CHAPTER 4

EFFECT OF CONCENTRATION ON THE SHAPE OF ETCH PITS ON CALCITE CLEAVAGES.

4.1 Introduction:

Calcite is one of the commonest and most widely distributed of all minerals; hence many workers have studied the etching of these crystals. It is therefore, worthwhile to review briefly the earlier work on etching of calcite cleavages. In most of the cases studies were made from the crystallographic point of view. [See for example, Honess, (1918); Royer, (1929); Honess and Jones, (1937); Himmel and Kleber, (1937); Boos, (1943); etc.etc.] . They concluded that the geometrical symmetry of crystals was always revealed by etch figures produced by optically inactive etchants. They had used optically active and inactive etchants which usually included organic and/or inorganic acids. It was also observed that the lowering of symmetry of etch figures occurred by the use of optically active etchants. This was found to be true for composite etchants containing a very small amount of optically active etchant. Novak, (1935).

The shape of an etch figure is dependent on the nature, concentration, composition and temperature of an etchant. Thus the earlier workers reported the occurrence of different shapes on cleavage faces of calcite due to various types of etchants. Even with the same etchant, the change in concentration had a significant effect on the shape of etch pits (Watt, 1959; Stanley, 1959; Pandya and Pandya, 1961 etc.). In all cases the diluent used to change the concentration of an etchant is distilled water in which calcite is very sparingly soluble (0.008 gm/litre). It is thus clear that with the same etchant, either concentrated or diluted, the chemical reaction is not materially changed. However, the rate of reaction with a cleavage face of calcite changes and this gives rise to production of etch pits of various shapes. This obviously points to the unusual characteristics of calcite cleavages. The present author has carried out a detailed systematic optical and interferometric study of etch patterns on cleavage surface of calcite. It is observed that even with the same concentration of an etchant, the rate of stirring of the solution has a marked effect on the shape of etch figures.

In most of the cases earlier workers have used acetic acid and hydrochloric acid as etchants which are optically inactive. To facilitate comparison with their etching work, the present study was made by using the above two etchants only. The shapes of etch figures produced by these etchants are functions of concentration and other conditions such as rate of stirring etc; and are discussed in this part.

With the recognition of imperfections in nearly perfect crystals (Seitz, 1952) and their vital role in controlling various structure-sensitive properties, the etch technique has assumed greater importance. It is nowadays widely used to detect and study dislocations in crystals. Several workers have reported dislocation etchants for calcite cleavages and the present author has offered detailed critical comments on these etchants.

4.2 Experimental:

Natural crystals of calcite were obtained from various localities in India. [Sivrajpur, Pawagarh, Broach (Gujarat State), Rajasthan State etc.] . The crystals are fiarly big with their sizes ranging from 1 cm to 15 cms with cross sectional area of the order of 3 cms x 3 cms. A big crystal was selected and etching work was carried out on small pieces obtained by cleaving such a crystal. Calcite crystal was cleaved in the usual way, i.e. by giving a sharp blow with a hammer on a razor blade kept in contact with the crystal along the cleavage direction. The cleavage surface was fully immersed in a still etchant of known concentration for desired time of etching at room temperature. The concentration is usually expressed by the quantity (volume) of acid contained, in total volume of 100 c.c. Thus 10% concentration means 10 c.c. of acid in 100 c.c. of total solution. Distilled water is used as diluent. After etching the crystal for a given period, it was kept in running distilled water for sometime. It was then dried by the hot air blower. Etching time was varied from a few seconds to a few minutes for obtaining etch pits of required sizes, resolvable under a low power objective. The study of etch pattern on calcite cleavages in the initial stages of etching required the use of high power objectives. The contrast in the etch pattern under high magnification and resolution is usually poor. This is therefore, enhanced by depositing silver film on the etched surface by thermal evaporation technique described in Chapter 2. It was found that silver could not be removed fromm the surface of calcite without damaging its microstructure. Hence silver film was not deposited on a crystal cleavage which was subjected to multiple etching for the purpose of studying etch patterns in depth. High resolution microscopic technique with a variety of illuminations and multiple beam interferometry were used to study the etch patterns on the cleavage faces. In all cases the central region of the cleavage surfaces was investigated in detail. This was necessitated by the fact that the edges from which the cleavage had propagated, were regions of high distortion.

