P A R T III

DETAILED MICROTOPOGRAPHICAL STUDY OF CRYSTALS.

CHAPTER 3

MICA

The term mica is a group name applied to a large number of minerals that have certain physical and chemical characteristics in common. Chemically they are all silicates, usually orthosilicates of aluminium with potash and hydrogen and generally magnesium and ferrous iron. Fluorine may be an important constituent. Less common varieties contain ferric iron, sodium and lithium with, more rarely rubidium and cesium. Still more uncommon varieties contain vanadium, barium, manganese and chromium.

Since mica is a silicate, some general information on silicates with special reference to mica will not be out of place. The silicates comprise the largest chemical group among minerals. They show a wide range in composition which is frequently very complex in character. X-ray investigation, however, has revealed important fundamental facts concerning their atomic structure and thrown much light upon the intricate problem of their composition. It is now established that the fundamental structural unit of all silicates has a tetrahedral shape with four oxygen atoms being at the corners of the tetrahedron. These SiO_4 groups

may be linked together in various ways to form indefinitely extended series. According to W. L. Bragg, a silicate should be regarded as a structure having a constant number of oxygen atoms in the unit, with a constant number of places for metal and silicon which can be filled by these elements in varying proportion m consistent with a balance between valencies. The silicates are classified as anhydrous and hydrous depending upon whether or not they yield water upon ignition. Those silicates giving water upon ignition are to be regarded as basic or acid silicates. A line of demarcation between the strictly anhydrous and hydrous silicates cannot be sharply drawn, since with many species which yield water upon ignition, the part played by the elements forming water is as yet uncertain. Mica is included in the second group - hydrous silicates, since they yield water upon ignition mostly from 4 to 5 per cent. Doubt is cast as to the propriety of placing the micas in the second group since water given out on ignition is probably to be regarded in all cases as water of constitution and hence they are not properly hydrous silicates.

Second type of classification of silicates depends upon the type of linking of SiO_4 tetrahedron with other

tetrahedrons, with appropriate sharing of either oxygen atoms or silicon atoms or both. On this basis, silicates may be classified as neosilicates, sorosilicates, phyllosilicates etc. In the SiO_4 tetrahedrons of silicates, some of the silicon atoms may be replaced by aluminium, beryllium, boron or other atoms. According to this classification, micas belong to phyllosilicates [sheets of tetrahedrons type formula Am (B_2 X 5n).] The phyllosilicates have SiO_4 groups which are united to other SiO_4 groups by having three oxygen atoms in common. No SiO_4 group has more than one oxygen atom in common with any other SiO_4 group, each SiO_4 is thus linked to three other SiO_4 groups. This results in forming layers. Such SiO_4 sheet should have Si_2O_5 for its composition. The Si-O tetrahedra are grouped together in a hexagonal like ring which apparently accounts for the common pseudo hexagonal character of the mica crystals. The result of this typical grouping is the formation of layers. Minerals of this structure are characterized by eminent cleavage parallel to these layers. They have good basal cleavage because of the lack of any ionic (i.e. electric) attraction between different planes of atoms and also the wide spacing

between these planes. This is why the micas have a perfect basal cleavage, the so-called micaceous structure.

General Description of the Micas:

The members of the mica group are monoclinic but pseudo-hexagonal in habit. Distinct terminated crystals are very rare. The usual crystals of all the micas are thin basal plates of hexagonal outline; in all of them the prism angles (110 ∧ 110) and also (110 ∧ 110) i.e. on the basal section plane angles) are very nearly 60° & 120°. The very perfect basal cleavage parallel to (001), giving thin tough and more or less elastic laminae, is the most striking feature of the micas. They are characterized by the weak birefringence in cleavage flakes and basal sections combined with strong birefringence in transverse sections.

Percussion Figure:

A blow with a somewhat dull-pointed instrument on cleavage plate of any mica develops a six-rayed star, one line being more distinct than the other two. This strongly characterized line is parallel to the clinopinacoid or plane of symmetry i.e., is parallel to (010) plane, whereas

the others are parallel to the prismatic edges (prism faces). The percussion figure thus makes it possible to determine the position 010 (and hence the optic orientation) in any cleavage piece of mica, even though no crystal faces are present. Pressure instead of a blow on mica cleavage surface, (001), produces six-rayed pressure figure whose lines are perpendicular to those of the percussion figure. In this figure, more often only three and sometimes only two branches are developed. These lines due to pressure figures are connected with gliding planes inclined some 67° to the plane of cleavage.

Twinning is common in mica; the twinning plane being (110) and the composition face (001) or (110).

Classification of Micas:

Micas are classified in various ways depending upon the particular general property chosen for classification.

From the view point of commercial importance, they may be divided into two general groups (1) those used for their physical properties; including muscovite, phlogopite, biotite, sericite and vermiculite, and (2) those used

for their chemical content, including lepidolite and zinnwaldite (lithium) and roscoelite (vanadium).

They may also be grouped according to the position of the plane of the optic axis. In the first class belong those kinds for which optic axial plane is normal to b (010), the plane of symmetry, in the second class the axial plane is parallel to the place of symmetry. The micas of the first class include muscovite, paragonite, lepidolite also some rare varieties of biotite called anomite. The second class embraces zinnwaldite and most biotite including lepidomelane and phlogopite.

The position of the interference figure in the percussion figure on cleavage surface of mica is also used for the classification of micas (Rogers 1937). If the inter-ference figure lies between two rays of the percussion figure, then the third ray is the direction of the b-axis. These are micas of the first class and are shown in figure 8a. If the interference figure lies along one of the rays, then that ray is the direction of the b-axis. These are micas of the second class and are represented in figure 8b. Muscovite andlepidolite are micas of the first class, while biotite and phlogopite are micas of the second class.

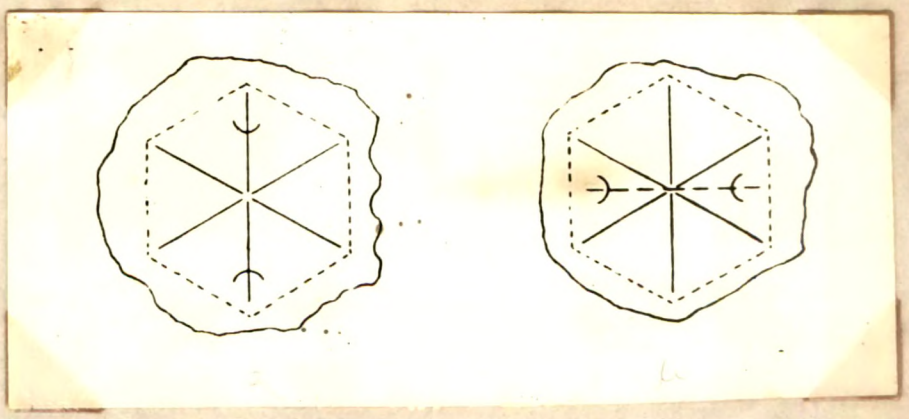


Fig 8

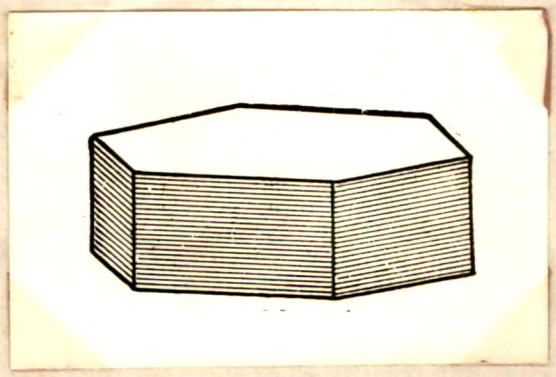
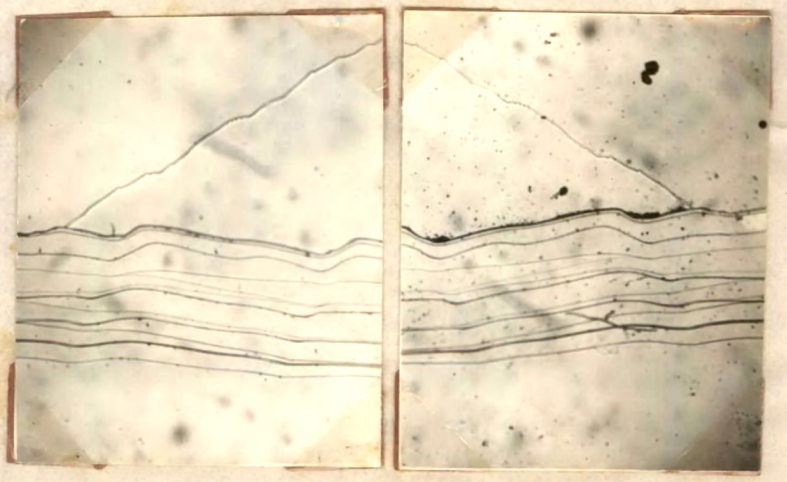


Fig 9



(a) (b)

Fig (10) ×170

Another basis of classification of micas is according to the number of atoms in the chemical formula (excluding O, H and F). They are then known as heptaphyllites and octophyllites.

The heptaphyllite micas are characterized chemically by having seven (or fourteen) atoms in the formula (excluding O, H and F) and optically by having an optic angle (the true angle between the optic axis, or the optic axial angle) usually of 30°, to 50° with dispersion $r > v$ (i.e. the optic axial angle in the red light is greater than the optic axial angle in the violet). This class consists of muscovite and its varieties and paragonite.

