# CHAPTER 6

## ECCENTRIC ETCH PITS ON CALCITE CLEAVAGES

### 6.1 Introduction:

It is shown that etch pits on calcite cleavage faces, are formed by the vicinal faces (planes). Further the pits become point-bottomed when these planes meet in a point which is of maximum depth. The present chapter is devoted to the study of point bottomed pits produced by etchants of various concentrations under different conditions of etching. The intersections of point-bottomed pits with the plane of observations, give rise to two dimensional geometrical figures such as a triangle, quadrilateral pentagon etc. It has been shown in earlier chapters that formation of these figures on cleavage faces of calcite is highly dependent on concentration of etchant, time of etching and condition of etching. When a crystal surface is

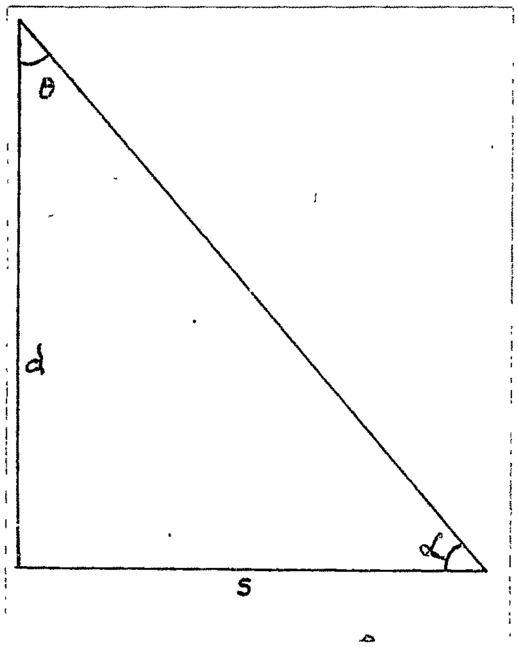



Fig. 6.1A

successively etched, pits formed at line defects increase their surface areas and depths, while pits formed at impurities or at point defects show large increase of surface areas and a relatively minor change in depths. If the line defect is perpendicular to the etched surface, centre of the geometrical figure on the surface may coincide with the depth point. If this point (depth point) coincides with centre of the geometrical figure the etch pit will be symmetrical about the centre. In this case the rate of etching should be isotropic in some definite directions i.e. for equilateral triangles, three directions, for squares (or rhombus), four directions etc. If rate of etching is unequal for these directions a different type of asymmetry results due to etchant though line defect may or may not be perpendicular to the surface.

The study of the asymmetry of the geometrical figure of an etch pit with respect to depth points is reported by many workers (Amelinckx 1956, Gilman et al 1958, Patel 1961, Pandya and Balasubramanian 1962, Patel and Goswami 1962, Patel and Desai 1965 and Patel and Raju 1969 etc.). Amelinckx was the first to study the asymmetry of etch pits produced in rock salt crystals and suggested the existence of inclined dislocations within the crystal. The inclination ($\theta$) (fig. 6.1A) of a dislocation line with a normal to the observation plane is determined by the formula $\tan\theta = \frac{\text{shift}}{\text{depth}}$ where shift is the distance between the depth point and the geometrical centre of the figure and depth of pit is measured from the point of maximum depth. On the basis of his observations on etching of diamond crystal cleavages, Patel (1961) had postulated the existence of inclined dislocations meeting the surface under observation. He has determined the asymmetry of a pit by introducing the term eccentricity in place of shift, and found the inclination of dislocation line by $\tan\alpha = {}^{\text{depth}}/_{\text{eccentricity}}$ (fig. 6.1A) where $\alpha$ is the angle between the dislocation line and a line in the observation plane. This angle is numerically equal to $90 - \theta$ where $\theta$ is the angle given by Amelinckx. The available literature on the study of the displacement of the depth point from the centre of geometrical figure revealed by etching shows that this displacement is considered to be due to inclined dislocations in the body of the crystal as mentioned above. However, no experimental evidence appears to have been put forward to show dependence of displacement on the concentration of an etchant. In the present work the definition given by Amelinckx will be used to study the asymmetry of pits i.e. eccentricity $= {}^{\text{shift}}/_{\text{depth}} = \cot\alpha = \tan\theta$. This definition is more helpful in understanding eccentricity of an etch pit. If the shift is zero, the etch pit is symmetrical, i.e. the eccentricity is zero, and greater the asymmetry of a pit, greater is its eccentricity. The present investigation shows very clearly that besides inclined dislocations, one must consider the concentration of an etchant, time of etching and condition of etching while determining the displacement of the depth point from geometrical centre. The present report deals with the eccentricity of pyramidal pits having different shapes of geometrical figures such as rhombus, hexagon, pentagon, triangle on the surface. Detailed study of displacement of depth point from geometrical centre (shift) and eccentricity is made on etch pits with rhombic outlines on the surface. This shape is particularly well suited for study due to occurrence of shift along directions <110> round the centre of geometrical figure of etch pits with sides parallel to the edges of the crystal. The etching study was carried out mainly on the oppositely matched cleavage faces of calcite.

## 6.2 Experimental procedure:

The experimental procedure for producing etch pits on the cleaved surface of calcite is same as reported in chapter 4. The specimens having low dislocation content are selected for work. The shift of the etch pits were measured by the filar micrometer eyepiece while the depth of the individual etch pits were initially measured by light profile technique which was then discontinued in favour of multiple beam fiezeu interference fringes for obtaining better accuracy in the depth measurement. The interferograms were taken under normal incidence of monochromatic beam (5461 A.U.) of mercury light. Low power objective under normal incidence was used to minimize the correction in the formula used for depth measurements (Tolman and Wood, 1952). The thickness of silver film deposited on the crystal surface by coating unit was adjusted by fixing time for thermal evaporation of silver under very low pressure so as to obtain maximum reflection and minimum absorption required for obtaining good multiple beam fiezeu fringes.

## 6.3 Observations and Results:

Fig. 6.1a (x 170) represents a photomicrograph of a freshly cleaved face etched by 0.25% glacial acetic acid for 30 seconds. The matched region on the counterpart was etched by 0.018% glacial acetic acid for 5 minutes and is shown in fig. 6.1b (x 170). It is to be noted that etching time was increased in second case for obtaining visible etch pits which were studied under high power objective. The size of etch pits in both figures are nearly same. There is a good correspondence between the rhombic etch pits observed in both figures. The pits in fig. 6.1a are symmetrical with respect to $[110]$ direction passing through the depth point but are not symmetrical with respect to the normal to this direction. It means that depth point is shifted in $[110]$ direction from geometrical centre. The pits in fig. 6.1b are nearly symmetrical with respect to both directions $[110]$ and $[\bar{1}10]$ passing through the depth points which are situated nearly on geometrical centres of the etch figures. The shift of depth points of the pits along $[110]$ from the geometrical centre will be referred to as a positive shift whereas negative displacement will be along direction $[\bar{1}\bar{1}0]$. Background etching was absent in both these figures. The distance between the depth points of any two pits (fig.6.1a) is almost equal to the distance between depth points of corresponding pits (fig. 6.1b). The surface shown in fig. 6.1a was re-etched by 0.25% glacial acetic acid for a further period of 30 seconds (fig. 6.2a, x 170), whereas the counterpart was re-etched for a further period of 5 minutes by 0.018% glacial acetic acid (fig. 6.2b, x 170). The detailed study of figures (6.1a and 6.2b) and (6.1b and 6.2b) has revealed interesting points of similarities and dissimilarities. In all these figures it is found that (1) The density of etch pits has remained constant. (2) Surface areas and volumes of etch pits have increased due to more time of etching. (3) The distance between the depth points of any two pits (figs. 6.1a, 6.2a) is almost equal to the distance between depth points of corresponding pits (figs. 6.1b, 6.2b). Hence the positions of depth points on etching and re-etching have either remained unaffected or have moved through equal distances along the same direction. (4) Displacement of the cleavage line PQ and P'Q' on etching and re-etching. (5) Development of stepped structure in many point-bottomed pits due to etching and re-etching.