4.3 Observations and Results:

(a) Change in shape of etch figures with change in concentration of hydrochloric acid.

It is known that calcite reacts very strongly with concentrated inorganic acids. Strong hydrochloric acid reacts violently with calcite to form highly soluble reaction products, calcium chloride, water and gaseous carbon dioxide. The later goes to the atmosphere. The etching is so fast that within a fraction of second, a large number of very big pits are produced. Further they overlap each other. As a result the use of such a strong etchant in general prohibits a detailed study of the etch patterns. Fig. 4.1 (x 150) represents a photomicrograph of a freshly cleaved surface etched in 90% HCl for less than a second. Point-bottomed pits with triangular outlines are observed in the figure. Most of these pits exhibited terraced structure. Outer boundaries of the tringular pits are curved.

Fig. 4.1 (x150)

Fig. 4.2 (x150)

Fig. 4.3 (x90)

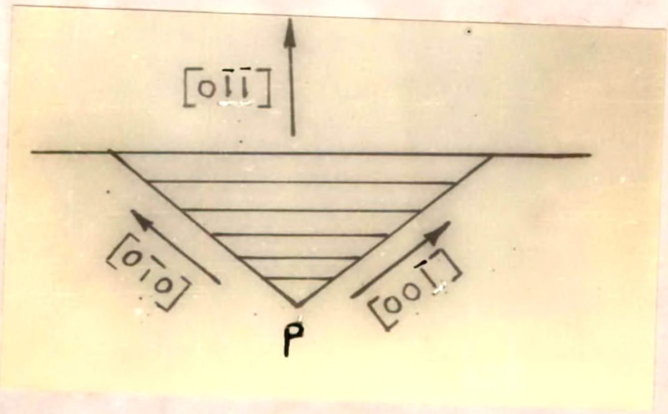

Fig. 4.3A

Fig. 4.4 (x170)

Fig. 4.5 (x170)

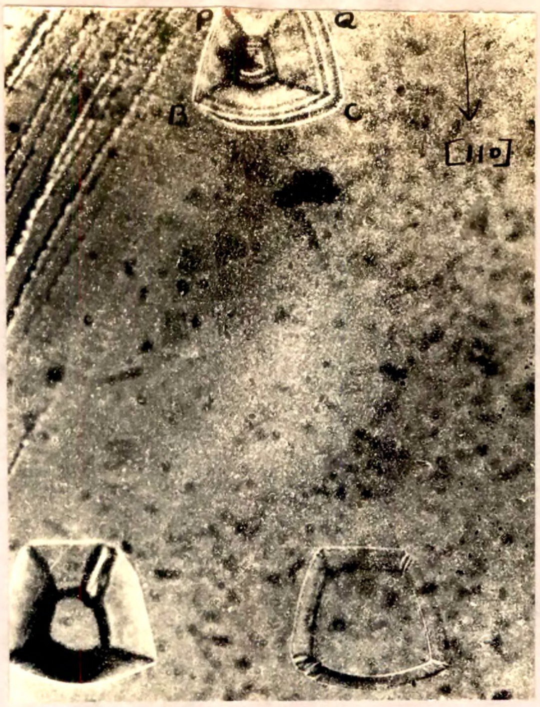

Fig. 4.6 (x170)

Fig. 4.7 (x170)