The octophyllite micas are characterized chemically by having eight (or sixteen) atoms in their formula (excluding O, H and F). This class embraces lepidolite, taenolite, biotite, and phlogopite.

General properties of Micas:

Micas, as already mentioned, are complex silicates which crystallize in the monoclinic system. They are characterized by a perfect basal cleavage, are relatively soft and fuse with difficulty. Thin plates are

usually transparent, but the thicker plates vary from transparent to opaque. Colours are white, yellow, amber, red, brown, green, grey and black.

Mica has several uses in industry. It is used for electric insulation, heat insulation. Due to its transparency it is utilized for furnace sight holes, glazing the fronts of stoves etc. It is also used as phonograph diaphragms and various sounding devices (submarine detectors). Ground mica is used extensively for decoration in wall paper, processional ornaments, fancy points, ornamental tiles and concretes. It is also used for lubrication, for calico printing, to prevent sticking of tar papers and for medicinal uses (in India only).

Several mica substitutes and synthetic mica are now available, but it is improbable that they will ever entirely replace natural high grade mica. It should be noted that India is the principal producer of muscovite and is the most important source of high grade sheet mica in the world, normally supplying about 65 per cent or more of the world's production.

The present author had made a detailed systematic

surface study of cleavage and etch patterns on the easily available muscovite and hence a very brief information on muscovite is given below.

Muscovite, so well-known as potash mica with a chemical formula $H_2 KAl_3 (SiO_4)_3$, is a silicate of potassium and aluminium and hydrogen, also often containing sodium, iron, calcium and fluorine. Muscovite mica, so named by J. D. Dana in 1850 from the old name muscovy glass, occurs (1) in granites pegmatites and granite aplites, (2) in schists and gneisses, often the main constituent of the mica schists, (3) in granites. Granite is about the only igneous rock in which muscovite occurs as an original constituent, (4) in sand-stones and sands as a detrital mineral.

Physical Characters:

The crystals are tabular in habit and pseudo-hexagonal or pseudo-rohombic, but are really monoclinic having perfect cleavage in one direction parallel to (001). (Fig. 9) The cleaved surfaces possess a high natural polish. Also secondary parting or slip planes parallel to (110) and (010). Its hardness varies from 2 to 3, specific gravity, from

2.8 to 3.1. Index of refraction, is from about 1.556 to 1.611. It is optically Biaxial, negative with birefringence 0.037 to 0.041 and axial plane is perpendicular to (010). Colour, varies from colourless, yellow, brown, red, green, and grey. Thin plates are transparent to translucent, thicker plates are transparent to opaque. As regards its tenacity, it is elastic.

On heating muscovite begins to loose its valuable electrical properties at about 550°C and gives off water rapidly at 700°C.

Cleavage of Muscovite Mica:

Mica cleavage surfaces have been intensively studied by Tolansky (1945, 1946, 1947) who has beautifully developed the powerful and sensitive technique of multiple beam interferometry. Tolansky and Morris (1947a, 1947b) made an interferometric survey of natural (1947a) and synthetic (1947b) micas. He observed cleavage steps to be either 20 A.U., its X-ray unit cell or its integral multiple. At times mica surface cleaves true to a single molecular plane. The step height along a cleavage line is constant proving that the surfaces separated by this line are "parallel".

Uptil now the cleavage steps observed were either an integral multiple of 20 A.U. or a single molecular lattice of 20 A.U. Courtney-Pratt (1950) reported the occurrence of a cleavage step 1.5 times the crystal lattice spacing.

Direct experimental evidence by an interferometric technique is given for the existence of a screw dislocation in muscovite mica (Amelinckx, 1952a). A step ending in the middle of a cleaved face with a step height of 140 A has been observed. The point where the step ends is considered as the point where a screw dislocation emerges from the surface. The screw dislocation has Burgers vector of some seven unit cells long. The phenomenon is suggested as a possible explanation for the various mica and chlorite structures. Further proof of the phenomenon is supplied by the observation of growth spiral on biolite crystals (Amelinckx and Dekeyser 1953). It has been suggested from this and X-ray observations (Amelincks 1952b) that polymorphic forms of micas are polytypes in accordance with Frank's mechanism of spiral growth.

The present work is chiefly concerned with the etching of mica crystals, but it was thought desirable to study the oppositely matched cleavage faces, before they were

subjected to etching. The matching of two counterparts was optically studied by Pandya (1954) who reported the one-to-one correspondence between the matched areas. Here the areas on the cleaved surfaces which were observed for matching are followed up during the etching work.

For study, three varieties of muscovite mica were supplied by the Director of Industries and Commerce, Andhra Pradesh. Out of these, one variety which was opaque was found to contain many inclusions and was therefore, not studied. The remaining varieties were studied in the present work. So far as the cleavage study was concerned there was no difference between the cleavages studied from the samples. The etching work did show some differences in the two samples.

Figure 10a (X 170) is a phase contrast picture of a typical cleavage system of muscovite whereas Figure 10b (X 170) represents the phase contrast photomicrograph

of the counterpart. It is seen that there is perfect one-to-one correspondence between the cleavage systems on the two counterparts obtained by cleaving the crystal. It was suggested that during the act of cleavage the - pattern although unaffected by itself might have moved. To ascertain this point, the thin muscovite was cut in a definite shape and a small hole was produced in the centre. It was then cleaved and the counterparts were silvered and the cleavage systems in the two specimens were studied. The two counterparts were then placed together so that the holes on the two completely coincided and the shape of the crystal was maintained. It was then examined in transmission with a relatively low power objective so as to have good depth of focus, so that both the pieces could come in view simultaneously. It was found that there was complete correspondence with the matched cleavage patterns and that there does not appear to be any relative displacement of the cleavage patterns.

Several samples (about 100 pairs) were studied by

phase contrast microscopy and the following points were observed for the cleavage systems on the cleaved crystals.

(i) The cleavage lines are distributed at random starting from the end where the needle is inserted. Cleavage lines, representing discontinuities in levels vary considerably in length. In general, four types of cleavage lines were observed: (a) Curved or straight cleavage lines, (b) Y-shaped cleavage lines, (c) V-shaped cleavage lines and (d) Single cleavage lines ending in the middle of the surface .

Regarding the frequency of the occurrence of the cleavage lines, curved or straight cleavage lines are most frequent. The Y-shaped cleavage lines are more ~~freuqne~~ frequent than the V-shaped cleavage lines whereas from the many samples examined only one sample showed a single cleavage line ending on the middle of the surface. This shows the extreme rarity of such lines. In some samples cleavage lines turn abruptly through near about 90°. Cleavage lines crossing each other were not observed on any sample so far examined. In some samples the cleavage lines run in one general direction whereas in others it is not so. Between the cleavage lines areas are found to

be optically uniform, extending in some cases upto several square centimeters. At a V-point in the V-shaped cleavage lines the step heights on both the counterparts do not agree, whereas at all other points there is a perfect agreement between the step heights and optically and interferometrically there is a perfect agreement on the two counterparts.

Regarding the concentration of cleavage lines on a given specimen, it is found that on an average the number of cleavage lines per unit area are smaller on muscovite crystals than those observed on calcite cleavages, although both are said to have perfect cleavages.

Etching of Muscovite

Introduction:

Etching figures may be said to be definitely shaped solution cavities produced by the momentary or prolonged action of some natural or artificial solvent upon the faces of crystals, the shape and distribution of the cavities being attributable to the solvent and the molecular configuration of the crystal face on which they occur. Good accounts of the study of etch figures are given by Honess

(1927) and by Desch (1934). In recent years, the etching of crystal faces is taken up to investigate structural defects. notably the line defects (dislocations and their movements) and the etch figures are studied by the highly developed new techniques. Since mica has a perfect cleavage and it is known (Tolansky 1948) that a good muscovite can cleave true to a molecular lattice over relatively large regions, even at times over areas of some square centimeters, it was felt that etch figures on such a highly cleaving muscovite, if studied, might furnish valuable information.

Several workers reported the study on etching of mica. Baumhauer made elaborate study on etching of crystal surfaces. He had studied the etching of zinnwaldite and muscovite micas (1879) by hydrofluoric acid (HF) and fused alkalies and observed the sharply defined five and six-sided etching figures.

Etching of muscovite mica was studied in detail by De la vault (1942, 1943, 1944a, 1944b, 1946a, 1946b). He used etching to study the rate of attack on crystalline surfaces treated with acids and alkalies . Two forms of etching by hot hydrofluoric acid were observed: (i) fairly regular pattern due to the chemical properties of the

crystal lattice, and (ii) an irregular disintegration probably due to imperfections or foreign inclusions. He discussed the patterns and the speed of etching (1942). He also studied (1946a) the rate of attack on muscovite by hydrofluoric acid at 100°C with concentrations ranging from 40, 20, 10 and 4 per cent of the acid, and solutions of the compound KF and HF acid with the composition (i) KF.4HF and (ii) KF.2HF, and 40 per cent HF acid at temperatures of 120°, 100° and 76°C. The etch figures thus produced were then studied. Reduction of the concentration of the HF acid from 40 per cent to 4 per cent was found to be accompanied by a decrease of the rate of attack from 30 to 1. Solution (i) was as effective as 10 per cent HF, whereas solution (ii) was only one-fifth as active. Regarding the effects of temperature, 40 per cent HF was 10-12 times more effective at 120°C than at 76°C.