The points of dissimilarity are as follows: (1) Slight displacement of depth point from geometrical centre is observed for pits in fig. 6.2b as compared to corresponding pits in fig. 6.1b. The depth point has moved in the downward direction, i.e. $[\bar{1}\bar{1}0]$ from the geometrical centre. Hence the shift is negative while in fig. 6.1a and 6.2a shift is positive. (2) Shift is not same for all etch pits in above figures. However, shift is more in fig.6.2a than the corresponding pits in fig. 6.1a. (3) Change of point-bottomed pit into flat-bottomed etch pit (E and E' in figs. 6.1a and 6.2a).

Further etching of these surfaces (figs. 6.2a and 6.2b) destroyed the geometry of the pits. Fig. 6.2A (x 170) represents the photomicrograph of the same region of the surface shown in fig. 6.2a etched by 0.25% glacial acetic acid for a period of 30 seconds. The sides of pits are rough and have mottled character. The shift of the depth point is more than that observed in fig. 6.2a.

From the above observations, it can be said that nature and magnitude of the displacement of depth points with respect to geometrical centre depend upon the concentration of etchant and etching time. The different concentration of the etchant may produce etch pits with positive shift, negative shift or nearly zero shift in rhombic etch pits.

If a freshly cleaved surface etched by an etchant of a particular concentration for producing rhombic etch pits having negative (or positive) shift is re-etched by other appropriate concentration of the same etchant which does not produce any change in the shape of etch pits, the depth point on re-etching changes it position, giving rise to a change of the shift. Following pairs of observations show conclusively that displacement of point of maximum depth of a pit from geometrical centre depends upon the concentration of the etchant.

Fig. 6.3a (x 170) shows the photomicrograph of a freshly cleaved surface etched by 0.012% glacial acetic acid for 15 minutes. Point-bottomed rhombic etch pits are observed along with some flat-bottomed etch pits and a horizontal cleavage line. The lines of intersections emanating from the depth point are clearer than the boundaries of pits. Dislpacement of the depth point from geometrical centre is in [$\bar{1}\bar{1}0$] direction i.e. shift is negative. The same region of the surface re-etched by 0.25% glacial acetic acid for 30 seconds, is shown in fig. 6.3b (x 170). The direct measurement of shifts by filar micrometer eyepiece show very clearly that the average shift of the pits in fig. 6.3a is greater than the corresponding average shift of pits in fig. 6.3b by 5.5 microns only. Depth point has moved in the same direction (line of symmetry) from the geometrical centre in both the figures. Hence, the (negative) shift is decreased due to second etching. It is shown earlier that 0.25% glacial acetic acid produces a positive shift, whereas 0.018% concentration of this acid induces a negative shift. Hence the successive etching of freshly cleaved surface by these two concentrations reduces the shift value. Fig. 6.4a (x 170) is a photomicrograph of a freshly cleaved calcite surface etched by 0.25% glacial acetic acid for 40 seconds, whereas fig. 6.4b (x 170) shows a photomicrograph of the above surface re-etched by

0.012% glacial acetic acid for 10 minutes. The shift of the depth point is positive and has the average value of 4.0 microns (fig. 6.4a). The positive shift for the corresponding pits in fig. 6.4b has disappeared producing nearly zero shift. This has therefore given rise to nearly symmetrical pits. It should be remarked here that for pits produced by a given concentration of an etchant the displacement of the depth point from the geometrical centre irrespective of its algebric sign increases with the etching time. The above observations have shown very clearly that desired shift along directions $\langle 110 \rangle$ (+ve, -ve or zero) can be obtained for most of the pits by suitably changing the concentration and time of etching.

The study of successive etching of the same surface under high resolution for determining quantitatively the variation of shift with other parameters is desirable. However, this is not possible for this crystal, for the study under high resolution requires the deposition of silver film. After the study of this silvered crystal, it is not possible to remove the silver film without damaging the surface. Further the quality of etch figures which are produced at line defects deteriorates on multiple etching of the same crystal face. Due to these reasons it is decided to study several pairs of oppositely matched faces etched under varied but controlled conditions as shown below:

(1) Etching of matched cleavages by an etchant of constant concentration under static condition with (a) identical periods of etching (ref. figs. 6.5a and 6.5b) (b) different periods of etching ( table 6.1, column a,b,c).

(2) Etching of matched cleavage counterparts by etchant of different concentrations for (a) different periods of etching under static condition (figs. 6.6a and 6.6b) and (b) same period of etching under static condition (table 6.2, column d,e,f,g,h and table 6.3 column i).

(3) Etching of oppositely matched cleavage faces by etchants of constant concentrations for different periods of etching under different conditions (static and dynamic) of etching, (figs. 5.4a and 5.4b, chapter 5; table 6.3, column j).

Figs. 6.5a and 6.5b (x 170) are the photomicrographs of a pair of cleavage counterparts etched by 0.25% glacial acetic acid for 40 seconds. It is clear from these figures that (i) pits are asymmetric and their densities on the matched faces are constant, (ii) the average shift of all these pits on both the photomicrographs are nearly equal and positive. This is also found to be true for average depths of etch pits determined by multiple beam interferometry. However, the depths and shifts in case of individual pits vary within a certain range (see table 6.1, column a), (iii) a flat-bottomed pit A' in fig. 6.5a corresponds with a point-bottomed pit A in fig. 6.5b.

The photomicrographs (figs. 6.6a and 6.6b, x 170) show the matched cleavage faces etched by 0.05% and 0.005% glacial acetic acid for 2 minutes and 45 minutes respectively. Fig. 6.6a shows pits with positive shift whereas negative shift is observed for the pits in fig.6.6b. Further the eccentricity and shift of depth points of pits in fig. 6.6b are more than those of the corresponding pits (fig. 6.6a).

Even the condition of etching affects the position of depth point with respect to geometrical centre. The changes in shift (nature and/or magnitude) is observed for both condition of etching (static and dynamic), (figs. 5.4a and 5.4b, chapter 5).

Figs. 6.7a and 6.7b (x 120) show interferograms of the matched counterpart etched by 0.008% glacial acetic

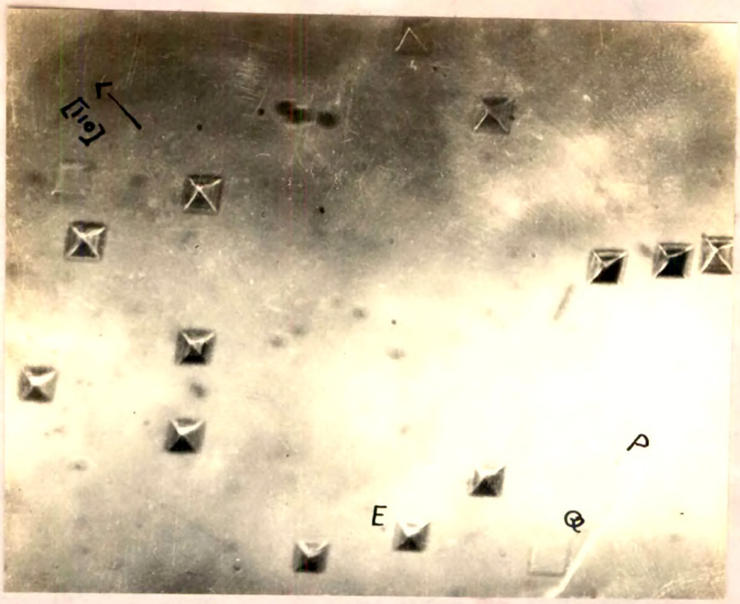



Fig. 6.1a ( x170 )