Planes forming the pits intersect one another in straight lines. The orientation of these pits can be found with the help of percussion mark. Pits are symmetric with respect to projection of longer lined of intersection (namely AO in figure) on cleavage faces. This is in the direction $[110]$. While MN which is perpendicular to AO and parallel to the tangent at the midpoint of the curved line BC is in the direction $[1\bar{1}0]$. In some cases small triangular shaped pits are found at the centre of the bigger triangular pits. These small etch pits may exhibit different outlines such as rhombic, septagonal, pentagonal etc. It will be shown, in what follows that above shape of etch pits can also be observed on the calcite cleavage faces at low concentration of hydrochloric acid. It is further clear that a few pits are overlapping and many pits are likely to overlap each other on successive etching for a small increase of etching time, (about a second) on a given crystal face. Background pitting is also found on the surface. It is observed that with the decrease in concentration, there is a change in the directions of boundaries (AB and AC) of triangular etch pit. Fig. 4.2 (x 150) is a photomicrograph of a crystal surface etched by 60% HCl for less than a second. It is clear from the figure that one boundary of the tringular pit (such as BC) becomes nearly straight with direction $[1\bar{1}0]$. Further curvilinear character of the boundary BC mentioned above is more in the point-bottomed pits than in the terraced pits. The curvatures of the other two boundaries such as AB and AC in point-bottomed and terraced pits are nearly same. The pits have assorted sizes and small background pits are also observed. Besides the ratio $^{BC}/_{AB}$ in fig. 4.2 is slightly more than the ratio of the corresponding sides $^{BC}/_{AB}$ in fig. 4.1. This is due to change of concentration of the etchant. Pits are nearly symmetrical about the line AO which is in the direction $[110]$ and passing through the centre of the ~~th~~pit. This direction also represents line of symmetry of crystal face. Orientation of etch pits was determined with the help of percussion mark produced on the cleavage face. Fig. 4.3 (x 90) shows a photomicrograph exhibiting the etch pattern produced by etching freshly cleaved surface by 30% hydrochloric acid for a second at room temperature. On this etched surface a percussion mark was produced in the usual way. The percussion figure consists of a large number of parallel lines which are identified as slip lines generated from the point of impact P and on one side of it, along the direction$[\bar{1}\bar{1}0]$ and bound by the cleavage direction$[\bar{1}00]$ and $[0\bar{1}0]$ fig. 4.3a (sketch diagram) . Slip line and lines in cleavage direction meet at a point P and form an isosceles triangle on the cleavage surface. The etch pits with isosceles triangular outlines (fig. 4.1, 4.2, 4.3) on the surface have opposite orientation with respect to percussion mark. This orientation will henceforth be referred to as negative orientation. If the outline of an etch pit has orientation similar to that of percussion mark, the etch pit has a positive orientation. The comparison of etch pit shapes in three photomicrographs (Figs. 4.1, 4.2, 4.3) shows very clearly the effect of change of concentration of hydrochloric acid. With a very high concentration (about 90%) all sides of triangular etch pits are curved. With the decrease of concentration by 30%, the base BC (Figure 4.2) becomes less curved than the other sides. When the concentration was further reduced by 30%, the isosceles sides AB and AC become more rectilinear than the base BC (Fig. 4.3). Further on the ~~right~~ left hand side of a percussion mark, a small pit 'P' with pentagonal outline suggests the development which should be effected for converting the shape of triangular etch pit into other geometrical figures. The curved base (BC in Fig. 4.3) is divided into two equal parts and vertex A is truncated. These changes give rise to an irregular pentagonal pit. The simultaneous production of triangular and pentagonal pits on the same cleavage face is usually rare. The division of the curved base into two lines is symmetrical about the line of symmetry $[110]$ of the crystal face. It appears that truncated side at the vertex A is parallel to $[1\bar{1}0]$, i.e. the base of the percussion mark. This will be elaborated a bit later. It is thus clear that when the concentration of hydrochloric acid at room temperature was progressively reduced from 90% to 30% for etching, the geometrical outlines of etch pits became more and more rectilinear without changing its triangular shape. Further change in concentration by 5% (i.e. use of 25% HCl acid) has produced a change in the shape of the etch figures. Fig.4.4 (x 170) is a photomicrograph showing quadrilateral etch pits obtained by etching a freshly cleaved surface by 20% HCl for 1 second. The outline of etch pits in this figure, is that of a curvilinear quadrilateral which is obtained by truncating the vertex of curved isosceles triangular etch pits. The length of the side developed at the vertex A (Fig. 4.3) and shown as PQ in Fig. 4.4 is comparatively very less than the opposite curved side BC. The average ration BC:PQ is more than 4. The quadrilateral shape is maintained for the change of concentration from 25% to 15% hydrochloric acid.