The rate of attack was also studied by comparing the growth of corrosion figures on the two surfaces obtained by cleaving, one surface being attacked longer than its counterpart (De la vault 1944b). This method has the advantage of being unaffected from accidental factors such as mechanical deformation, inclusions which cause disaggregation during attack and hence render the measurements of loss in weight of little value.

It should be noted that no precise measurements on the etch patterns were made and all the drawings were made by hand, and reports were chiefly directed towards the study of the quickness of attack on muscovite cleavages.

In the present work etching of muscovite was effected by two etchants (i) hydrofluoric acid (HF) and (ii) fused alkalies, sodium hydroxide (NaOH) and potassium hydroxide (KOH) and their mixtures with different proportions. A preliminary study on the etching by HF acid (Pandya and Pandya 1958) and a detailed report on the etching of muscovite by fused alkalies (Pandya and Pandya 1959) have already been reported. Independently and at about the same time Patel and Tolansky (1957a) reported the optical study on the etching of muscovite mica by HF acid by the techniques essentially similar to those employed in the present investigation.

The investigation of etch phenomena was taken up on the two varieties of muscovite mica (Andhra Pradesh). Although the etch patterns are essentially the same, the etching time required to produce almost identical matured etch pits are noticeably different. With the etching by hydrofluoric acid this is more noticeable as the etching ~~by hydrofluoric acid this is more~~ period is spread over a

number of hours, whereas in the case of etching by fused alkalies where the etching period varies from seconds to a few minutes, the difference is not quite appreciable. This variation of etching time indicates the compositional variation in mica. This aspect is not studied in detail in the present work.

In both the cases of etching, the experimental procedure for observing the etch patterns is the same and is given below.

Muscovite mica was cleaved and silver films were deposited on the freshly cleaved surfaces by the technique of thermal evaporation in high vacuum described earlier. The surfaces were examined under a microscope before they were subjected to etching. It is found from the observations that this practice of examination of cleavage surfaces before etching was not found essential and later on discontinued. The surfaces were cleaned by hydrogen peroxide and running water and exposed to etching by either hydrofluoric acid or fused alkalies. They were then examined under high power microscope objective at different stages of etching after cleaving and depositing silver films over them. All the recent optical techniques briefly described in chapter two were used to examine the surfaces. Both the surfaces

by cleaving
obtained/were compared after etching each time.

Acid Etchant:

The etching of mica was carried out at room temperature in the 40 per cent hydrofluoric acid vapour or liquid. Patel & Tolansky (1957a) have studied the etch attack by acid vapour. In acid vapour, very prolonged exposure for etching was found necessary to obtain the mature pits of the same size as those obtained by immersing the crystal in liquid acid for a shorter time. The difference in etching was one of degree alone and nothing else.

A typical photomicrograph of the etch pits produced on a freshly cleaved surface by dipping it in liquid acid for 20 hours is shown in figure 11 (X 212.5). The etch figure appears to be a parallelogram shaped cavity, the diagonals of the geometric figure being perpendicular to each other, so the parallelogram is a rhombus. The orientation of all the pits is the same. The pit corners like A are not strictly sharp but are slightly rounded, although the opposite corner is sharp. Note also the random distribution of etch pits.

Figures 12a and 12b (both at x 360) represent the same region of the specimen etched for 8 hours and 24 hours

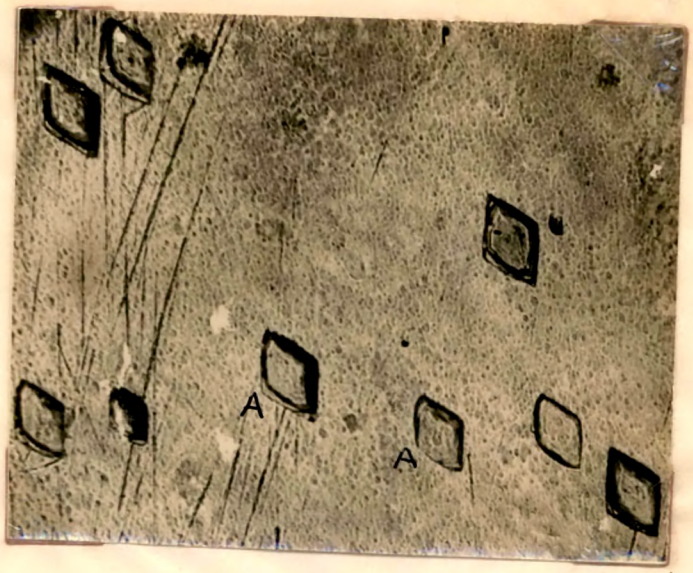
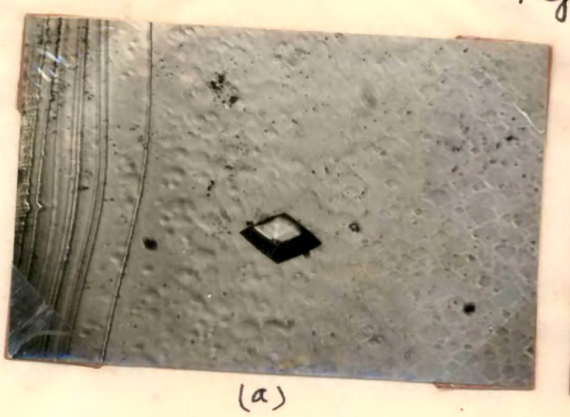


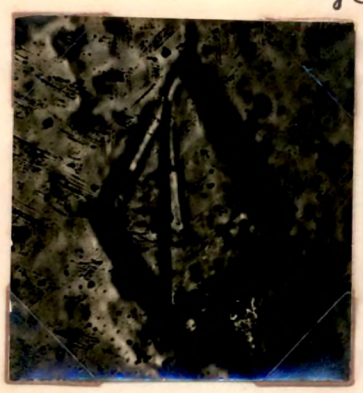
Fig (11) x 212.5



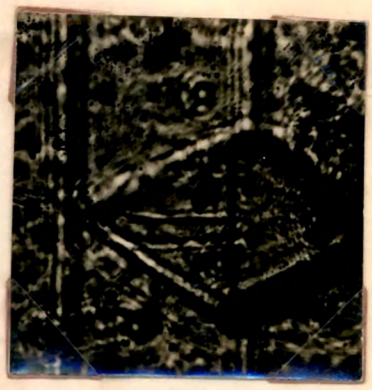
(a)

(b)

Fig (12) x 360



(a)



(b)

Fig (13) x 992

respectively. The cleavage lines which were there before etching were used as landmarks for locating the region. The figures show a set of cleavage lines and an etch pits. It is clear from the figures that the sharpness of the cleavage line which was observed before etching gradually decreases with the advancement of etching. Moreover, the increase in etching of the same region does not give rise to the increase in the number of pits but the etching figures that were formed at the start of etching began developing in length, breadth and depth. This goes on up to a particular etching time, (depending upon the concentration and temperature of the etchant) beyond which new pits begin to form and the existing pits begin to overlap each other. The etch pattern becomes complicated and it becomes increasingly difficult to arrive at a conclusion from a study of such patterns. The fact that the successive etching does not produce new pits, but the existing pits enlarge, suggests that these pits are located at some special defects in the crystal. This point is considered later on in deciding the origin of pits.

The increase in length and breadth of an etch pits is not accompanied by a proportionate increase in depth. In

fact, the depth of a pit increases slightly at first with etching but apparantly ceases to increase after a certain time and the lateral development of the pit goes on with increase in etching time. This is clearly shown by the quantitative studies made on the pits by the precision multiple-beam-interferometry and light profile microscopy, and is reported later on. On the consideration of depth, the larger pits can be classified as being of two types: (i) flat-bottomed and (ii) point-bottomed. In the former case the depth is approximately uniform in the pit, whereas in the later case the depth changes at various points, increasing from the side to the pyramidal point.

The photomicrographs also show that the whole surface is attacked, has become rough and is covered with smaller pits the density of these pits ($\sim 4 \times 10^6$ cm^2) being greater than those of larger etch pits. From the beginning of the initial etch attack, the smoothness of the surface has disappeared, and the degree of roughness of the surface increases with the enhancement of etching. It is reported that cold acid has no sensible effect on the mica over a considerable period of time (De la vault, 1942) but the present study has indicated that it is affected by the cold acid at room temperature from the very beginning and if the specimen is kept in the acid for few hours, the effect

is markedly visible under a low power microscope. That the muscovite is etched from the beginning is shown by the roughness of the surface. A multiple-beam-interferogram over such a surface clearly shows this character. It is more vividly revealed by the application of thin film technique (Tolansky & Omar 1952b). The etched specimen becomes more brittle with the etching and after a certain time depending upon the thickness of the specimen, the surface becomes so brittle that it could not be handled.