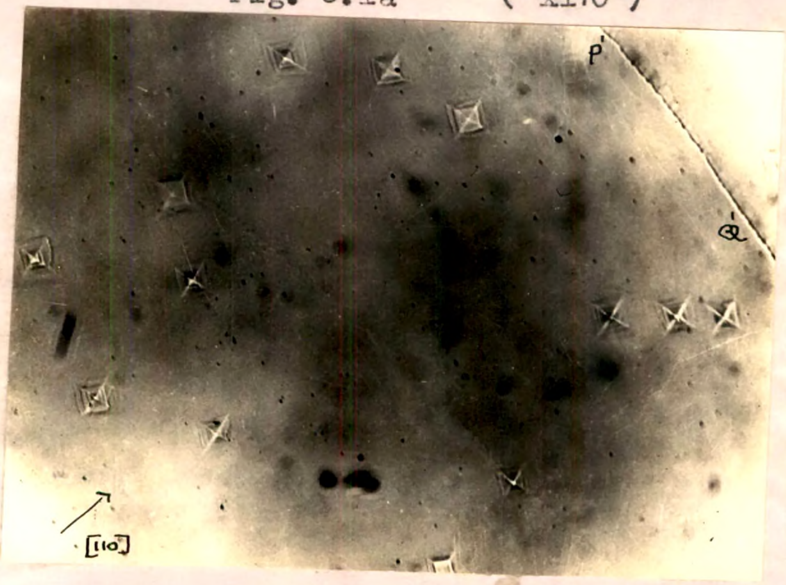
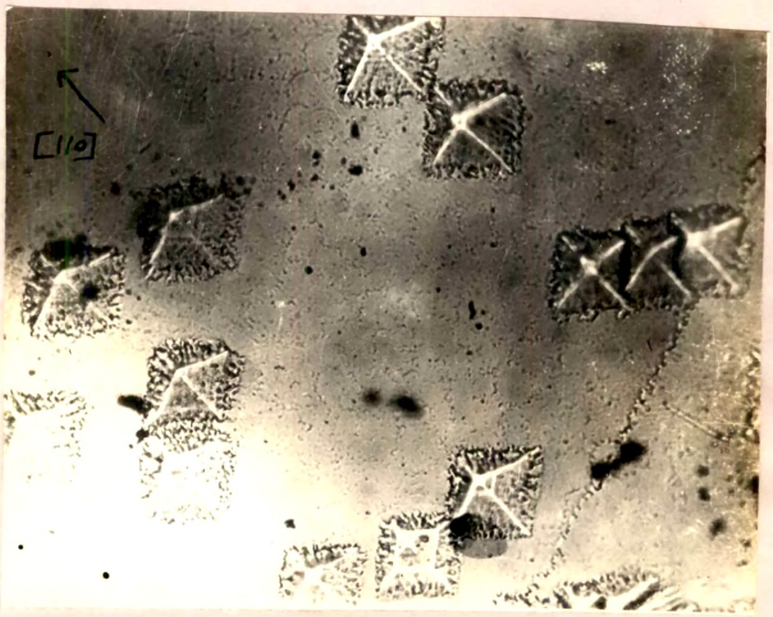



Fig. 6.1b ( x170 )


Fig. 6.2a (x 170 )


Fig. 6.2b (x 170 )




Fig, 6.2A ( x 170 )


Fig.6.3a ( x170 )

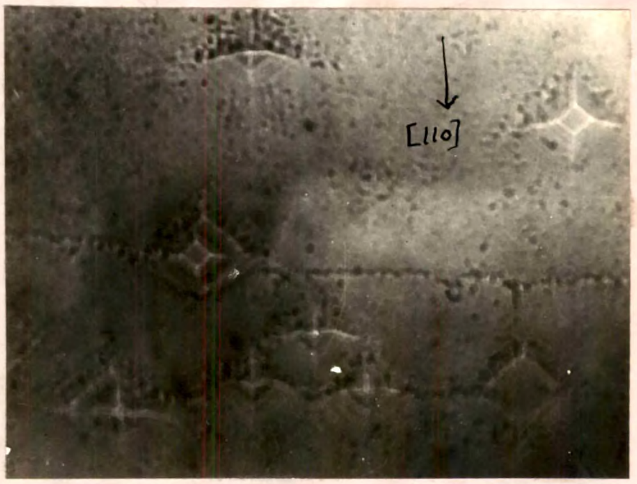



Fig. 6.3b ( x170 )

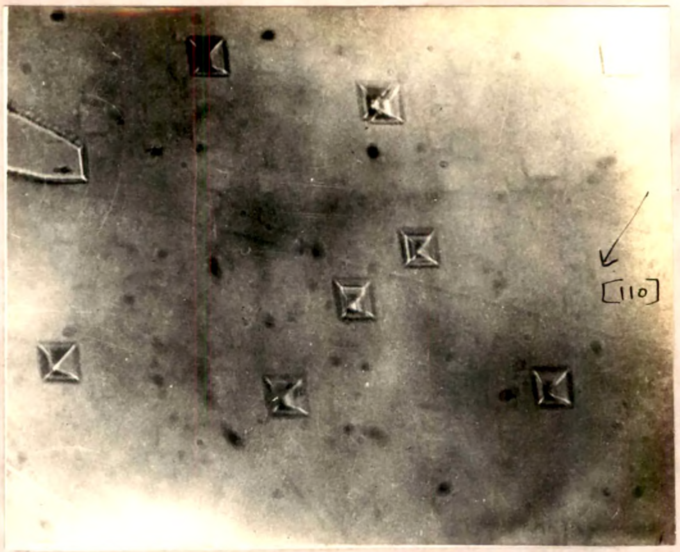



Fig. 6.4a ( x170 )


Fig. 6.4b ( x170 )

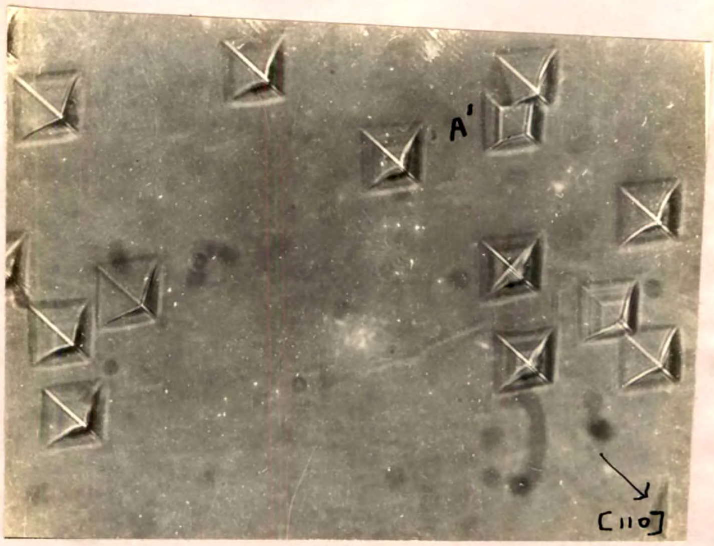



Fig. 6.5a ( x170 )


Fig.6.5 b (x170)

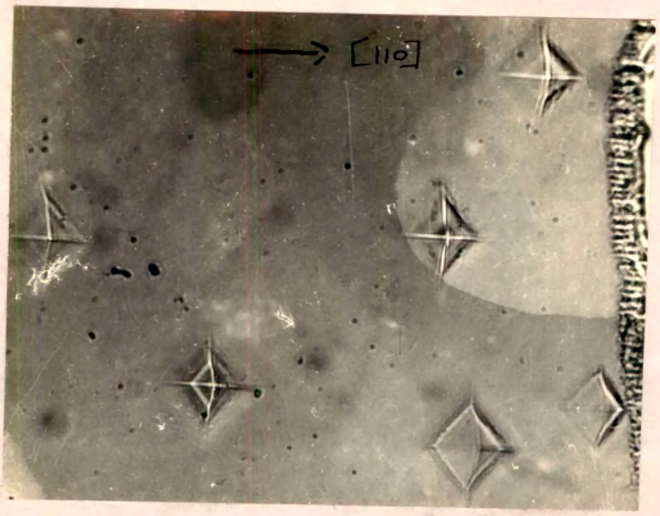



Fig. 6.6a ( x170 )


Fig. 6.6b (x170)

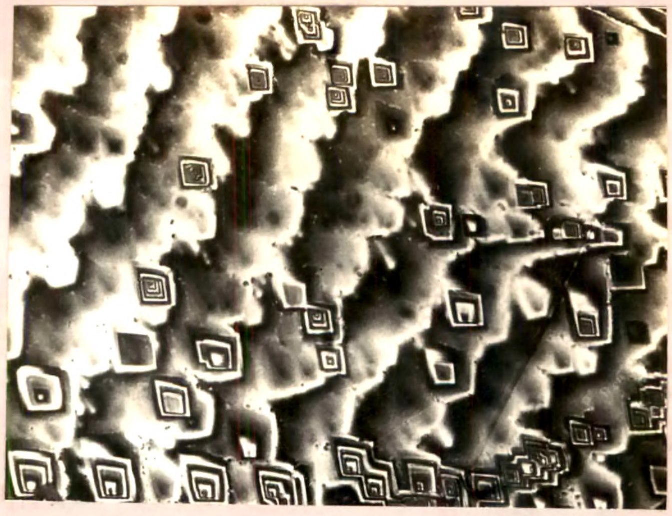


Fig. 6.7a ( x120 )