With further decrease in concentration from 15% to 5%, the curvilinear boundary BC (Fig. 4.4) of the quadrilateral pit was segmented into two parts giving rise to etch pits with irregular pentagonal outlines on the cleavage surface of calcite. This is shown by photomicrograph [Fig. 4.5 (x 170)] obtained by etching a cleavage surface by 10% hydrochloric acid for one second at room temperature. During these changes of concentration, the length of the various sides are ranging as shown below.

TABLE No: 4.1

DIMENSIONS OF PENTAGONAL ETCH PITS OBTAINED BY THE CHANGE OF CONCENTRATION FROM 15 % to 5 % HCl.

Obs. No.	Cons. of HCl.	Length of sides with direction in Microns. BS	SC	PQ	QC	PB	Ratio $\frac{BS}{QP}$	$\frac{SC}{QP}$	$\frac{CQ}{QP}$	$\frac{PB}{QP}$
		[0 10]	[100]	$[\bar{1}10]$	[350]	[5 30]				
1	5%	10	10	9	20	20	1.11	1.11	2.22	2.22
2	7%	14	14	9	28	28	1.75	1.75	3.5	3.5
3	10%	22	22	9	40	40	2.44	2.44	4.44	4.44
4	12%	26	26	8	42	42	3.25	3.25	5.25	5.25
5	15%	25	25	7	44	44	3.57	3.57	6.30	6.30

When the concentration of hydrochloric acid was reduced from 5% to 1.5%, the shapes of etch figures are found to be quite unusual. The shape becomes quadrilateral. The formation of quadrilateral etch marks by the use of hydrochloric acid of concentration ranging from 5% to 1.5%, is almost opposite to the formation of pentagon from quadrilateral etch pits (produced by the concentration ranging from 15% to 25% HCl). Segments BS and SC unite t o form a smooth curvilinear boundary BC with a corresponding increase of opposite side PQ and a decrease of adjoining sides PB and CQ. In the case of pentagonal etch pits (Table 4.1), the ratio $^{PB}/_{QP}$ varies from 2.22 to 6.3, the corresponding variation of the ratio is 1.0 to 2.0 in quadrilateral pits in Fig. 4.6 (x 170) which shows a photomicrograph of a cleavage surface etched by 2% HCl for 2 seconds. Point-bottomed quadrilateral pits are observed. The side opposite to the curved line of pit is parallel to the slip line and pits are symmetrical about the line [110] passing through the projection of a point of maximum depth on the cleavage plane.

It is hard to explain the occurrence of pits with regular pentagonal outlines on a cleavage surface, on the basis of homogeneous filling of space. However, these pits do exhibit the symmetry of the crystal face viz. line of symmetry along [110]. Fig. 4.7 (x 170) shows a photomicrograph of surface etched by 1% HCl for 8 seconds. It exhibits clear point-bottomed and nearly regular pentagonal pits. They are produced by the hydrochloric acid with concentration ranging from 1.5% to 0.5%. The change in concentration of this etchant shifts depth point (the projection of point of maximum depth of pit on cleavage surface) with respect to the geometrical centre of the pit.

Pit T in Fig. 4.7 is noticeable different from other pits. It is very likely that the defect revealed by the formation of this pit might have moved vary rapidly during etching. However, there is not much experimental evidence in this regard.

It is generally understood that when the concentration is gradually reduced, the attack along normal direction is comparatively decreased, thereby giving rise to larger amount of lateral dissolution. As a result the deterioration of the surface would be more. This has been observed for crystals etched by acids of lower concentrations (Keith and Gilman, 1960). However, in the present work etching at lower concentration has not resulted in the deterioration of freshly cleaved surface. This is due to highly reactive character of the substance. For a concentration of the order of 0.25% HCl, septagonal etch pits were produced on the cleavage face of calcite. [Pandya and Mehta, 1969] . Fig. 4.8 (x 170) is a photomicrograph of a freshly cleaved calcite surface etched by 0.25% HCL for 15 seconds. Among the many sides which bound this pit, LP, PQ, QM, CS and SB have low inclices of direction whereas BL and CM have high indices and are parallel to BP and CQ of a regular pentagonal pit shown in Fig. 4.7. Here again the pits are symmetrical about the line of symmetry of the crystal face. When the concentration of HCl acid is further reduced, unexpected