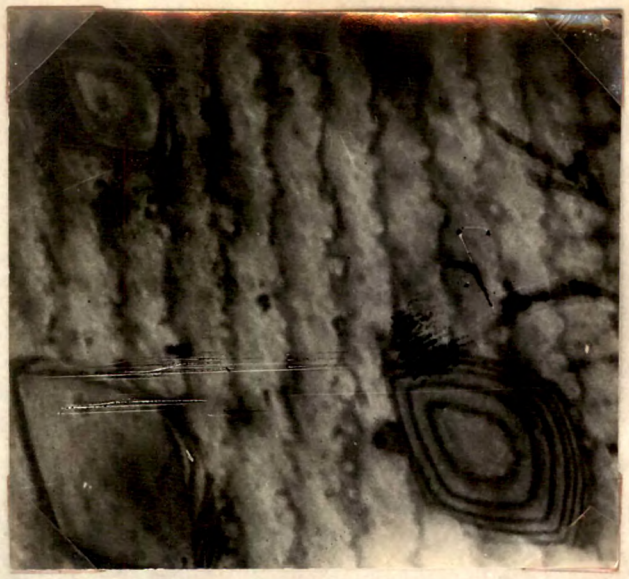
Unlike the etch figures of figure 11, the pits shown in figures 12a and 12b are very sharp in outline. This is because of the slow rate of etch. This point is very important in the study of etching of crystal surfaces, because with the increase in etching, the patterns become complex and the very features, sought for study, are obliterated and hence no useful information can be secured. In some cases advanced etching is intentionally used to bring out clearly certain surface features.

Thus the photomicrographs (figures 12a and 12b) show that the etch attack on cleaved muscovite gives rise to (i) the general etching of the crystal surface covered by smaller pits and (ii) randomly dispersed larger pits, some of them being (a) pyramidal and others, (b) flat-bottomed.

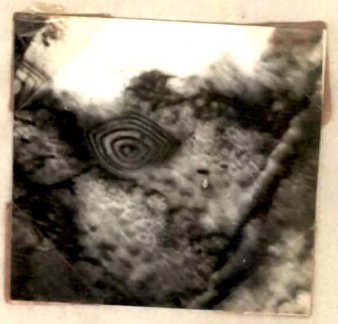
Measurement of the depth of etch figures:

For measuring the depth, recourse is made to the powerful techniques of light profile microscopy and multiple-beam-interferometry. Figures 13a, 13b (X 992) show profile pictures taken on an etch figure. The depth of the pit is measured along its major and minor diagonals. They are respectively 2 and 2.2 μ.

At the hands of an expert, multiple-beam-interfero-metry is a sensitive tool for revealing quantitatively steps of the order of atomic diameters. The present author has occasionally used this technique to measure the etch pit depth. A multiple-beam-interferogram over an etched surface of mica (etching time 20 hours) is shown in figure 14a (x 44). It ⁎ not only gives the depth but also the roughness or smoothness of a surface is elegantly indicated The coarse nature of the fringes and the nature of the surfaces interposed between the fringes clearly show how mottled a surface becomes on etching. This matt character is observed from the beginning of the etch attack. In the initial stages of etching, this feature is not readily observed by multiple-beam-interference pattern observed under a low power objective, but it was very nicely disclosed by the application of thin film technique (Tolansky and

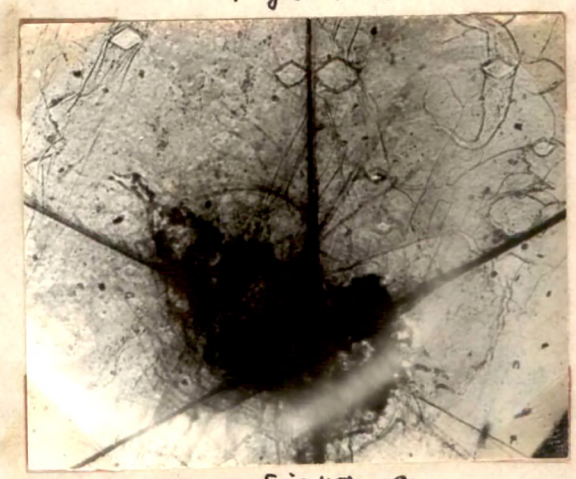


(a)

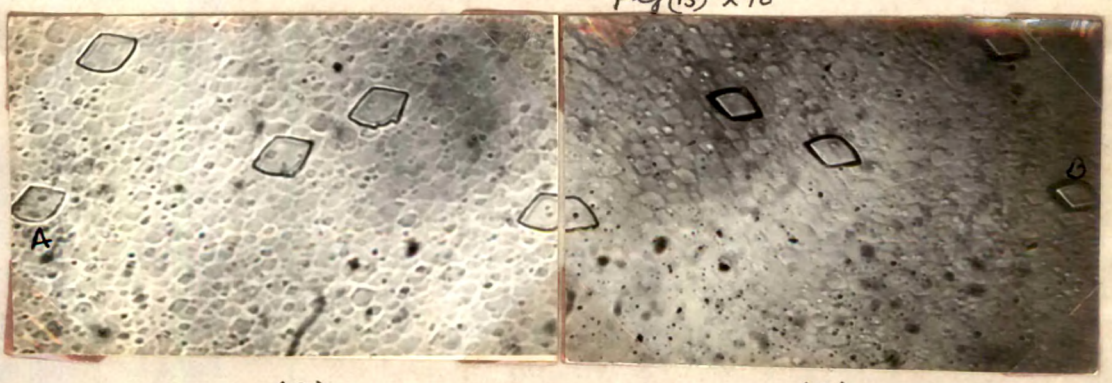


(b)

Fig(14) x 44



Fig(15) x90



(a) (b)

Fig(16) x 170

and Omar 1952). The depth to which a pit descends is calculated by counting the number of fringes in a pit and multiplying it by $\lambda/2$ where λ is the wavelength of green mercury light (5410A). They are 1.6 μ and 0.8 μ respectively. A high dispersion multiple beam interferogram over an etched figure is shown in figure 14b (x 44). The depth of the etch figure is 1.6 μ. Many such interferograms were observed and in fact the quantitative data reported later on were based on the utilization of this and the light profile technique. From the studies it is observed that the depths of all the etch pits are not identical and the variations in depth among them could not be correlated. This suggests that the imperfection that is associated with pits is not equally distributed in depth on the surface.

Orientation of the etch figure:

The orientation of the etch pits with reference to the percussion mark has been determined. Percussion mark was produced by a dull-pointed and on the freshly cleaved surface which was then etched. To compare the effect of the blow, it was also produced on an etched specimen which was then re-etched for a smaller period. There was found to be no change in the percussion mark, but in the latter case the surface becomes more rough and

distorted. The etch pits have their short diagonals parallel to the stronger ray of the percussion figure (figure 15, x 90) which in turn is parallel to the plane of symmetry, the b-pinacoid. Thus with the help of the etch figure, one can ascertain the plane of symmetry of the crystal devoid of external crystalline shape.

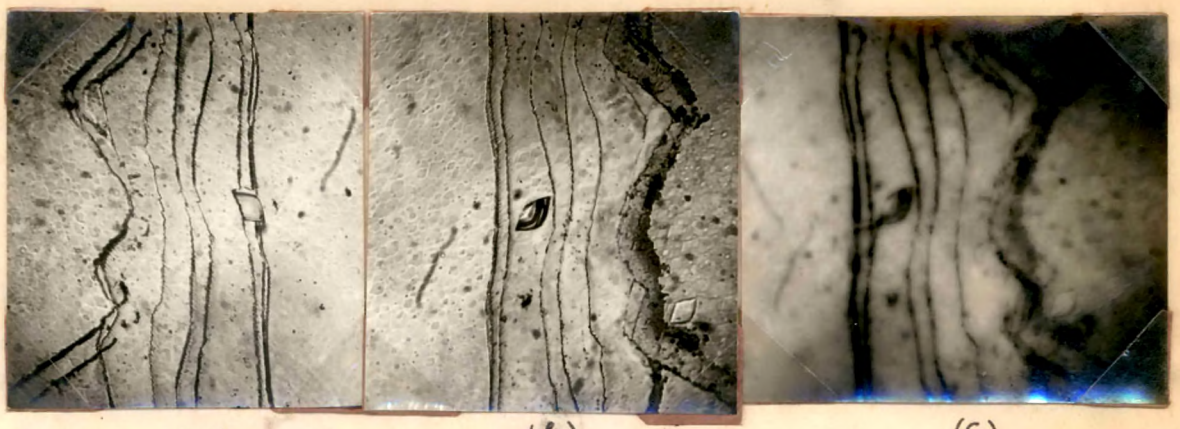
Matching of the Cleavage Counterparts:

It is reported on the section of the study of muscovite cleavages that the cleavage patterns on the two counterparts obtained by cleaving a crystal are identical and in particular the set of cleavage lines observed on one face is completely reflected in shape and position on the other. In order to examine the effect of etching on the results so far obtained from the studies of the unetched virgin cleavage surfaces, etching studies of the cleavage counterparts were taken up. The experimental procedure consists in subjecting simultaneously the cleaved counterparts to the etch attack of HF acid at room temperatures (i.e. from 30°C to 33°C). After a definite duration of etching time, the same area on both the counterparts was studied. Several samples were observed and similar features were observed in all cases.