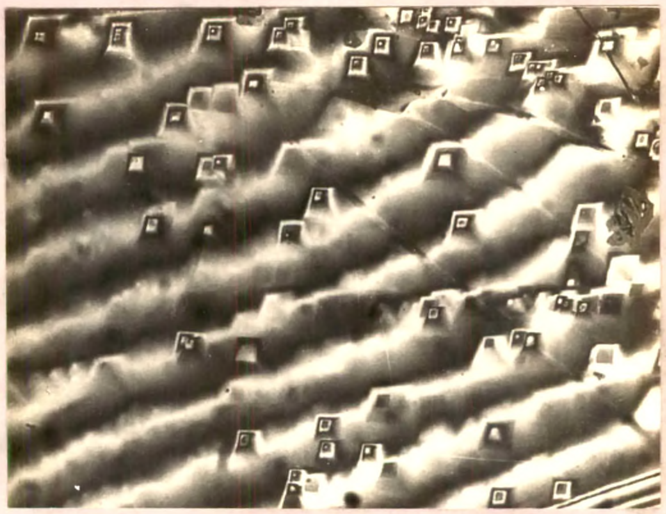


Fig. 6.7b ( x120 )

Fig. 6.7c        ( x90 )

Fig. 6.7d        ( x90 )

acid for 5 minutes and 15 minutes under dynamic and static condition of etching respectively. Though time of etching is more for static etching, depth and surface areas of pits are more for the pits produced under dynamic etching than those formed under static etching. Shift of individual pits is measured by filar micrometer eyepiece. It is observed that shift is positive for pits in fig. 6.7a while it is negative for corresponding pits in fig. 6.7b. Measurements of shift, depth and eccentricity of individual pits are given in table 6.3j. Similarly interferograms taken over the matched cleavage surface of calcite, one etched by 0.25% glacial acetic acid for 2 minutes and other by 0.012% glacial acetic acid for 10 minutes are shown in figs. 6.7c and 6.7d (x 90) respectively. It is clear from the figures that magnitude of shift is not same. Shift is more in fig. 6.7c than in fig. 6.7d. Depth point is in direction [110] (fig. 6.7c), while depth point is in direction $[\bar{1}\bar{1}0]$ from geometrical centre in fig. 6.7d. The shifts of individual pits were measured by filar micrometer eyepiece and depths of the corresponding pits were calculated by counting number of fringes in pit. Eccentricities of pits were measured from shifts and depths (table 6.3i). Similarly interferograms of several pairs of cleaved faces etched under various conditions were taken. The quantitative measurements of shift by filar micrometer eyepiece and of depth by multiple beam interferometry were taken and

TABLE NO: 6.4

AVERAGE ECCENTRICITY OF RHOMBIC PITS PRODUCED BY DIFFERENT CONCENTRATIONS OF GLACIAL ACETIC ACID.

| Obs.No. | Concentration | Average eccentricity |
|---|---|---|
| 1 | 0.35 % | + 3.87 |
| 2 | 0.25 % | + 3.25 |
| 3 | 0.22 % | + 2.87 |
| 4 | 0.15 % | + 2.58 |
| 5 | 0.025% | + 1.79 |
| 6 | 0.022% | + 1.31 |
| 7 | 0.015% | - 3.22 |
| 8 | 0.012% | - 5.46 |
| 9 | 0.01 % | - 7.1 |
| 10 | 0.008% | - 8.43 |

calculation of eccentricity of rhombic etch pits produced by different or same concentration of glacial acetic acid, for different or same time of etching etc. are given in the tables 6.1, 6.2 and 6.3.

A composite table 6.4 is also prepared out of these tables giving average values of eccentricity of pits for different concentrations of etchant. These observations are then graphically studied by plotting graph of log. concentration versus eccentricity.

## 6.4 Discussion:

The observations have clearly brought out the following points. (1) The concentration of an etchant and time of etching are vital factors affecting the positions of the depth point when all other parameters are kept constant. (2) The average eccentricity of etch pits remains constant for a given concentration of an etchant and for different period of etching.

Many workers tried to explain the occurrence of shift of depth point by postulating the existence of inclined dislocations, emerging on the surface under observation. The present author firmly believes that this interpretation has not taken into consideration, all the factors affecting the position of depth point with respect to geometrical centre. It is crystal clear from the perfect matching of pits on oppositely matched cleavage faces etched by same and different etchants (e.g. HCl, HAC, HCOOH etc.) of varied concentrations for different periods of etching, that all these are dislocation etchants. The study of the shift of depth point and eccentricity of the pits has shown that if all these pits are at the site of dislocations, some pits are likely to be of different types, due to different geometries of dislocations in crystals. This is made more clear by the photomicrographs (figs. 6.8a and 6.8b, x 170) of matched cleavage faces one etched by 0.005% glacial acetic acid for 45 minutes and the other etched by 0.02% of same acid for 7 minutes. The figures are indeed remarkable for the simple reason that when one is superimposed over the other, depth points of most of pits except the pits marked $A_1$ and $A_2$ (fig. 6.8a) and $B_1$ and $B_2$ (fig. 6.8b), coincide with one another. The depth points of pits $A_1$ and $B_1$ donot lie on the shorter diagonal of the plane figure of rhombic pits but are away from it. In fig. 6.8a it is on the right side of the shorter diagonal for pit $A_1$ whereas in fig. 6.8b it is on the left side of the shorter diagonal of corresponding pit $B_1$ on matched cleavage counterpart. It is obvious that the dislocation line passing through them i.e. through the original block of the uncleaved crystal, is inclined, in the plane other than (110) , with the surface under observation. The displacements of depth point from the symmetrical line for pit $A_1$ and $B_1$ are 2.0 microns and 1.1 microns while depths of the above pits are found to be 1.09 microns and 0.54 microns respectively (fig. 6.8A). Hence the inclination of the dislocation line with a line in the plane (110) is $63^{\circ}$ 48'. This inclination is absolutely uneffected by change of concentration and time of etching. Further the correspondence of terraced flat bottomed pit $A_2$ (fig. 6.8a) with a line-bottomed pit $B_2$ having terraced structure (fig. 6.8b) can be understood on the basis of dislocation loop (fig. 6.8B). All the boundaries of pit $B_2$ (fig. 6.8b) are not equal. Boundary along X direction is nearly half of the boundary along Y direction. This helps one to conjecture that pit $B_2$ is the combination of two pits whose origins are situated too close to be distinguished. Hence the depth point of pit $B_2$ is replaced by a line along Y direction. The corresponding pit $A_2$ (fig. 6.8a) is flat-bottomed etch pit due to non-existence of dislocation line after certain time of etching. The complete coincidence of depth points of other corresponding pits on figs. 6.8a and 6.8b suggest that if these pits represent the emergent points of dislocations, these dislocation will not be of the type mentioned above.

The etch pits which are symmetrical about [110] are produced at the tips of dislocation lines lying on the (110) plane and intersecting observation plane (100).

