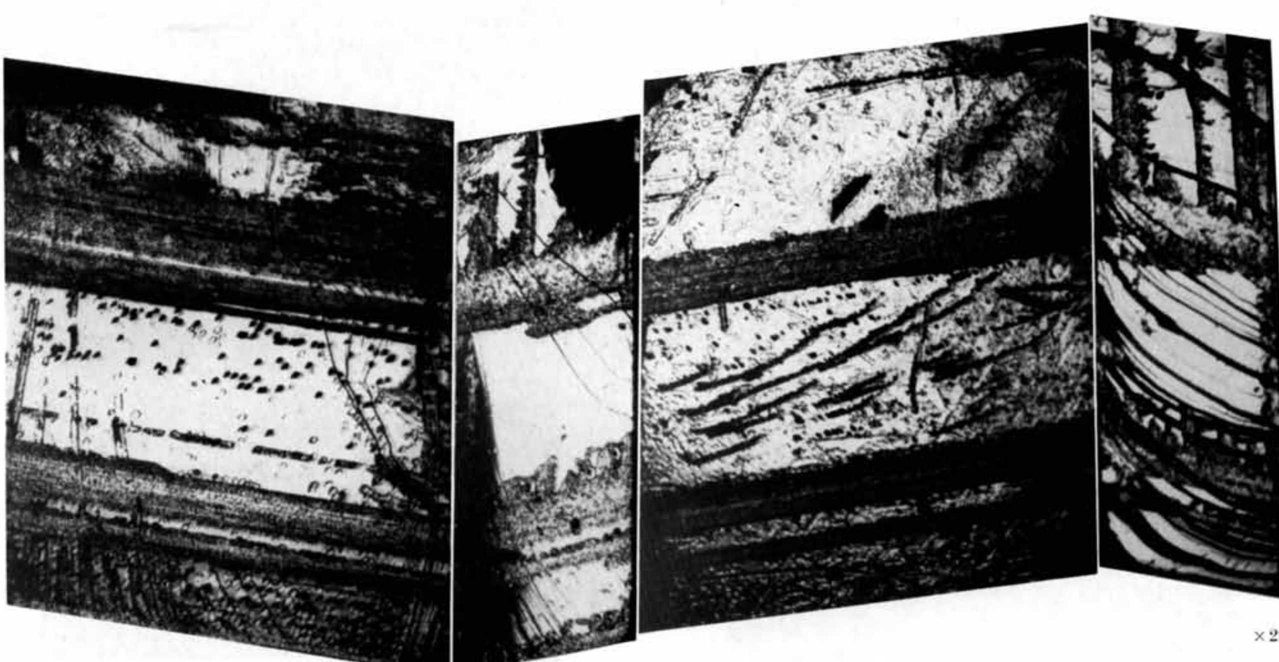


Fig. 9. Displacement of etch pattern across the large cleavage step. ×33



×22

Fig. 10. Correlation of etch pattern on the four faces of a small cleaved out block of calcite.

linear etch pattern might have been formed along with edges of imperfect layers deposited during growth. The calcite crystals were of rhombohedral habit. The growth layers make an angle of about 75° with the cleavage face. The displacement observed in Fig. 9 across the cleavage step and the height of the measured step are such that the angle made by the imperfect layers with the cleavage face is about 73°.

The question arises as to how far within the body of the crystal does such a pattern extend. We have obtained an answer to this question by using the method adopted by Patel & Tolansky (1957) for diamond. A small block of calcite was cleaved out and etched on all faces. A remarkable correlation appears in the patterns of the faces. These etch patterns are shown in Fig. 10 (×22) which is an exploded view, showing relation between the faces. Distinctive regions exhibiting different degrees of attack are seen. In one region the pits are widely distributed and in the other linear arrangements of densely populated pits are formed. These linear arrangements reveal the growth stratigraphy of the crystal.

It is clear that the stratigraphical pattern goes right through the body of crystal. Indeed, the etch has revealed the true history of growth of the calcite. The crystal sheets growing layerwise might have grown under different conditions. Such sheets of different thicknesses, maintain their individuality through the whole crystal block and this accounts for the similar etch pattern appearing on the four cleavage faces as shown in Fig. 10.

The implication seems to be that growth conditions (temperature pressure, impurities etc.), whilst effectively constant for each region differ markedly for successive regions.

It might well be that the growth is controlled by two separate rates:

(1) Sheets with isolated pits might have grown slowly.
(2) Sheets with densely populated pits have probably been deposited fairly rapidly.

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Plane Groups on Polyhedra

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Simple mosaics are given for the plane groups and the conditions for fitting these on the surfaces of polyhedra are discussed. All the basic polyhedra are considered, and a list is drawn up of the various possibilities. Some application to the structure of viruses is suggested.

Introduction

A mosaic is a two-dimensional array of congruent shapes which completely covers the plane without overlapping. For this array to belong to one of the 17 plane groups, it must be invariant to certain symmetry transformations. If the basic shape has no symmetry, the shapes must be in the general positions of the plane group.

The simplest possible such shape will give the simplest possible mosaic which fully describes the plane group. As any antisymmetry or colour-symmetry plane group is isomorphic with one of the plane groups, the mosaic for this plane group will be the most appropriate for adaptation for all the isomorphic groups.

Belov *et al.* (1956, 1957, 1958) have given mosaics for antisymmetry and colour-symmetry plane groups, but these do not all agree with the principles laid down above. Thus Belov & Belova (1957) use a mosaic isomorphic with Fig. 1 to describe the colour-symmetry groups numbered I*a* and III*a* in their paper. Fig. 1 contains numerous planes of symmetry, which do not become planes of true or colour symmetry in the diagrams of Belov & Belova. Moreover Fig. 1 is not the most appropriate mosaic to use to describe