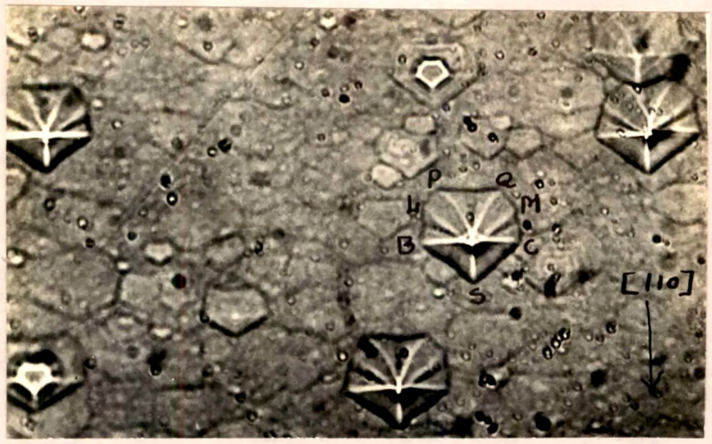

Fig. 4.8 (x170)

Fig. 4.9 (x170)

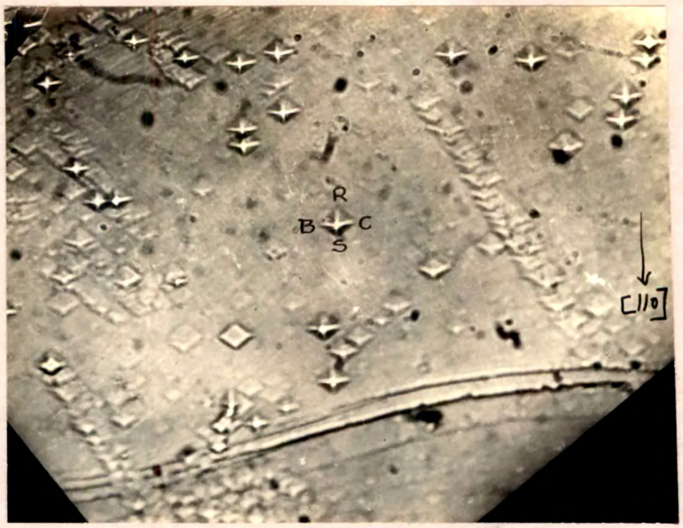

Fig. 4.10 (x170)

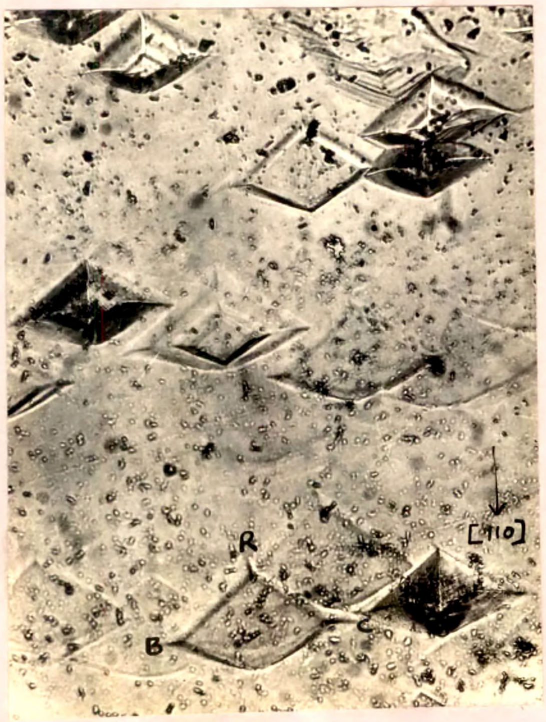

Fig. 4.11 (x 170)