The present author has made very detailed study about the effect of a wide range of concentrations of glacial acetic acid on the eccentricity of etch pits and found that for a given range of concentration, the geometrical shape of etch pits remains unchanged. When the concentration range was taken from 0.5% to 2% of glacial acetic acid, the shape of pits was found to be hexagonal on the etched surface of calcite cleavages. Figs. 6.9a and 6.9b (x 90) show photomicrographs of cleavage counterparts etched by 1.6% glacial acetic acid for 15 seconds. Almost all pits are point-bottomed with hexagonal outline on the surface. Further the displacement of depth points from geometrical centre of all these pits are positive. Figs. 6.9c and 6.9d (x 90) are the interferograms of the surfaces shown in figs. 6.9a and 6.9b respectively. Depths of the etch figures can be easily found by counting the number of fringes and multiplying it by $\lambda/2$ and shift can be measured by filar micrometer eyepiece. Depth point is shifted in [110] direction from geometrical centre because density of fringes is more along OS than along OA where O is depth point. Shift and eccentricity of the hexagonal etch pits produced by different concentration of glacial acetic acid are given in table 6.5. Similarly tables 6.6 and 6.7 are prepared from the observations of shift and depth of pentagonal and triangular pits produced by various ranges of hydrochloric acid. It is interesting to note that for the whole range of concentrations i.e. from 0.5% to 2 %, of HAc the shift has a positive value. Average eccentricity and shifts are same for pits (figs. 6.9c and 6.9d) on both these figures.

For some hexagonal pits, it is not possible to obtain the depth points on the diagonal along [110] which is line of symmetry. Their displacements are on the right (pits A and B, fig. 6.10a) and left (pits A' and B', fig. 6.10b), sides of this diagonal having direction [110]. Figs. 6.10a and 6.10b (x 170) are obtained by etching the cleavage counterparts by 0.8% and 1.5% glacial acetic acid for 30 seconds respectively. This is similar to the case of pits formed in figs. 6.8a and 6.8b. Hence in this case also it is possible to explain their occurrence on the basis of inclined dislocations. From the measurement of shifts and depths for these pits, the inclinations of the dislocation lines with the normal to the cleavage plane are found to be 32° and 40°. Further the pits with depth point congruent with those of the corresponding pits (figs. 6.10a and 6.10b)

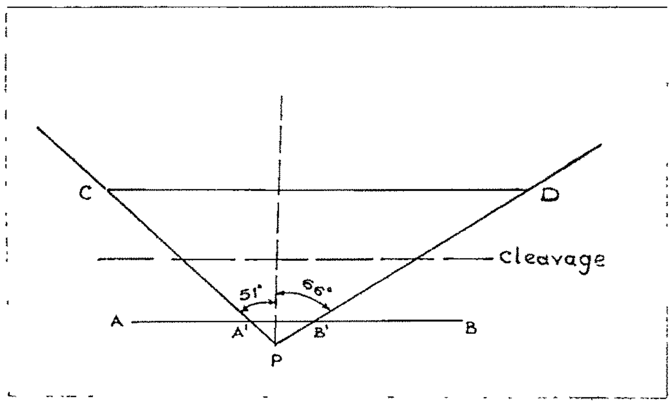



Fig. 6.12

are also observed. They are similar to those discussed in figs. 6.8a and 6.8b for **rhombic etch** pits. These observations are further supported by the following photomicrographs, (figs. 6.11a and 6.11b; x 200) which are obtained by etching the oppositely matched faces by 0.4% and 0.6% glacial acetic acid for 30 seconds respectively. It shows rhombic pits (figs. 6.11a) whereas hexagonal pits are found on its counterpart (fig. 6.11b). The following points are worthnoting, (i) Depth pointsof rhombic pit marked A (fig. 6.11a) and corresponding hexagonal pit A' (fig. 6.11b) are on opposite sides of diagonal PQ having [110] direction. (ii) There are other rhombic and hexagonal pits (such as C and C') for which the depth points lie on diagonal PQ. (iii) The hexagonal pits $R_1$ and $R_2$ have depth points on the opposite sides of the diagonal having direction [110] and depth points lie on the line [100] whereas corresponding pit on fig. 6.11a is shown by the formation of a single comparatively large pit with a line centre having direction [100] . This can be explained if one assumes a pair of inclined dislocations meeting at a point (P in fig. 6.12). When the crystal was cleaved and the resulting cleaved surfaces were subjected to etching the points nearer the vertex of these inclined dislocations would etch differently than those of the individual dislocations. In this process the resulting pit at these points is a parallelogram instead of two close rhombic pits, whereas on the oppositely matched face, the dislocations are separated enough to produce two different hexagonal pits. The depth points of pits $R_1$ and $R_2$ are found on the left and right side of diagonal along a direction [110] . Further these inclined dislocations meeting at a point make different angle with the line in (110) plane. From the measurement of shift and depth, the inclination of individual dislocations are found to be $51^{o}$ and $66^{o}$ with normal to the cleavage plane. The converse is also found to be true when a single pit A' (fig. 6.13b) corresponds with two pits forming a parallelogram (A in fig. 6.13a) rather than the rhombus as shown in the photomicrographs (figs. 6.13a and 6.13b; x 170) which are obtained by etching cleavage counterparts by 0.01% and 0.007% of glacial acetic acid for 7 minutes and 45 minutes respectively. This can also be explained by considering a narrow loop of dislocation. Figs. 6.14a and 6.14b (x 90) show interferogram of the matched counterpart etched by 1% HCl for 7 seconds. It is clear that depth of all pits are not equal. Depth point of pit marked as A and A' (fig. 6.14a) is shifted left from the line of symmetry by observing the density of fringes along OB and OC, while depth point of corresponding pit a and a' (fig. 6.14b) is shifted right from the line of symmetry by observing the density of fringes

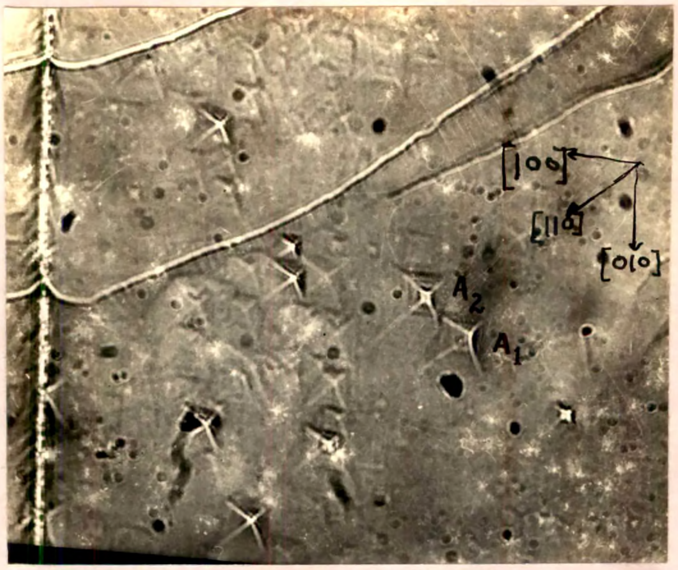



Fig. 6.8a ( x170 )

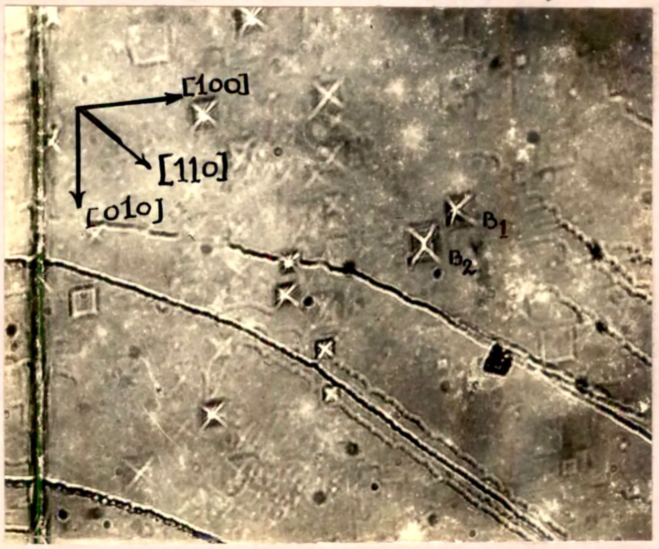



Fig. 6.8b ( x170 )

