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Etching of Mica Cleavages

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An optical study is made of the etch patterns produced by hydrofluoric acid on muscovite, phlogopite, and biotite mica cleavages. As usual two types (*a*) large isolated pits and (*b*) small widely distributed pits are observed. Large isolated pits with different shapes and different orientations have been observed on the one cleavage face. On oppositely matched cleavages correspondence has been observed with regard to the number and positions of the large isolated pits but not with regard to their shapes. Pits are observed growing within the pits and both can have different shapes; the structures of such pits are studied by light-profile microscopy. Correspondence between the etch patterns on the opposite sides of a thin mica sheet has been established by taking pictures in transmission. Instead of individual isolated pits individual pairs of pits are observed. The etch patterns on the two sides of a thin sheet of mica show a displacement effect. The mechanism of formation of such pairs is discussed and they are attributed to the existence of linear dislocations lines running in the body of the crystal. The displacement of the etch patterns on the opposite sides of thin mica sheet has been explained as due to (1) different rate of development of the pit in opposite directions, and (2) existence of inclined dislocations in the body of the crystal. The implications are discussed.

Introduction

It has long been known that etch figures play an important part in the study of the dislocation contents and the surface defects of crystals. Experiments on etching of mica have been reported by amongst others R. De la Vault (1943, 1944), Patel & Tolansky (1957), Pandya & Pandya (1959).

Such observations were restricted to muscovite mica. Patel & Tolansky (1957) have reported that two types of etch pits, (*a*) small widely distributed pits and (*b*) relatively large localized isolated pits, are produced by etching mica cleavages with HF acid vapour. No explanation however has been given for their formation. In the present investigation we have tried to investigate the cause of one of the two types of pits and these studies have been extended to biotite and phlogopite micas. Interesting results have been obtained.

Experimental

We have available samples of phlogopite, biotite and muscovite micas which we have established by multiple-beam interferometry to be good crystals. The biotite was obtained through the Geological Survey of India from Gudur (Andhra Pradesh) and from the Geology Department, Jammu and the phlogopite from Trvandrum.

We find that selected samples of these micas can be cleaved true to a single unit cell over regions at times exceeding a square centimeter. A selected piece of mica was cleaved and the two separated faces were immersed in a solution of hydrofluoric acid at a temperature of about 25 °C. We describe our observations in two parts, (*a*) observations on biotite mica and (*b*) observations on phlogopite mica.

Biotite mica

Figs. 1(*a*) and 1(*b*) (×100) show the etch patterns on the two oppositely cleaved faces of a piece of biotite mica from Gudur etched for 10 minutes. Attention is drawn to the following features.

(1) Whereas in muscovite mica it would need about 24 hours etch to produce the pits of this size, here it requires only 10 minutes. The rate of development of pits on this mica is quite large as compared with that of muscovite mica.

(2) The individual isolated pits occur at about 3000 per sq.cm. as against about 400 per sq.cm. as reported by Patel & Tolansky (1957) on Indian muscovite mica.

(3) The pits are closely similar in size.

(4) The number and the positioning of the pits on each face are such that they mirror image those on the other face.

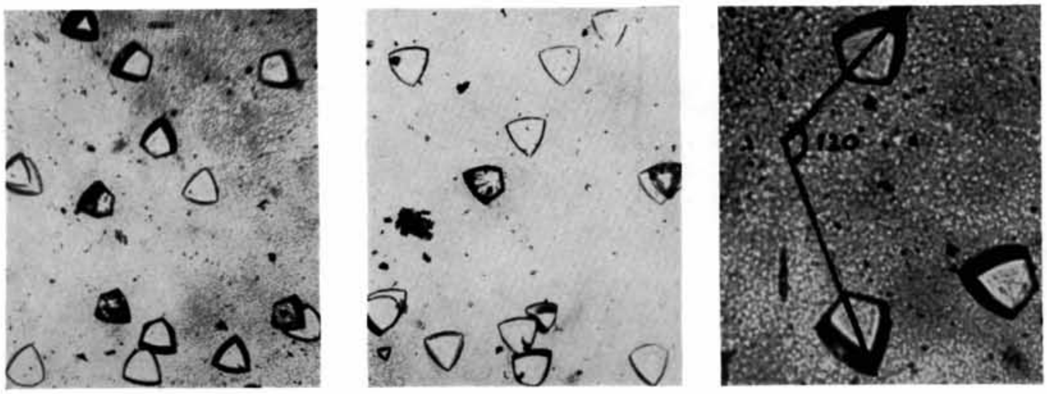
(5) The shapes of all the pits are not identical. Some are triangular in shape with rounded sides whilst others are four-sided.