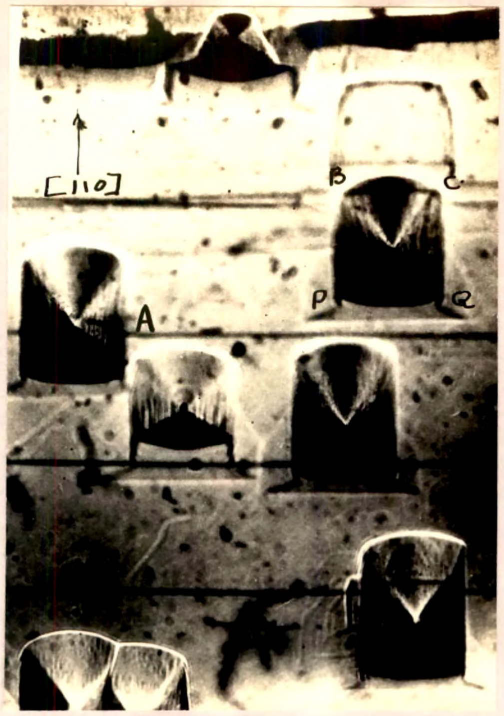

Fig. 4.12 (x170)

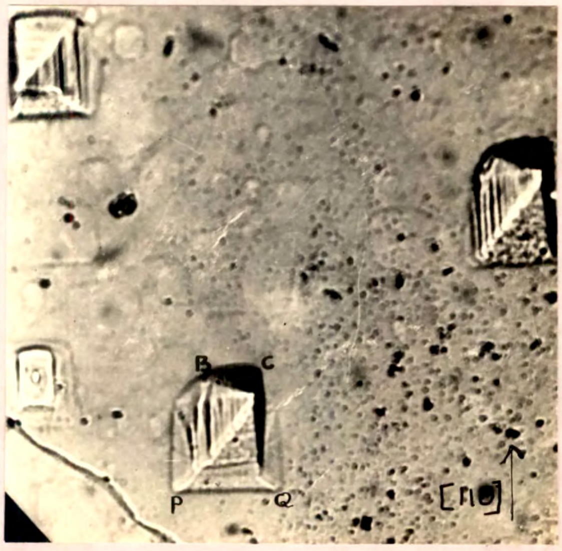

Fig. 4.13 (x170)

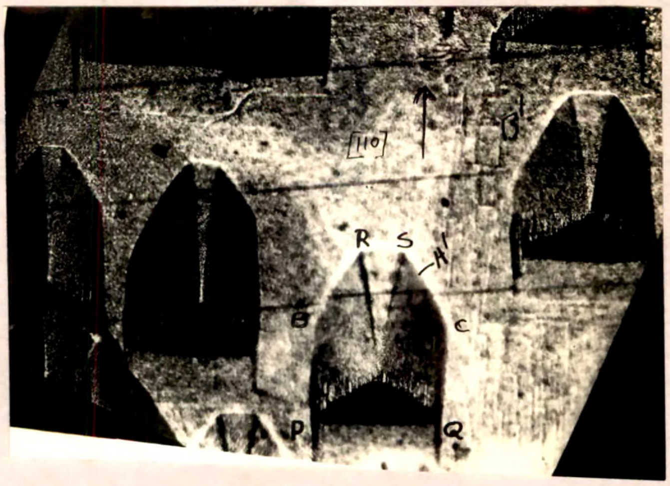

Fig. 4.14 (x170)

Fig. 4.15 (x170)

Fig. 4.16a (x170)

Fig. 4.16b (x170)

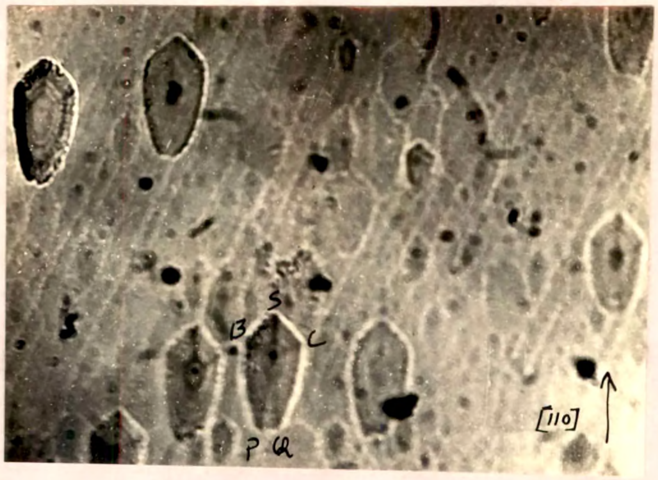

Fig. 4.17a (x170)