Figures 16a and 16b (both at x 170) show the same

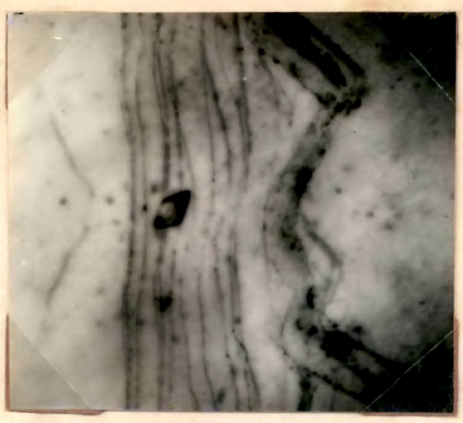
area of cleavage counterparts etched for 20 hours. They consist of pits which have complete correspondence on either surface and the number and location of etch pits has not changed. One important point to be noted is that rounding of a pit corner, shown at A (figure 16a) is oppositely oriented to that of the corresponding pit in figure 16b shown at B. This feature is brought out only because of some advance etching. Otherwise the pits being fairly symmetrical, low etching would not have disclosed this point but would have shown the patterns as mirror images of each other. Moreover, the sizes of the corresponding pits on both the pictures are somewhat different. Although, both the parts were simultaneously exposed to etching, the reason of unequal sizes which is obviously due to unequal etching is not quite clear. Out of the several paired samples examined, some samples did show this point, the representative of which is shown above. Such paired samples were rejected for quantitative measurements to be reported later on and only on those samples which show the pits to be identical so far as the outward shape is concerned, measurements were made.

Figures 17a and 17b (both at x 170) show the etched cleavage counterparts with set of cleavage lines and pits, the etching time being 10 hours. A close examination



(a) (b) (c)

Fig (17) × 170



(17d)

(18a)

(b)

(c)

Fig (18) × 170

of the two pictures will at once show that with the appearance of cleavage lines on the pictures, the matching picture is not so simple as it was with the above pictures, figures 16a and 16b, depicting the pits. In figure 17a the etch pit is between the first two cleavage lines on the right hand side, while the same etch pits (figure 17b x 170) is found to be between the second and the third cleavage lines on the left hand side of figure 17b. This indicates the possibility of the movement, on etching, of either the cleavage lines or the pits. These are discussed in detail below. The location of etch pit on the extreme right in figure 17b is also of interest. The corresponding pit is not found in figure 17a. This is the feature found common in many paired samples examined by the author. Patel and Tolansky (1957b) have dismissed the occurence of such pits by saying them as 'rogues', but the present author feels that by calling them as 'rogues' the existence of such pits could not be accounted for. One possible explanation for this is that the imperfections existing in the crystal are not properly distributed throughout the volume of the crystal and the pits may not be associated with the line defects. The presence of line defects, notably dislocations, implies their equal distribution on either of the matched counterparts and their subsequent

-ance
appear/by etching and hence complete matching will be secured. Since the pits were not matching in all cases even though some of them might be at dislocation sites one could only say that the etchant is not a suitable one so as to discriminate between the various defects by revealing them as etch pits.

Figures 17c and 17d represent the superimposed pictures of 17a and 17b x in two possible ways. In figure 17c, the cleavage lines exactly coincide with one another giving rise to the displacement of the etch pit along the direction of the major diagonal, whereas in figure 17d, the pits were made to coincide so that a shift in the cleavage line is seen. Successful attempts have been made to differentiate between the two possibilities. For deciding this, it is imperative that there should be some fixed mark which is unaffected by etching. This fixed mark may be a small hole penetrating both the matched region or a scratch on a crystal surface or a cleavage line on the
the crystal which is intentionally unexposed
rear face of/either by etching one side of the crystal in vapour or by immersing the crystal in the etchant in which case the rear face was coated with a thin layer of wax. After etching the wax was removed by placing the crystal in boiling hot water for sometime and then washing it with lukewarm water and dried.

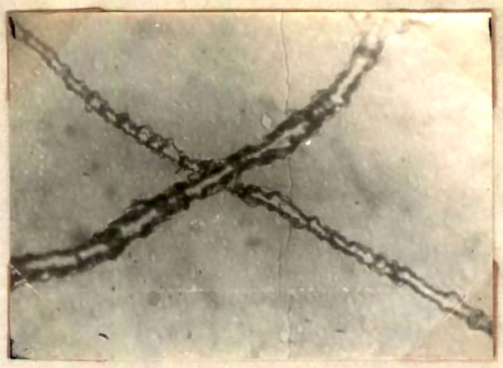
It is already shown that the act of cleavage through the crystal does not change the position nor the shape of the cleavage pattern. Thus a cleavage line is unaffected by the process of cleaving and hence it can be used as an ideal landmark for determining the two possibilities created by etching.

Experiments were made by using both the fixed marks, viz., a scratch in the matched regions (or a small hole in it) and a cleavage line in the rear unetched face.

The fiest set of experiments consists in producing a scratch on the etched specimen which was then re-etched for a shorter period and the patterns in the two cases were compared. Although, the procedure for scratching the crystal and then taking the scratch mark as a fixed one is apparantly objectionable, as it induces local deformation. Even then it is adhered to because of the fact that these very experiments are helpful in deciding the origin of etch pits.

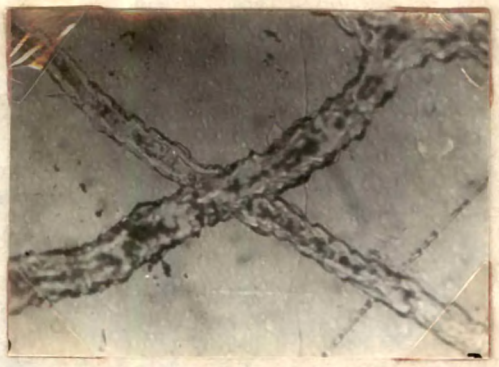
Figure 18 a (x170) represents a region consisting of pits produced by dipping the specimen for 10 hours and a scratch made by a needle. The same region is re-etched for a further smaller period of six hours and is shown in

figure 18b. Figure 18c is the composite picture secured by superimposing figures 18a and 18b. The result is very evident from the figure. Although a local deformation is caused the pits do not change their places, but are simply enlarged due to further etching. The scratch is also etched and widened. Furthermore, the same figure shows crudely (a finer proof is afforded later on), that the centres of the pits had not changed and therefore in the present case the pits remained stationary on etching and even on the exertion of local deformation in their vicinity. Also note that no appreciable number of new pits have been created due to scratching. This result, along with the fact that the sharpness of a cleavage line before etching decreases with increasing etching (which appears to be due to unequal etching along the cleavage line), leads one to conclude that the etching affects the cleavage line appreciably and makes it to displace from its original position. This is also shown by the photomicrographs of figures 19a, 19b and 19c(x 170). Here in the etched specimen, two scratches were made by a needle in such a way that a portion of the cleavage line is intercepted between them and in effect with the scratches forms a triangle. Mark also the position of the pit on the right hand side of the figure and on the upper part of the scratch. The further etching for six hours (figure 19b)



(a)

Fig (20a) x 70



(b)

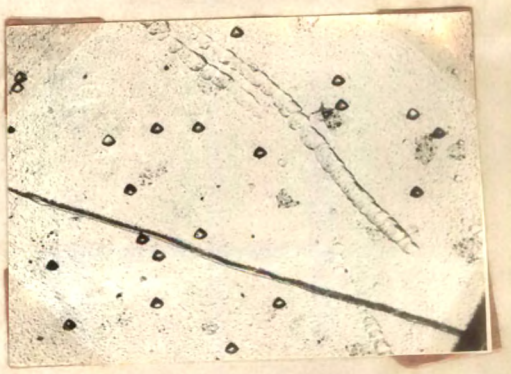
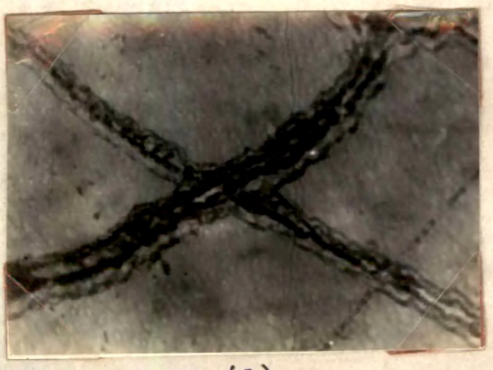


Fig (20a) x 90



(c)
Fig (19) x 170

Fig (20b) x 750

simply widens the scratch and enlarges the pit. On superimposing the two pictures so that the centres of the scratch lines coincide exactly as far as practically possible with one another it is observed that there is a shift of cleavage line (figure 19c) and the location of the etch pit has not changed. The centre of the etch pit has not changed. Although, this - the last point - is not rigourously verified in this case, a separate precision experiment was conducted to examine this point. In this experiment a sharp cleavage line on the rear unexposed and very thin mica crystal was taken as a reference line. The mica crystal selected was a very thin one so that the regions of interest consisting of a cleavage line in the front and back surfaces can come simultaneously in focus in a medium power objective. The surface was observed every time after etching, for 10 hours, 16 hours and 22 hours and it was observed that the centres of the pits remained stationary and that the line had moved.

All these experiments indicate that etching of a cleaved mica crystal induces the displacement of cleavage lines and steadiness of the pits. Now next point is to decide whether the movement is parallel or not. For this, the figures 17a, 17b and 17d and also figures 19a, 19b and 19c are subjected to severe examination. In figures 17a or 17b the first two cleavage lines are somewhat curved ~~straight~~ and the

rest of the lines are curved with a variable curvature. From figure 17d which represents the matched regions of figures 17a and 17b so that the pits exactly coincide it is apparent that the movement is not parallel, the first two lines run approximately parallel, whereas the rest of the lines are unparallel, to the corresponding lines on the other counterpart. Since some of the lines are curved, the orientation of the lines is also a determining factor.