(6) The four-sided etch pits are oriented in any one of the three definite crystallographic directions.

(7) If the longer diagonals of the four-sided etch pits are produced towards the nose of the pit they intersect at an angle of 120° as shown in the Fig. (1(*c*)).

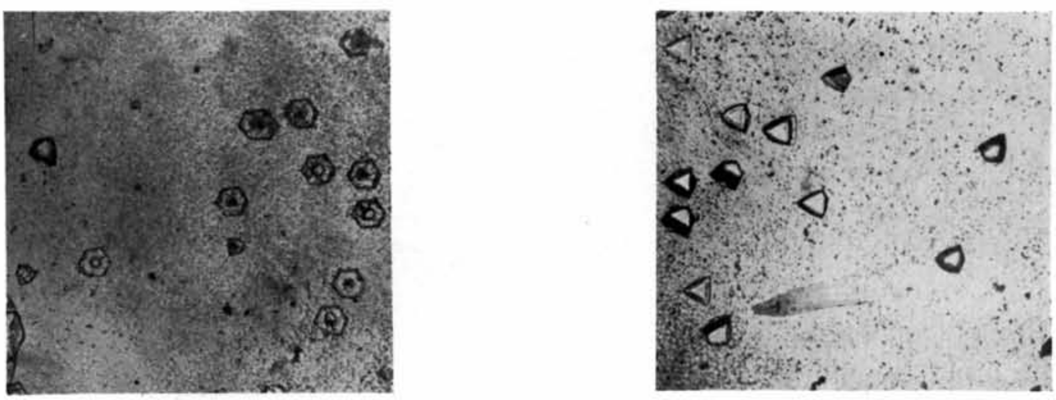
The pits of particular shape on one face do not always have a corresponding pit on the matched face of similar shape. The following conclusions are drawn:

(1) Some triangular pits have the corresponding pit on the matched face as a four-sided figure.



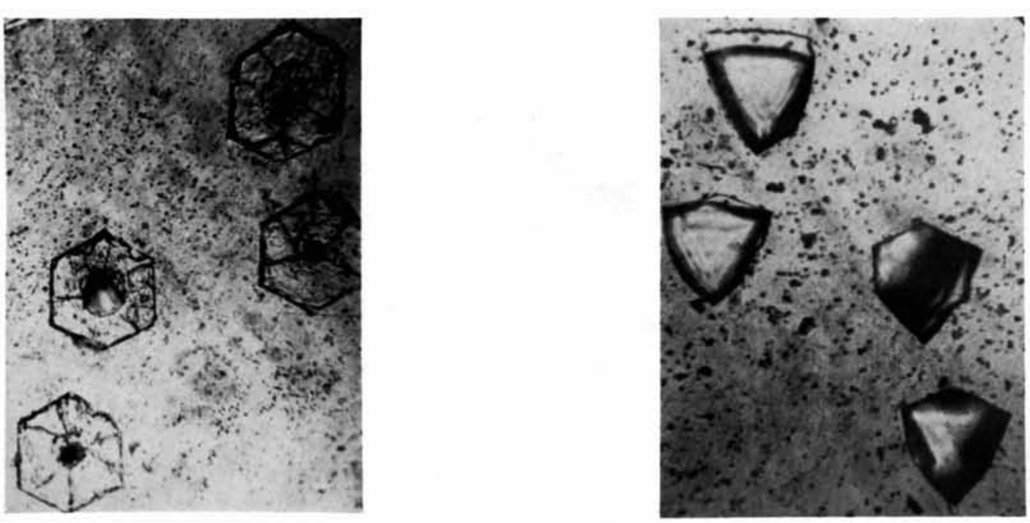
(a) (b) (c)