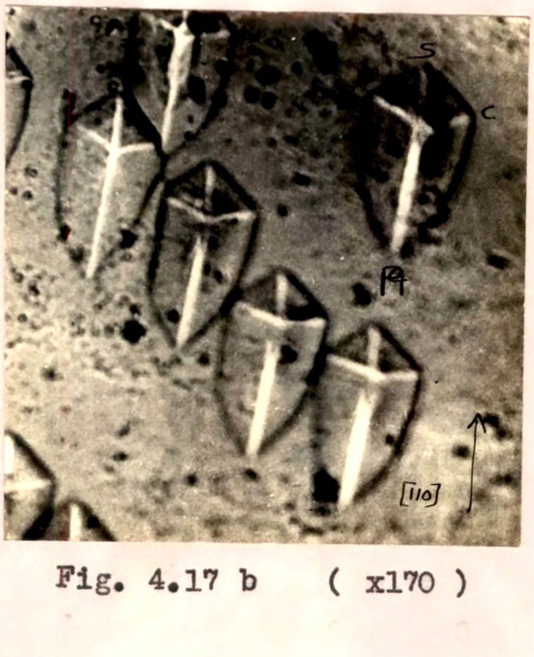

Fig. 4.17 b (x170)

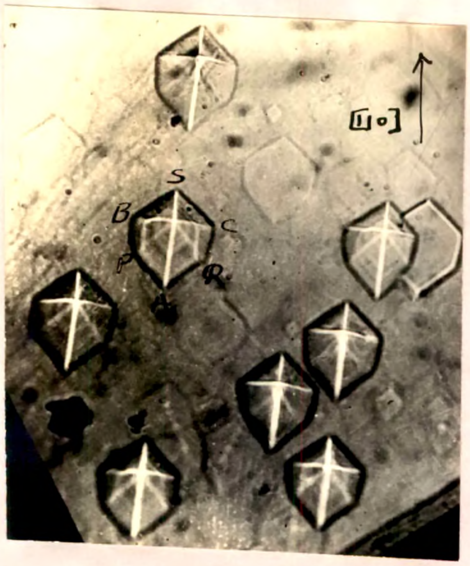

Fig. 4.18 (x220)

Fig. 4.19 (x220)

Fig. 4.20 (x170)

interesting observations are obtained. With a further decrease of concentration by 0.05%, i.e. up to 0.20% of hydrochloric acid, the lengths BL and MC decrease with a corresponding large increase of LP and QM having low indices of direction. Figure 4.9 (x 170) represents a photomicrograph of a freshly cleaved surface etched by 0.18% of HCl for 30 seconds. The lines BL and MC of septagonal etch pit in Figure 4.8 disappeared completely and an irregular pentagonal etch pit is formed. PQ has direction $[1\bar{1}0]$ whereas the directions of the remaining boundaries are along $\langle 100 \rangle$. The length of PQ diminishes with increase of dilution of HCl and at a concentration of 0.15%, length of PQ becomes zero and as a result rhombohedral etch pits are formed Fig. 4.10(x 170) represents a typical photomicrograph of a freshly cleaved surface of calcite etched by 0.1% hydrochloric acid for 23 seconds.. The etched surface exhibits background pitting with large number of point-bottomed pits with rhombic outline, scattered over the whole surface. The boundaries of these pits are parallel to the edges of the crystal. The lines of intersection of planes forming a pit, are more prominent and well defined than boundaries of pits. It is of interest to mention that the projection of point of maximum depth on cleavage surface (depth point) does not coincide with the geometrical centre of the plane figure. This gives rise to the formation of asymmetrical etch pits along $[1\bar{1}0]$. Seperation between depth points and geometrical centres of etch pits in direction $[110]$ has been observed in many cases for various shapes of etch pits and all these are discussed in Chapter 6. It should be mentioned here that separation between the depth point and geometrical centre of a plane figure is a function of concentration, composition of etchant, time of etching etc.