The composite picture of figures 19a and 19b which show the same region etched for 10 hours and for a further period of six hours, suggests that for straight cleavage lines the movement is approximately parallel. It is found that for a segment of the cleavage line such as that in figures 19a, 19b and 19c, the displacement is nearly parallel but if the measurement of the displacement is spread over a considerable length it is found that the displacements are variable indicating that the shift is not completely parallel. Further discussion of these points is taken up later on.

Fused Alkalies as Etchants:

Etching of cleavage surfaces of muscovite were also studied by subjecting them to the action of fused alkalies at higher temperatures, for NaOH the temperature being 330°C to 500°C and for KOH, 370°C to 500°C. Etching was also studied

at intermediate and lower temperatures. It will be seen from the following study that all the observations made by using HF as an etchant are exactly reproducible barring the fact that the etch pits are triangular in shape and hence the obvious difference in the quantitative measurements.

De la vault has also studied the etching of muscovite by alkalies (1944a, 1946b). His observations (1944a) show that sodium hydroxide reacts more vigorously than KOH at the same temperature, but gives a more rounded figure. Furthermore the figure produced by bases seem to be oriented inversely to those given by HF. All of the figures also appear to be derived from the fundamental hexagon. He has also used various mixtures of NaOH and KOH(1946b) and studied the rapidity with which the reactions took place. The mixtures of NaOH and KOH, (with different proportions) etch out 0-42 μ/min. from muscovite at 350°C whereas the same reagents dehydrated 5 minutes at 750°C etch out 2-3 times as much. At higher temperatures ($\sim$ 700°C) potash cake dissolves the muscovite much more rapidly. This shows the influence of temperatures to be much more than the activity of mixture at 380°C. During these studies it is observed that the resistance of muscovite to etching is greater than that of the phlogopite. The etch figures produced by sodium hydroxide are elongated isoscales triangles whereas those produced by potassium hydroxide were

flattened isoscales triangles. In contrast to his earlier assertion (1944a) no hexagonal patterns were observed.

In the present investigation, the work which was started by using HF as an etchant has been extended with other etchants, notably fused alkalies, for comparative study.

To etch the crystal at higher definite temperatures an electric oven or furnace is required. For this purpose, a horizontal rectangular muffle furnace manufactured by Wild Barfield Electric Furnaces Ltd., Watford, Herts, is used. It consists of:

(i) the muffle, with lead outs and connections in the rear, spring-loaded door and protective atmosphere.

(ii) temperature regulator, comprising an energy regulator control unit.

(iii) temperature indicator in the form of a thermo-electric pyrometer designed for mounting separately from the muffle and together with associated thermocouple and compensating leads, and

(iv) safety devices.

As the crystals were to be etched at particular fixed temperature, it was necessary that the divisions and scale markings on the control knob were first calibrated in terms of the pyrometer readings by trial and error. Sodium hydroxide, potassium hydroxide (and mixtures of the two in varying proportions) were used as etchants. Sufficient quantity of the etchant was first heated in a nickel crucible to the required temperature. The crystal to be etched was then dropped inside the fused mass at the steady temperature and was removed from the etchant soon after the required etching time was over. It was then transferred to a small dish containing concentrated nitric acid which removed the solidified melt from the surface leaving the crystal very clean. It was further cleaned with the usual reagents and then silvered for microscopic examination.

It was noticed that when the melt was previously used for some period for etching in the etching experiments at a particular temperature and if the same melt was re-used at the same (or lower or higher) temperature, the effect of the melt in producing the etching was found decreased to a marked extent. This meant that due to chemical reaction the etchant was completely or to a greater extent used up in the previous etching and hence it could not show the full etching action

again. This could be seen by a simple experiment. A crystal was cleaved and one of the cleavage counterparts was etched at a fixed temperature for a definite time (5 seconds). Then some four more crystals were etched. The remaining counterpart is now etched for the same time (five seconds). After the appropriate cleaning, matched regions on both the counterparts were studied under high power microscope. It is found that the one surface which was etched first - showed very large pits as compared to those observed on the last etched counterpart, showing thereby the differential chemical reactions although the specimens were given the same treatment, viz., etching time and temperature were kept the same. In order to avoid this ambiguity, the crystals were always and every time etched in a fresh quantity of the etchants, sodium hydroxide, potassium hydroxide and the mixture of the two in various proportions at different temperatures.

To carry out the study, the specimens were etched by immersing them in fused alkalies, viz., sodium hydroxide and potassium hydroxide in a nickel crucible, the range of temperatures being 330°C to 500°C for sodium hydroxide and 370°C to 500°C for potassium hydroxide and etching times varying from a second to about two minutes. They were examined under high power microscope at different stages after cleaning and depositing silver films over them.

As reported earlier on the etching of muscovite by HF acid, here also the etch pits can be classified into two groups.:-

(i) micropits developed at random over the whole surface. The concentration of these pits is of the order of 6×10^6 per cm^2.

(ii) large localized isolated pits of which some are pyramidal and some are truncated or flat-bottomed.

Figure (20) x 70 shows the results obtained by etching with sodium hydroxide at 340°C, whereas figure (21) x 90 represents the same with potassium hydroxide at 370°C. In the figure (20a) x 750 is shown the initial stage of etching by fused potassium hydroxide. All these figures clearly show the different types of pits, these being elongated isoscales triangles in case of sodium hydroxide etching and short isoscales triangles resulting from the action of potassium hydroxide.

These elongated isoscales triangular pits are strictly oriented with their medians to the base parallel to the pinacoidal direction. Figure (22) x 90 shows this orientation with reference to the percussion marks obtained

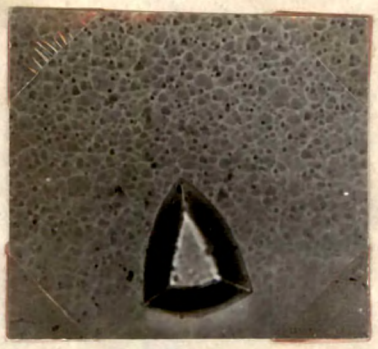
in the usual way. The stronger ray of the percussion star which is parallel to b-pinacoidal direction and the triangles are situated as seen in figure (22) x 90. This should be compared with the orientation of the pits produced by HF acid and is shown in figure (15) x 90, where the shorter diagonals are parallel to the b-pinacoidal direction.

The etch pits in case of alkalies are triangles as opposed to parallelograms for hydrofluoric acid and the shapes of the triangles due to sodium hydroxide and potassium hydroxide are apparantly different. For the pits due to sodium hydroxide and potassium hydroxide etc., respectively, the vertices are on a isoscales triangle with equal angles of 65°, and 50° respectively as shown in figures (24)x 360 and (25) x 360 respectively. Thex sides are rounded as seen in these figures. Etch figures obtained by using mixtures of the alkalies in varying proportion are isoscales triangles intermediate between the above isoscales triangular etch figures.

Figures (23a) and (23b) x 992 and (23c) x 992 show different types viz., the first two being flat-bottomed and the third one being pyramidal etch pits with profile microscope; their depths are 4.3 μ, 2.3 μ and 0.5 μ respectively. It should be noted that figures (23a) and (23c) consist of distinct steps. This phenomenon is usually ~~xxxxxxx xf~~

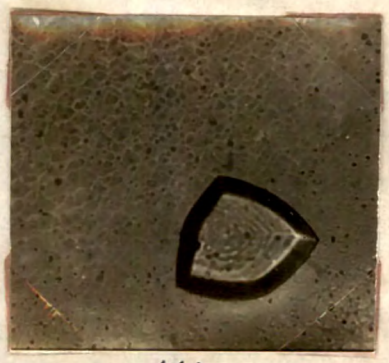
Fig(21) x 90

a



(a)

(b)

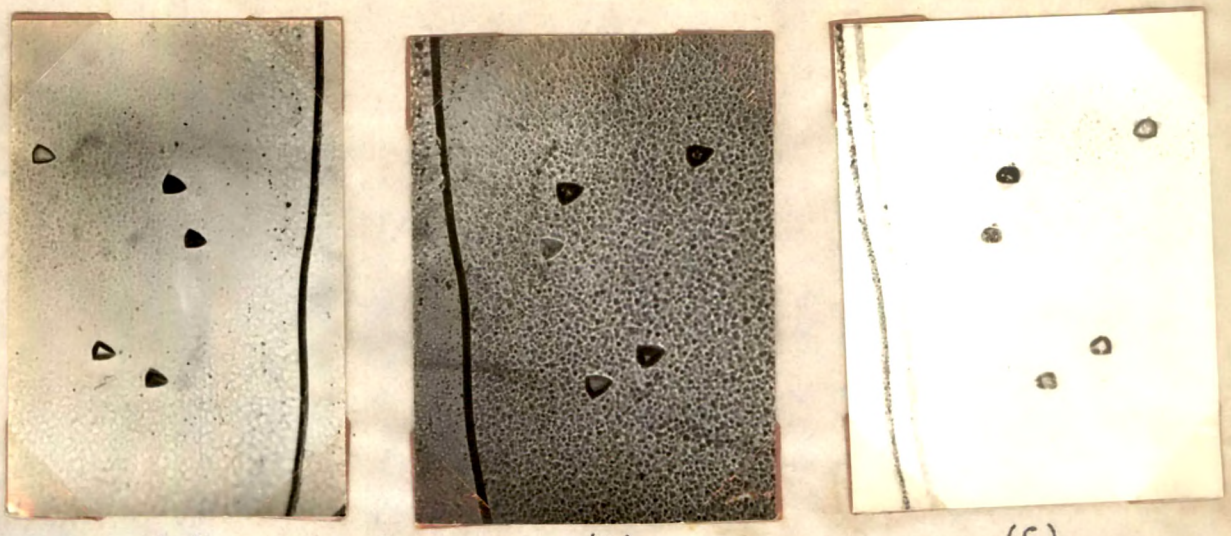


(b)