Fig. 1(*a*) and Fig. 1(*b*) (× 100). Etch patterns on matched faces of biotite mica from Gudur.
Fig. 1(*c*). Etch figures of different orientations.



(a) (b)

Fig. 2(*a*) and Fig. 2(*b*) (× 175). Etch patterns on matched faces of biotite mica from Jammu.



(a) (b)

Fig. 3(*a*) and Fig. 3(*b*) (× 750). Magnified photograph of Fig. 2(*a*) and Fig. 2(*b*).

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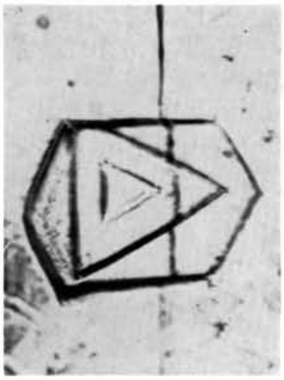

Fig. 4.

Fig. 5(*a*).

Fig. 5(*b*).

Fig. 4 (× 480). Light profile shadow across a hexagonal pit. — Fig. 5(*a*) and Fig. 5(*b*) (× 175). Etch patterns on matched faces of phlogopite.

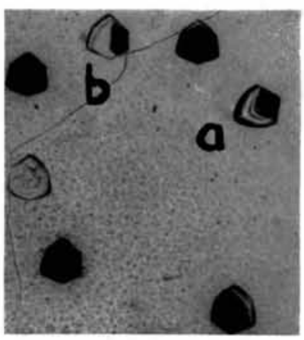

Fig. 6(*a*).

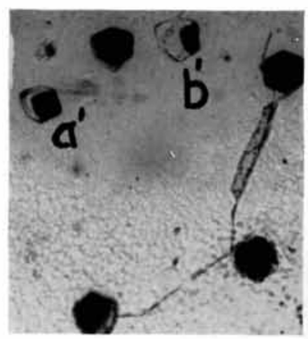

Fig. 6(*b*).

Fig. 7.

Fig. 6(*a*) and Fig. 6(*b*) (× 175). Etch patterns on the two sides of mica sheet. — Fig. 7 (× 175). Transmission photograph on phlogopite.

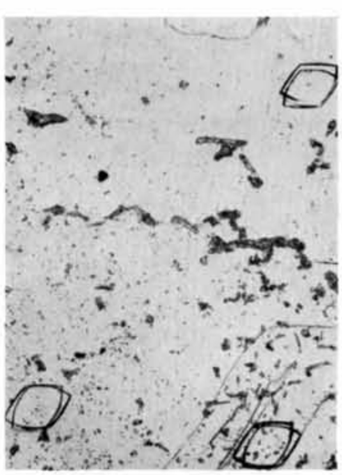

Fig. 8.

Fig. 9(*a*).

Fig. 9(*b*).

Fig. 8 (× 175). Transmission photograph on muscovite. — Fig. 9(*a*) and Fig. 9(*b*) (× 300). Etch patterns on muscovite after 30 hours and 54 hours of etch taken in transmission.

(2) Some triangular pits have a corresponding triangular pit on the matched face.

(3) A pit having four sides has never been found to have a corresponding four-sided pit on the matched face.