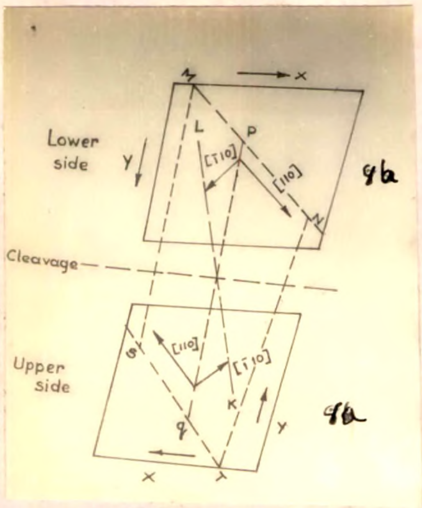



Fig. 6.8A

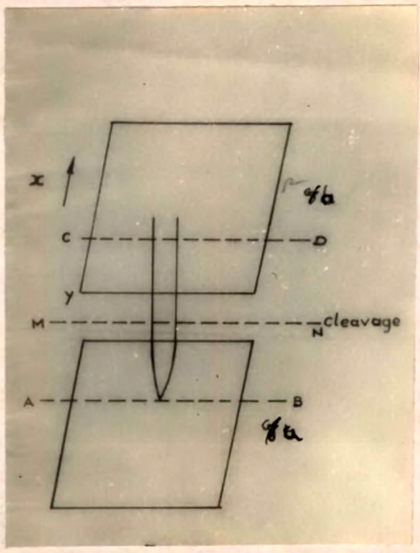



Fig. 6.8B


Fig. 6.9a ( x90 )

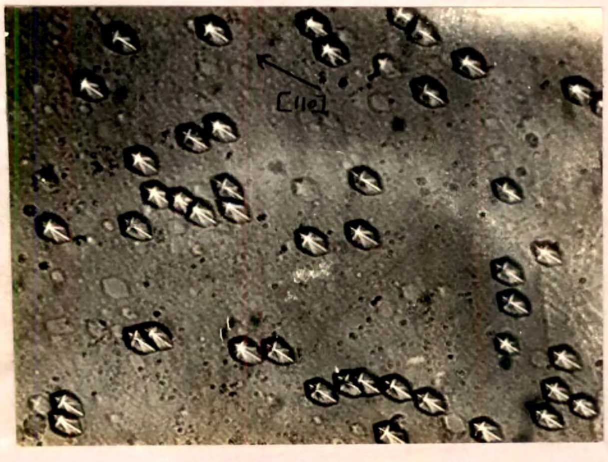



Fig. 6.9b ( x90 )


Fig. 6.9c ( x90 )

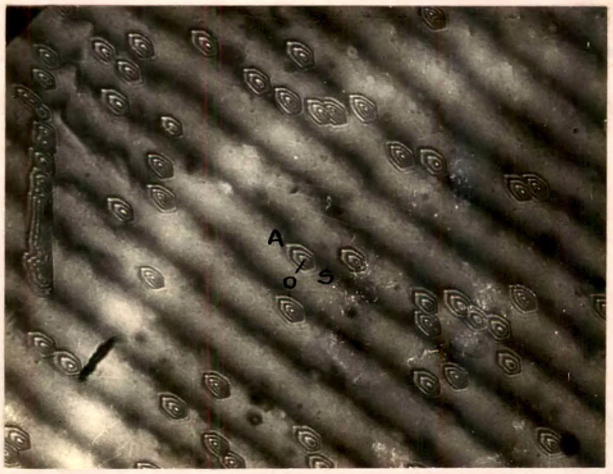



Fig. 6.9d ( x90 )

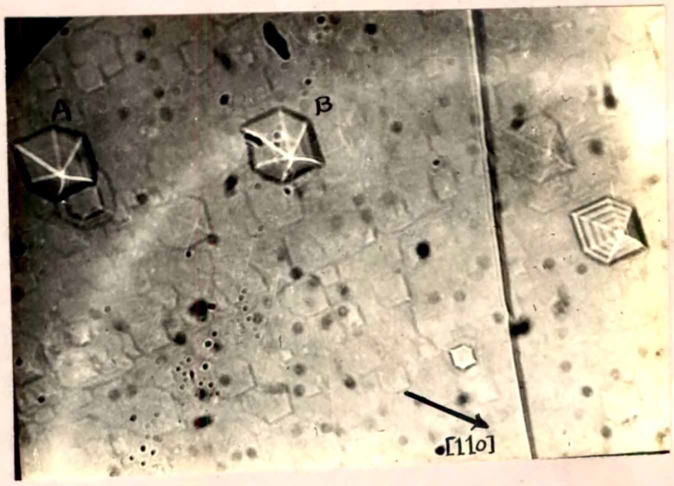



Fig. 6.10 a ( x170 )


Fig. 6.10b ( x170 )

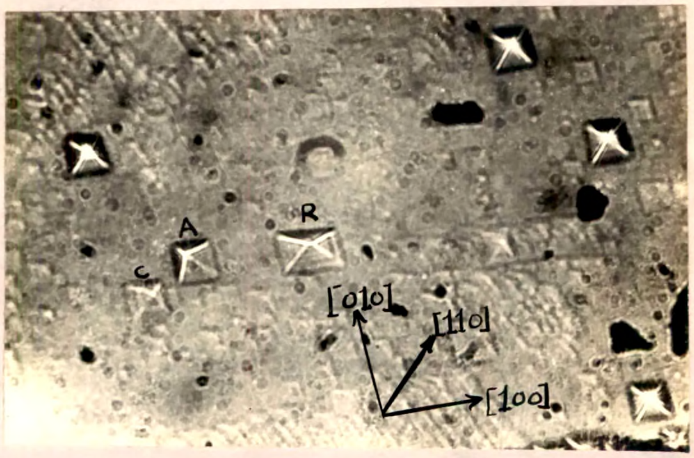



Fig..6.11a ( x200 )


Fig..6.11b ( x200 )

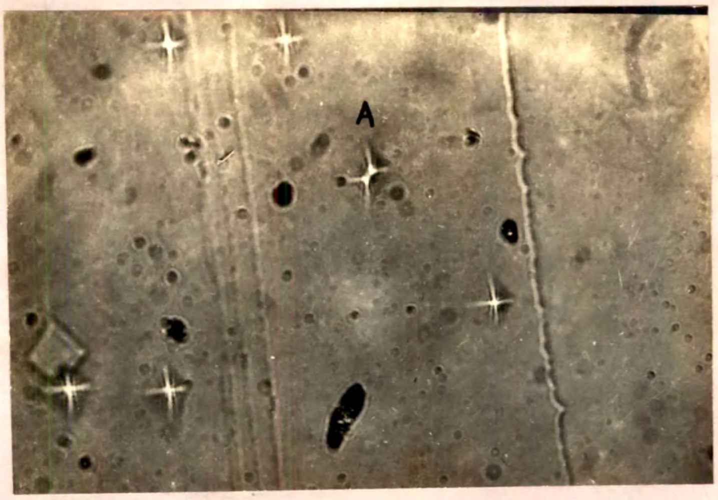



Fig. 6.13a ( x170 )


Fig. 6.13b ( x170 )

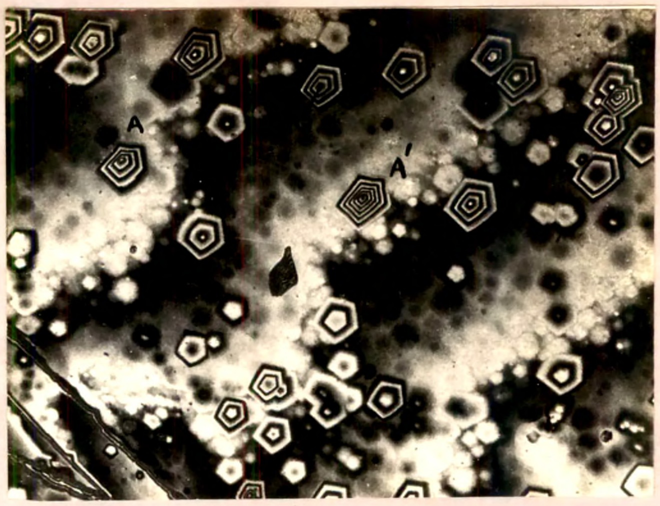



Fig. 6.14a    ( x90 )