Fig(22) x360

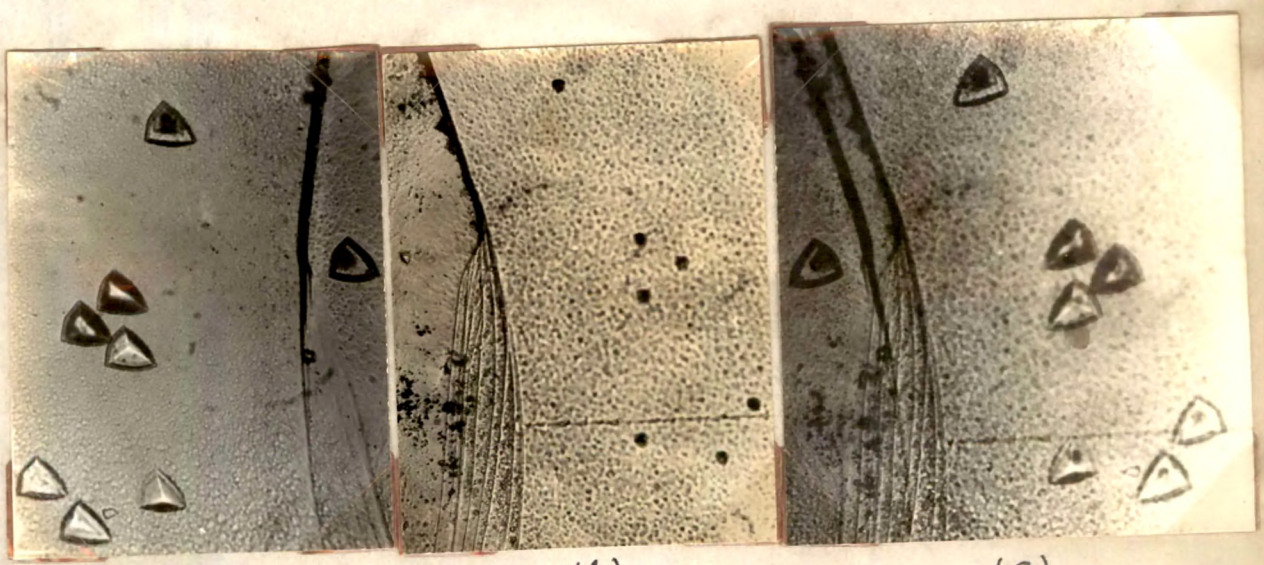
(c)

Fig(23) x 992



(a) (b) (c)

Fig (24) x 360



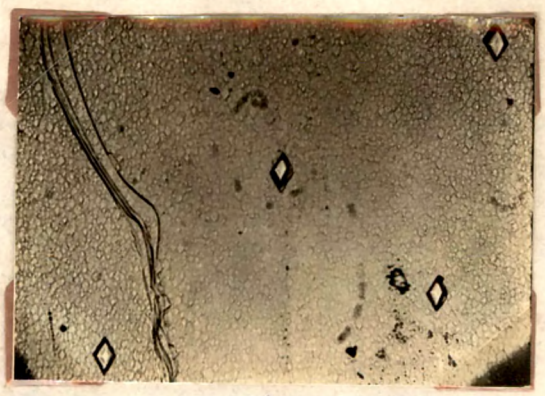
(a) (b) (c)

Fig (25) x 360

observed in pits on crystal surfaces, the pits being formed due to advance incremental etching. It appears that the step have no quantitative connection with each other and are apparently randomly formed. Such step like structure is also observed in pits produced by hydrofluoric acid.

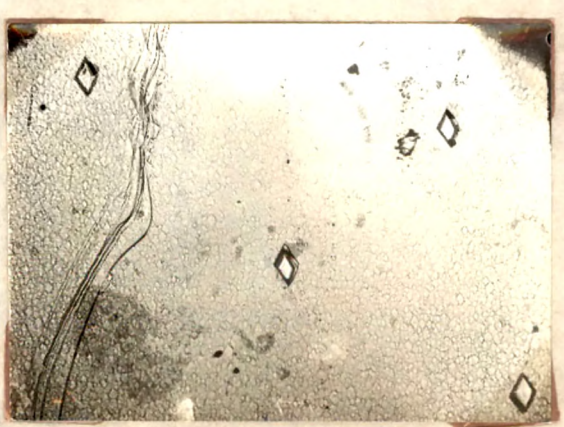
Figures (2ϕa) x 360 and (2ϕb) x 360 show the matched faces etched by sodium hydroxide at 360°C for five seconds. Figure (2ϕc) x 360 is obtained by superposing the negative of the two faces one over the other. This clearly shows that there is a perfect matching of the pits but the cleavage lines are displaced. The orientation of these pits on the two faces are also opposite and not exactly like mirror images and this is expected since the cleavage faces oppose each other. This point was not noticeable in the case of matching by hydrofluoric acid as the pits were symmetrical (when the etching rate was low). The experiments already reported to decide the occurrence of either the cleavage line displacement or pit shift are also performed here by drawing a scratch over it. A cleavage line on the back surface could not be used as a reference fixed mark as it was difficult to prevent it from etching, since to etch the specimen it was necessary to dip it in the fused etchant. For preventing the back surface from etching, an experiment was, however, tried without much

success. In this experiment the specimen to be etched is placed on a pyrex glass plate with the surface, to be prevented from etching, facing the glass plate which was kept at a temperature corresponding to the etching temperature and the fused mass of the etchant was poured over it. Although etching takes place only on the front surface, yet the glass plate (which is also attacked), being hot, requires some time to come to room temperature, this cooling period being enough to bring about the sufficient advance etching which makes the measurements on individual pits to be of little value. However, a simple experiment is performed which consisted in studying the V-shaped cleavage lines on the matched counterparts through the successive stages of etching. In the earlier studies on cleavage surfaces of muscovite , it is shown that such lines are not very frequent and hence number of samples were, therefore, required to be cleaved to obtain such lines. It is an established fact (Tolansky 1948) that the cleavage lines on the matched faces represent elevations and depressions respectively. In the present case, V.shaped line is an elevation on one face and a depression on its counterpart. If the cleavage lines displace on etching it is expected that elevation will go on dissolving and finally annihilate with the surface whereas the depressed region will become wider and wider on successive etching. This did happen on the cleavage surface of muscovite (an also on calcite to be described later on)



(a)

(b)



(c)

Fig(26) X 360

etched by fused alkalies, and thus confirmed the earlier observations on the shift of the cleavage lines on etching.

The results arrived at were indeed the same as those already obtained in the case of matching of faces etched by HF acid. The etching by fused potassium hydroxide of the matched cleavage counterparts leads to the identical results.

Figure(25a) x 360 shows one face etched by sodium hydroxide at 360°C and figure (25b) x 360, the counterpart etched by potassium hydroxide at 400°C. Figure (25c) x 360 shows the print obtained by superposing the two negatives for comparison. There is one-to-one resemblance with regards to the pits but the cleavage lines have moved.

Figure (26a) x 360 illustrates one face etched by 40 per cent hydrofluoric acid whereas in the figure (26b) x 360 is shown the counterpart etched by sodium hydroxide. Figure (26c) x 360 is a print obtained ~~sodium hydroxide~~ by superposition of the two figures (26a) and (26b). Again there is a point-to-point correspondence with regards to the number and positioning of etch pits but a shift of the cleavage lines is seen.

Some typical measured depths on an interferogram are 1.35 μ to 2.16 μ obtained by counting the number of

fringes in the pits and multiplying them by $\lambda/2$ where λ for the green mercury light is 5461A.

Cleavage Shift and Etch Pit shape:

It is qualitatively established that on etching cleavage line is displaced and the pits remained stationary. No such displacement on etching is known for slip and twin lines. Cleavage shift on etching is therefore the characteristic and distinguished property of the cleavage lines. Attempt is now made to have a quantitative estimation of the displacement and its correlation with the etch pit dimensions.

Table I gives the dimension of the parallelogram shaped etch pit, its depth, and the shift of the cleavage, whereas Table II shows measurements on the isoscales triangular etch pits produced by sodium hydroxide at 360°C.