Figs. 2(*a*) and 2(*b*) (×175) shows etch patterns produced on matched faces of biotite mica obtained from the Geology Dept., Jammu, and etched for 15 minutes at room temperature. The pits observed on these faces are either triangular or hexagonal. Again, a hexagonal pit never corresponds with a hexagonal pit on the oppositely matched face. Figs. 3(*a*) and 3(*b*) (×750) are magnified pictures of a selected region of Figs. 2(*a*) and 2(*b*) illustrating quite clearly that triangular pits correspond with hexagonal pits on the opposite matched face.

Phlogopite mica

Figs. 5(*a*) and 5(*b*) (×175) show etch patterns on the cleavage faces of phlogopite mica, etched for 25 minutes. Two types of pits are observed as in biotite mica. The more densely populated pits are triangular in shape, strictly crystallographically oriented. The individual isolated pits are not all of the same shape. On both the faces some of the pits have triangular outline while the others are elongated hexagons with a triangle inside the hexagon. The triangle inside the hexagon has the same orientation as those in the densely populated triangular pit regions. So far as the correspondence of pits on the matched cleavages are concerned this is similar to biotite mica. Fig. 4 (×480) shows a light-profile shadow (Tolansky, 1952) running across a hexagonal pit. The profile shadow indicates that the triangular pit is at a lower level (0·58 micron) than the hexagonal pit. The depth of the base of the triangular pit below the cleavage face is 1·40 microns.

Many of our observations do not fit the views on the shape and orientation of etch pits on mica cleavages suggested by earlier investigators. As the shape and the orientation of the pits depend upon the molecular structure of the face and that of the etchant, the pits of different orientation and shapes observed on the same face etched with the same etchant can be explained by postulating local changes in the molecular structure, which may be assumed to be confined to few molecular layers; in the process of cleavage, the cleavage goes through in such a manner that at some places the region of a particular molecular structure remain with one part while on the other part the molecular structure may be different. This explains the observations made on matched faces. If these matched faces are now etched, the correspondence, so far as the number and positioning of the pits are concerned, will be maintained while the orientation and shape may differ.

It may be assumed that the local change in the molecular structure is only a few interatomic distances in extent and hence may escape detection by other methods. But it could be easily detected by etching because once the pit nucleates with a particular shape and orientation it maintains both on further etching so long as it extends in the region of same molecular structure. The importance of etch methods therefore can easily be recognized.

Inclined dislocations

Our views differ from one of the possible conjectures made by Patel & Tolansky (1957), namely that the individual isolated pits originate at chemical impurity centres which lead to lattice distortion surrounding the impurity and not at the dislocations which produce the lattice distortion. In order to support the view that isolated pits originate at dislocations and not at other surface defects the following experiments were carried out.

A thin sheet of biotite mica from Gudur (India) 0·003 cm. thick was cleaved off and both the sides were simultaneously exposed to etchant for 15 minutes. Figs. 6(*a*) and 6(*b*) (×175) show the etch pattern taken on both the faces of the mica sheet thick silver being deposited after etching. Six etch holes are clearly seen in both the figures. The regions one above the other on both faces of the mica sheet can be identified by the positions of the etch holes. It is observed that there is no correlation in the etch patterns except the holes and they are quite independent. Noteworthy is the fact that holes are formed only at selected places and that some of the holes have etch boundary. Such etch boundaries with some of the holes are clearly seen in Figs. 6(*a*) and 6(*b*) (×175) in which, in pits marked a, a' and b, b', the holes have been developed only in small regions of the pits. It is quite clear that corresponding to pits a and b on one face there are pits a' and b' on the other. This correspondence can be explained by postulating the existence of linc dislocations in the body of the crystal. This is diagrammatically explained in Figs. 10(*a*) and 10(*b*) where aa', bb' and cc' in Fig. 10(*a*) represent dislocation lines assumed to be perpendicular to the cleavage faces while in Fig. 10(*b*) they run inclined to the cleavage faces. In cleaving, the two cleavages on the two sides of the mica sheet

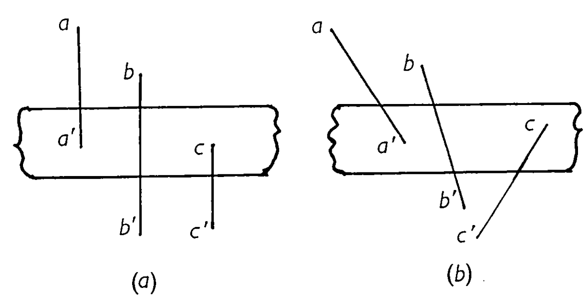

Fig. 10.