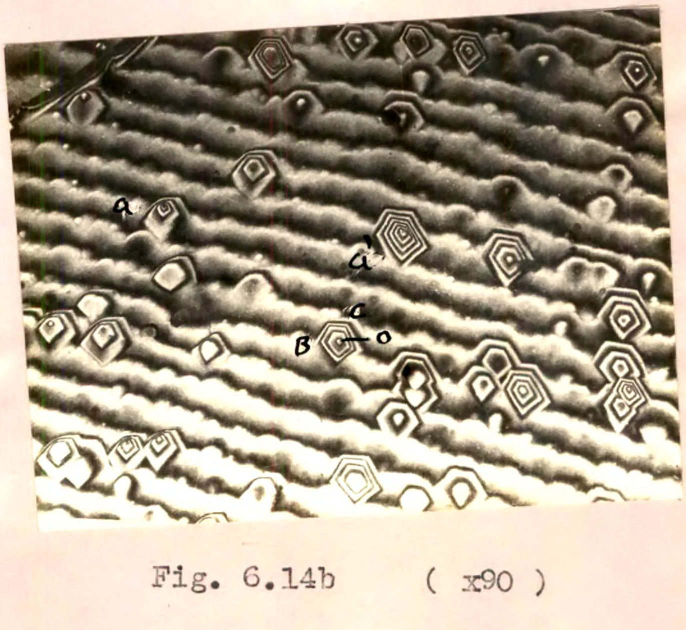



Fig. 6.14b    ( x90 )

along OB and OC. This suggests that these pits are formed on inclined dislocations which are not in plane (110). If depth points of corresponding pentagonal pits on matched surface are shifted in opposite directions from the line of symmetry (as shown in pit B , B' of figs. 5.6a and 5.6b of chapter 5),, they are formed on the inclined dislocations. It means that dislocation lines where pits are formed are not lying in the plane (110).

When depth points of etch pits produced by different concentrations of various acids (such as HCl or HAC) are not lying on the line of symmetry, the pits may be formed on the tips of inclined dislocations. If depth point of pit is shifted right (or left) from the symmetry line, depth point of corresponding dislocation pit (which may be of different shape) on matched surface is shifted left (or right) from the line of symmetry. This is clear from the figures 4.26a and 4.26b of chapter 4, where depth point of rhombic pits A', C, C' (fig. 4.26a) are shifted from the symmetry line opposite to those corresponding rectangular pits a', c, c'. These pits are formed at inclined dislocations.

The displacement of the depth point from the geometrical centre is a function of concentration and inclination of dislocation line with the cleavage plane. While considering the origin of etch pits on a crystal surface one must consider the following cases:

(i) Isotropic etchant and dislocation lines or loops inclined at angles other than 90° with observation plane.

(ii) Isotropic etchant and dislocation lines or loops inclined at 90° with observation plane.

(iii) Anisotropic etchant and dislocation lines or loops having characteristics shown in (i) and (ii).

When an etchant producing etch pits is isotropic and is capable of revealing dislocations normal to the plane of observation, the resulting etch pit will be symmetrical and the point of maximum depth exactly coincides with the geometrical centre of regular outline of the etch pit on a cleavage surface. However, if the dislocation lines are inclined at angles other than 90° with the observation plane, the etch pits will be asymmetrical i.e. the depth point does not coincide with geometrical centre.

If the dislocations not lying in plane (110) are inclined at angles other than 90° with the observation plane which is etched by an anisotropic etchant, the pits will be asymmetric. Depth point will not coincide with the geometric centre. In the present case such asymmetric pits are observed on the calcite cleavage surface (see for example figs. 4.26a and 4.26b; 5.6a and 5.6b; 6.8a and 6.8b). The depth points for such pits donot lie on direction [110] .

If the dislocations lie in the plane (110) and antisotropic etchant (such as HCl or HAC) is used to produce etch pits on the surface at the emergent points of dislocations, the pit will be symmetrical about a direction (110) which is a trace of plane (110) normal to the observation plane (001) and containing these dislocations. This direction is also a characteristic of the etchant used to reveal a set of dislocations. In the present work such pits having symmetry line along [110] are observed due to anisotropic action of an etchant (say HCl or HAC of appropriate concentration). For these etch pits, the point of maximum depth does not coincide with the geometrical centre of the plane figure (see, for example figs. 6.1a, 6.2a, 6.2b etc.). It is thus clear that if the dislocations belonging to (110) plane and meeting (001) plane are revealed by etching, etch pit must be symmetrical about a direction $[110]$. This is a predominantly governing factor for producing pits having various geometrical outlines on a cleavage surface. Thus, pyramidal pits having triangular, rhombic, pentagonal, hexagonal and septagonal outlines on a cleavage surface produced by an etchant whose concentration is systematically varied will belong to this geometry of dislocations, if these shapes are symmetrical about $[110]$. This is exactly what has been observed earlier in many figures of chapter 4. It should be noted that although these pits are symmetrical about $[110]$ they may be eccentric. This will become more clear by considering an example of a pyramidal pit with rhombic outline (see for example fig. 6.1a, 6.2a) on the cleavage surface. If the depth point coincides with the geometrical centre, the pit is symmetrical about $[110]$ and $[1\bar{1}0]$. This shows that reaction rates along $[150]$ and $[\bar{5}\bar{1}0]$ which are normal to $[100]$ and $[0\bar{1}0]$ are identical. If the reaction rate along $[\bar{5}\bar{1}0]$ is greater (or less) than the rate along $[150]$ the pits with positive (or negative) eccentricity are produced. In the case of hexagonal etch pits produced by glacial acetic acid with concentrations ranging from 0.5% to 2 %, the eccentricity is positive. This shows that the reaction rate along $[\bar{5}\bar{1}0]$ is greater than the rate along $[150]$. In this case reaction rates along $[1\bar{1}0]$ and $[\bar{1}10]$ do not appear to take part in changing the eccentricity of the pits because they are normal to $[110]$.

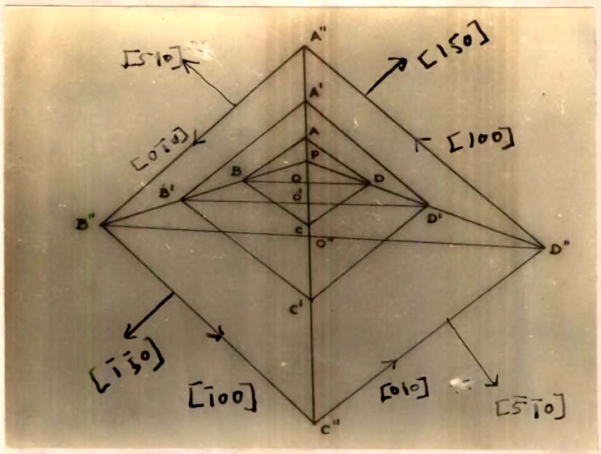
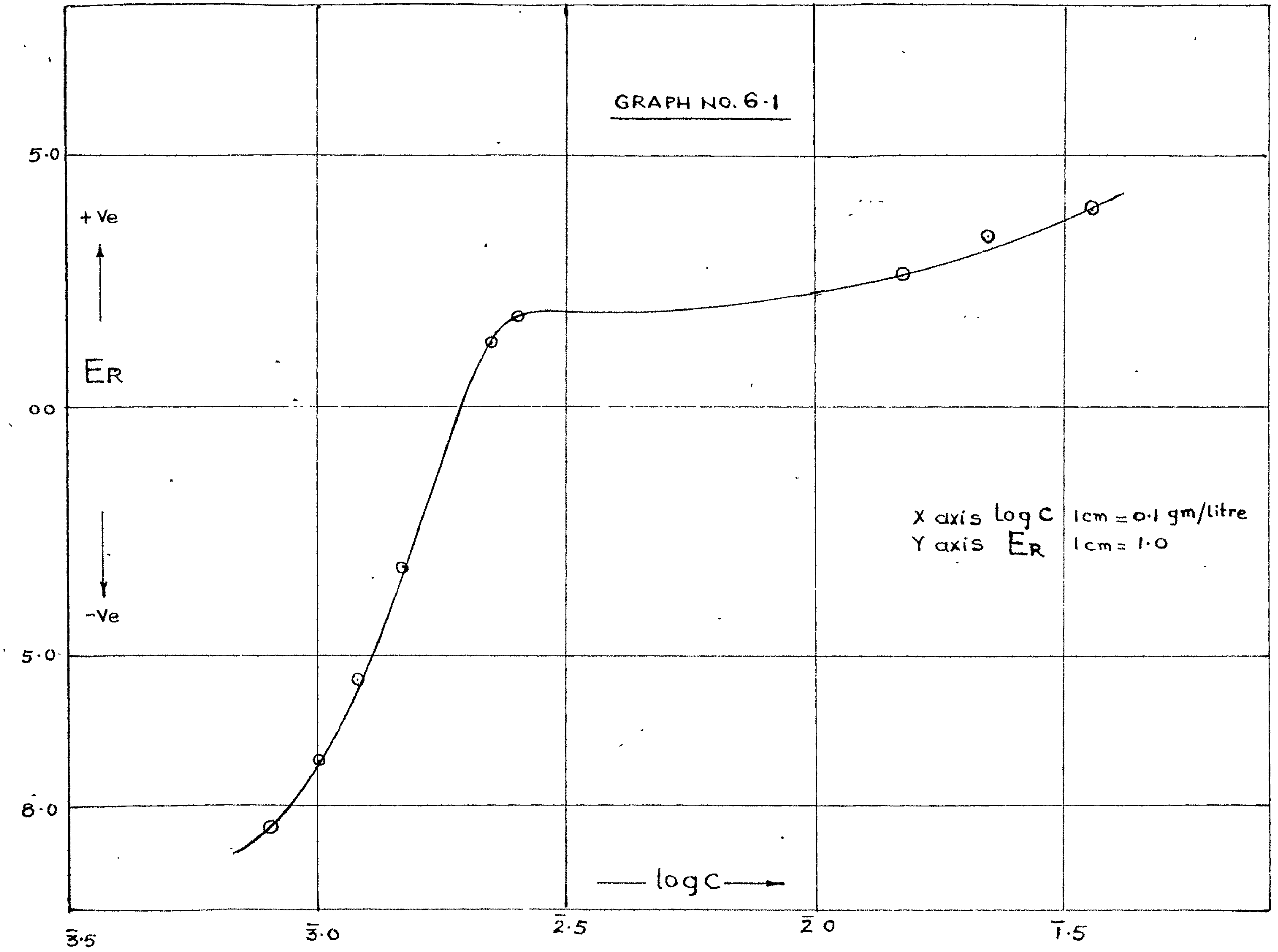