TABLE I

(Etchant 40 per cent Hydrofluoric Acid)

Side in cm.	Diagonal in cm.		Shift of cleavage line parallel to etch pit	Variation of shift	Depth of the pit, cm
	Long	Short			
2.57	4.40	2.65	4.25	4.25 - 2.8	0.75
3.25	5.50	3.45	5.40	5.4 - 3.5	0.83
3.79	6.65	3.70	6.62	6.62 - 3.9	0.87
5.47	9.15	6.00	9.02	9.02 - 6.2	0.90

TABLE II

(Etchant Sodium Hydroxide at 360°C)

Sides of etch pit in cm.			Length of the medians in cm.			Variation in Movement of cleavage line in cm.	Depth in cm.
a_1	a_2	a_3	M_1	M_2	M_3		
1.70	1.71	1.44	1.54	1.33	1.31	1.35 - 1.43	0.30
1.89	1.91	1.49	1.74	1.40	1.42	1.40 - 1.72	0.36
2.12	2.11	1.71	1.86	1.59	1.60	1.72 - 1.95	0.40

All measurements are shown at x 1800. They were made by comparator and by enlarging the negatives. In Table I cleavage shift is measured parallel to the long diagonal. The variation column indicates variation of measurements along the length of the cleavage line. Sizes of most of the pits were more or less equal, but there were appreciable variations in depth of the pits and hence depth measurements could not be relied upon. The measurements on the depth shown in the table represents the average depth.

It will be seen from the tables that accurate correlation between the cleavage shift and etch pit shape could not be predicted. Patel and Tolansky (1957a) have reported the shift of the cleavage line roughly corresponding to the

major diagonal of the pit. Measurements spread over the length of the cleavage line shows variation in displacement which was correlated by them with the values of the major and minor diagonals, taking into account the orientation of the cleavage line. The present observations show the general agreement.

From table II the cleavage displacement could not be correlated with any of the etch pit dimension. Tolansky and Patel (1957b) reported that the shift of the cleavage is equal to the side of a triangular etch pit.

The present author is of the opinion that it is premature to conclude from a number of observations obtained from a study of only one or two crystals. One should consider the fact that etch pits observed on crystal surfaces have various shapes ranging from a three sided geometrical figure to a six sided one, with various degrees of symmetry. Moreover, it is known that the shape of an etch pit depends upon a number of factors (time, temperature etc.), and in particular it is related with the symmetry of the crystal face. It is also important to know the entity with which the orientation of the cleavage line is considered. This should be thoroughly investigated with etch pits obtained on crystals showing very high (and also low) degree of symmetry. Before arriving at a definite conclusion from a

study of only one or two crystals, it is therefore worthwhile to study the shift on a number of crystals belonging to different crystal systems and its relation to the shape of an etch pit on these crystals.

Consideration of all these factors leads the author to think that these few observations are quite inadequate to arrive at a definite conclusion.

Discussion:

De la vault has carried out extensive work on the etching of all types of mica crystals from the chemical aspect of noting the quickness of attack of the different etching reagents and their mixtures. He has given a number of diagrams for the etch figures.

The triangular pits are expected with fused alkali as etchants, as pointed out by De la Vault (1946b). Although, it is known that potassium hydroxide is usually more caustic than the sodium hydroxide,it is observed in the present case that fused sodium hydroxide is having a faster reaction than potassium hydroxide. This could be explained on the chemical reaction on different atoms in the crystal. The temperature of an etchant is an important factor for the quickness of reaction and a separate experiment to study this effect was carried out. In one case etching was

carried out at a lower temperature for longer time and the other counterpart was etched at a higher temperature for a shorter time. The one etched at higher temperature showed faster reaction by way of larger etch pits. Higher temperature also effects the shape of an etch pit. It should be noted that from the beginning of etching all the pits obtained by fused alkali etchants, are curvilinear in outline, however, small the period of etching may be. Tolansky and Patel (1957), while studying the etching of octahedral faces of diamond in fused potassium nitrate have established that the rectilinearity of the pits formed on diamond depends in a sensitive manner on the temperature and rate of etch. The present author is of the opinion that this should be true not only for diamond, but also for all crystals requiring etching at high temperatures and as such he has carried out experiments on etching of mica by fused alkalies at lower temperatures. The melting points of NaOH and KOH are respectively 318.4°C and 360.4°C. Below this it is a solid mass. Caustic soda and potash in this experiment are employed in the form of powder. The etchant (NaOH) was kept at a temperature of about 100°C and the cleaved muscovite was placed in the middle of the thick layer of powder. It was kept for etching for 20 hours. The muscovite was then taken out and after appropriate cleaning

cleaning was thickly silvered for microscopic examination. Beautiful triangular pits having the sharp rectilinear outline were found on the surface. Although the alkali was in the form of solid powder, it preserved its caustic property at that temperature and reacted with the crystal. This is also found at still lower temperature, but in these cases the etching time was increased from few hours to several days. Encouraged by these results, the author extended these experiments at room temperature. A strong concentrated solution of the alkali (sodium hydroxide) was prepared at room temperature and the cleaved muscovite was immersed in it. After about a month, the specimen was taken out and properly cleaned and after depositing very thick silver film, it was examined. This also developed extremely small sharp triangular pits. Potassium hydroxide also gave similar results. The increase in etching period from a few seconds to several days with decrease of temperature from about 320°C to room temperature, is thus very marked.

These experiments show that the shape of an etch pit is determined by the rate of etching. The pits can be arbitrarily produced either of rectilinear or curvilinear outline. Moreover, after a certain temperature the shape of etch pit becomes curvilinear permanently, however, small etching

period is taken. But below that temperature, the pit shape is governed by the etching time, being sharp at low etching and curved at some corners with advanced etching.

The presence of flat bottomed pits indicates that the imperfections existed only upto the base and hence the reaction is not penetrating further preferentially but the attack is more on the sides. The etching on both faces of the same thin piece of mica show that there is no relation between the two and the number of pits and their locations are different in the two cases. This suggests that the imperfections associated with the pits are not much extended in depth. In one of the specimens studied, it was observed that larger etch pits were aligned themselves in a line. This observation suggested that the pits might be at dislocation sites, and accordingly in the preliminary report (Pandya and Pandya 1958) this possibility was hinted upon. Since such alignment of pits was observed on only one specimen, it was thought desirable to carry out detailed study on this and other samples. Subsequent detailed experiments conducted to check this result and thereby to detect dislocations and their movements gave negative results which led the author to suspect that the alignment of pits in a row might have been due to the etching of a crack or scratch in the crystal, formed possibly during the act of cleavage. This

point amply guards one against arriving at a hasty conclusion in etching experiments.

It is well-known that dislocations are responsible for the plastic deformation of crystals and as such the application of a sufficient amount of stress should therefore usually result in the movement of dislocations. If each pit represents a dislocation intersecting the surface, movement of dislocation should produce the movement of the etch pits on the strained crystal surface etched further for a smaller period of time, giving rise to new small pits near larger pits. Such movement is observed on other crystals (see, for example, Gilman and Johnston 1956). To achieve this, bending experiments were performed on mica crystals. Many workers have reported the bending of mica crystals to study the plastic deformation. Gross (1924a,b) studied the atomic structure of deformed crystals, particularly mica and rocksalt, in their reaction to the process of work-hardening and observed the bending of mica to be purely elastic. X-ray spectroscopic study of the bending of mica crystals by the use of Johann's spectrograph (Vainshatin et al, 1940) has been made to determine the mechanism of deformation. Their observations show that bent mica acts as a row of small crystals located close to each other. Plastic deformation of mica crystals has also been studied by investigating their surface structure by means of a monochromatic X-ray beam (Gogoberidge and Flerova 1940).

Their findings indicated the presence of twinning. None of the observations give any conclusive evidence regarding dislocations. This may be due to the fact that the idea of dislocation at that time was not firmly established and therefore did not receive serious attention of the workers and hence the investigation of plastic deformation from that point of view might not have been carried out. In the present investigation bending experiments together with double etch technique have been undertaken to locate and detect the dislocations and study their movements if any. Freshly cleaved mica crystal was etched for 8 hours in case of hydrofluoric acid etching and for 2 seconds by fused sodium hydroxide at 360°C and it was then bent by keeping it in between the gap of a V-shaped fork, one side of which is capable of movement by a screw so that the distance between the free ends of the fork can be altered, thereby inducing a change in the curvature of mica crystal. Decreasing the gap by the screw increases the curvature. After this treatment the crystal was re-etched for a smaller periods of 4 hours and 1.5 seconds respectively. The etch pits in the area of interest were then critically examined to observe their movement if any. Several pieces were used in this experiment and the bending was progressively increased so that the specimen was on the point of rupture. Even then no movement of the pits was observed. Another

experiment based on the matching of cleaved counterparts was also performed in which one surface was directly etched for the specified period and the other was given bending treatment in the same way as above and was etched for the same period. The two counterparts were then studied. This showed the perfect matching of the pits and the movement of the cleavage lines as reported earlier. It should be recalled that in the earlier experiments on matching a scratch was used to decide the movement of cleavage line or etch pits on etching. It was also remarked that no appreciable number of new etch pits were formed. Such a scratched specimen was also subjected to bending as mentioned above and was sunsequently etched. The observations disclosed no movement of either the new or old pits. All these experiments indicate that etch pits are not probably at dislocation sites.

The perfect matching of the pits obtained by two different etchants on the two counterparts of cleavage faces suggests that the isolated pits could be due to lattice distortions in these areas produced by some ~~cleavag~~ chemical impurity centres. If they were just chemical impurities or inclusions, the two different etchants viz., HF and NaOH would not necessarily have reacted at the same places and affected the counterparts equally.

Conclusion:

In conclusion it can be said that the pits originate at impurity centres, giving rise to lattice distortion, surrounding the impurity, in mica crystal and not at dislocation sites as found in several other crystals such as calcite as reported in the next chapter.