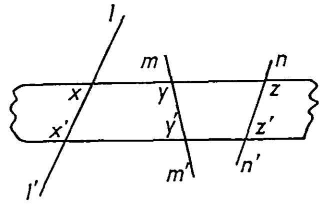

Fig. 11

have cut the dislocation lines leaving on each face a region of crystal distortion which when exposed to the etchant act as nucleating centres of etch pits producing the correlation in the etch patterns on the two sides. This is illustrated by Fig. 11 in which *ll'*, *mm'*, *nn'* represents the dislocation lines inclined to the cleavage faces which have been cut by the two cleavages thus leaving the region of distortion at *XX'*, *YY'*, *ZZ'* which become the centres of nucleation of etch pits; this explains the matching of the etch patterns on the cleavage flakes on both the sides. On prolonged etching holes will be formed at these sites earlier because the attack will start from both the sides. The correlation in the etch patterns on the opposite faces is clearly seen in Fig. 8 (×175) which is a photomicrograph of a region of a thin sheet, 0·003 cm. thick, of muscovite mica etched for 30 hours. This photograph is taken in transmission without depositing the silver films on the etched faces. This enabled us to photograph the etch patterns on both the faces of the mica sheet simultaneously. Fig. 7 (× 175) represents similar observation made on phlogopite. Attention is drawn to the following features.

(1) Instead of individual isolated pits, pairs of pits are observed.

(2) The pits have closely similar shape and size.

(3) The shape and orientation of each pair of pits reveal that in each pair one of the pits belongs to the etch pattern on one face while the second belongs to the etch pattern on the other face.

(4) There is a considerable amount of displacement in the etch patterns on the two faces.

(5) The displacements are in the directions of the shorter as well as the longer diagonals.

The relative displacement of the etch patterns may be attributed either to (*a*) different rates of development of pits in the directions of the longer and the shorter diagonal or (*b*) dislocation lines running inclined to the cleavage face.

In order to decide which of these two alternatives is responsible for the observed displacement, a thin sheet of muscovite mica was etched in two stages. Figs. 9(*a*) and 9(*b*) (×300) represent the etch patterns after 30 hours and 54 hours of etch respectively.

It is clearly seen that for each pair of pits the distance between (*a*) the shorter diagonals has remained the same and (*b*) the longer diagonals has been increased with the time of etch. It is therefore conjectured that displacement in the direction of the longer diagonal may be due to the different rates of etch while the displacement in the direction of the shorter diagonal may be due to the inclination of the linear defects as shown in Fig. 10(*b*). This was also confirmed with sheets of mica of different thickness, measuring the displacement of the etch pattern in the direction of the longer diagonal of the etch pit. The displacement in the direction of the longer diagonal was greater for greater thickness of the mica sheet.

The angle of inclination of the dislocation lines with cleavage faces was computed from the observations made of the displacement in the etch patterns on the opposite faces of three different mica flakes of different thickness.

	Thickness	Displacement observed	Angle of inclination calculated $\tan\theta = d/t$
1.	0·003 cm.	0·3 cm.	11° 42′
2.	0·005	0·4	9° 28′
3.	0·006	0·5	9° 51′

The angle of inclination has been calculated in the following manner. If t be the thickness of the mica sheet, d be the displacement in the etch pattern observed and θ be the inclination of the linear defect with the normal to the surface then $\tan\theta = d/t$. That there exist inclined dislocation lines in the body of crystals agrees with the findings of Patel (1961).

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