Fig . 6.15

Fig . 6.16 ( x340 )

With the increase in etching time up to a certain limit, it is found that the eccentricity of a pit does not change. However the shift changes in proportion to the depth, so as to maintain a constant ratio between them. Patel and Goswami (1962A) had shown the increase of shift with the progressive etching by citric acid. However, it appears that they have not taken into consideration the effect of concentrations or etching time on the value of shift. Fig. 6.15 shows a schematic diagram of development of etch pits with etching time. ABCD is a rhombic outline of etch pit on the observation plane for initial stage. Depth point P and geometrical centre are not coinciding. For the second stage if depth point is not moved, new positions of boundary of of pit are seen as A'B'C'D'. Geometrical centre of A'B'C'D' is O'. It is clear that depth point is moved with respect to O'. Similarly A''B''C''D'' is the third stage of development with O'' as geometrical centre. It gives more value of shift with increase in etching time. Irrespective of the position of dislocation, this happens.

It may be pointed out here that the total surface area of planes forming eccentric pits is usually greater than that of planes forming a non-eccentric (symmetric) pit, when the depth and surface area of pits on observation plane in both cases are identical. However, this factor


GRAPH NO. 6·1
5·0
+ Ve
E R
0·0
-Ve
5·0
8·0
log C
X axis log C 1cm = 0·1 gm/litre
Y axis E R 1cm = 1·0
$\bar{3}$·5
$\bar{3}$·0
$\bar{2}$·5
$\bar{2}$ 0
$\bar{1}$·5

does not appear to affect much the etching behaviour of the calcite cleavages.

The quantitative measurements of shift by filar micrometer eyepiece and of depth by multiple beam interferometry of individual pits with rhombic, hexagonal pentagonal and triangular outlines are made and given in the tables 6.1 to 6.4, 6.5, 6.6 and 6.7. The first four tables show the measurements made on pits with rhombic outlines whereas the remaining tables present the measurements on pits with hexagonal, pentagonal and triangular outlines respectively. These measurements were made on pits which are symmetrical about [110] . It is shown earlier that irrespective of geometry of dislocations meeting the observation plane, the eccentricity of an etch pit symmetrical about [110] is a function of concentration and condition of etching and can be changed to a desired value by using appropriate concentration of an etchant and/or appropriate condition of etching. This shows that the angles calculated from the determination of eccentricity are function of concentration of an etchant and/or conditions of etching. Thus for eccentric etch pits symmetrical about [110] , the only conclusion which can be drawn from the above study is that the pits are produced at dislocations lying in plane (110) with their projections in direction [110] on the observation plane (001). Several sets of measurements for a large number of etch pits produced on oppositely matched faces etched by the same etchant of identical or different concentrations for equal or unequal periods of etching under equal or unequal (dynamic or static) conditions of etching are taken and given in above tables. These tables show a very large variation of eccentricity If an average eccentricity is calculated for each of these concentrations and a graph of eccentricity versus log. C (for rhombic pits) be plotted the nature of the graph is as shown in graph 6.1. It is clear from the graph that the average zero eccentricity of etch pits on a cleavage surface corresponds to 0.02% concentration of glacial acetic acid. Attempt is therefore made to verify this conclusion by etching a crystal cleavage by 0.02% glacial acetic acid for five minutes (fig. 6.16, x 340). This figure is indeed remarkable because it shows almost all pits to be non-eccentric and symmetrical about [110] and [$1\bar{1}0$]. Similarly this etchant with concentration >0.02% produces pits with positive eccentricity irrespective of the condition of etching. Further if the concentration is less than the above, pits with negative eccentricity will be formed under static etching. However, for dynamic etching the eccentricity of etch pits may become +ve (table 6.3). For pits with hexagonal outlines, the variation in eccentricity is comparatively less for different concentrations. Similarly positive and negative eccentricity can be obtained with concentration which produces pentagonal pits. This leads to the up and down motion of depth point from the geometrical centre by the variation of concentration of an etchant. It is rather difficult to explain the variations in the value of eccentricity of individual etch pit produced on a cleavage surface under identical condition of etching. These variations may be due to a large number of factors which are as follows: (1) local dilution of etchant under static condition of etching. The dilution may be different for various pits, (2) variation of energy of dislocation lines or loops, when etch pits are formed, (3) dislocations network belonging to different crystallographic planes intersecting the plane of observation, (4) removal of $CO_2$ from a point on or near etch pit on a crystal surface (Dunlop & Wilkinson, 1961), (5) dislocations with impurities or without impurities in a crystal, (6) experimental errors due to limitations of measurements of shifts and depths (Adequate care is taken to minimize these errors).

Since many of these factors are operating actively on an atomic scale, it is rather difficult to estimate the contribution of each one of them in deciding the overall value of eccentricity of etch pits.

## 6.5 Conclusions:

(1) The shift and eccentricity of an etch pit depend upon the concentration of an etchant and condition of etching. For a given concentration of an etchant shift increases with etching time while eccentricity remains constant.

(2) By progressive dilution of an etchant (HCl or $H\overline{AC}$) which gives rhombic shape of etch pits on the cleavage face of calcite eccentricity regularly decreases from a positive value to a negative one.

(3) If a dislocation line lies in the plane (110), pits produced by HCl or $H\overline{AC}$ are symmetrical about the direction [110] passing through its geometrical centre. However, the etch pits become asymmetrical about this direction, when they are produced at dislocations lying in plane/s other than (110).

(4) The angle that a dislocation line lying in plane (110) makes with the normal to the plane of observation (001) cannot throw any light on the position of dislocation in this plane because this angle is a function of concentration of an etchant and the inclination of the

dislocation line. For dislocations lying in plane/s other than (110), the angle is only due to the inclination of dislocation line with the normal to the surface under observation. Hence it can be uniquely determined.

(5) Progressive change in a given range of concentration of an etchant produces regular changes in magnitudes of reaction rates along different directions, giving rise to changes in shift and eccentricity of etch pits, without changing its shape.

(6) Average value of eccentricity is nearly same for etch pits produced on matched cleavage faces under identical conditions of etching.