The pyramidal rhombic etch pits maintain their shape on the cleavage surface when etched by hydrochloric acid, having concentrations ranging from 0.01% to 0.14 %. It should be noted that for all concentrations between 1.5% and 0.01 %, relative change in the directions of boundaries BS and SC (Figs. 4.6 to 4.9) is not noticeable. However, shape of geometrical figure on the surface does change due to change in directions of other boundaries. Further the boundaries BS and SC are parallel to the cleavage edges of a rhomb with 'S' pointing in the same direction as the point of impact of a percussion mark. Use of HCl of still lower concentration reduces the sharpness of corner 'S' and indicates the tendency of the sharp boundary BS and SC to unite and form a curvilinear boundary, thereby giving rise to an isosceles triangular pit of negative orientation and a curvilinear base whose tangent at the mid point is parallel to $[1\bar{1}0]$. This is very clear from Figure 4.11 (x 170), which is a photomicrograph of a freshly cleaved surface etched by 0.001% HCl for 10 hours. Here etching time is enormously increased for obtaining visible etch pits under high power objectives. It should be remarked here that the pyramidal etch pits ~~which~~ with triangular outlines on the surface can be produced by etching a cleavage surface by a highly concentrated hydrochloric acid, (Figs. 4.1, 4.2, 4.3) and also by a very diluted HCl. These pits exhibit the same line of symmetry i.e. [110] passing through the depth point. Further in the former case the elongated triangles with acute angles are observed whereas very diluted acid produces short obtuse angled triangular etch pits with isosceles sides parallel to the direction <100>.

On going through the various shapes of etch pits produced on freshly cleaved surface of calcite crystals by A.R. quality hydrochloric acid (10 N) with concentrations ranging from 90% to 0.0001%, it is crystal clear that a complete cycle of etch pit shapes is depicted and that all shapes are symmetrical about the direction [110] and usually passing through the centre of the plane figure of a pit, projected on cleavage surface. Further for a given dilution all pits usually exhibit same geometrical outline irrespective of their origin on the cleavage surface. All these observations are summarized in table 4.2.

From the preliminary studies of etching of these crystal cleavages by other inorganic acids such as H_2SO_4, HNO_3, the present author is of the opinion that such spectrum of etch pit shapes can also be obtained. Hence, in the present work, these observations are not included. Since calcite is also easily attacked by organic acids, it is likely that the use of such acids diluted by distilled water within a given range, would produce pits of various shapes. However there are certain differences between the chemical actions of organic and inorganic acids on these cleavages. These differences are brought out more clearly in the next section which describes the etch action of glacial acetic acid on calcite cleavages.

(b) Change in shape of etch figures with change in concentration of glacial acetic acid.

Many workers [see e.g. Royer, (1929); Keith and Gilman (1960), Hanke (1961), Thomas and Renshaw (1965)] have studied the etching of calcite cleavages by organic acids. Royer had used different types of tartaric acids (d, ℓ and dℓ) as etchants for studying the effect of optically active and inactive etchants on the geometry of etch figures. Thomas and Renshaw also studied the etch figures produced by tartaric and malic acids. They suggested pits to be at sites of dislocations terminating on the cleavage surface. Hanke observed rhombic etch pits on cleavage face of calcite etched by glacial acetic acid. Keith and Gilman had used various organic acids such as formic, propionic, tartaric, acetic etc. for producing etch figures. They also studied the effect of concentration of formic, propionic and acetic acid on the quality of etch figures. They used the concentration of glacial acetic acid ranging from 100% to 10% and reported the production of rhombic etch figures by pure glacial acetic acid and of pentagonal etch pits by 50% and 10% glacial acetic acid. The diluent used in their work was distilled water. It will be shown in this section that some of their observations are at variance with those reported here.

Etch pits are not produced by pure glacial acetic acid on the cleavage face of calcite even if it is kept in the acid for more than 30 hours at room temperature. When it was diluted by distilled water by 2% (i.e. 98% acid) etch pits were observed on the face after prolonged etching for several hours. Fig. 4.12 (x 170) represents a typical light profile photomicrograph of a cleavage surface etched by 97% glacial acetic acid (by volume) for 18 hours at room temperature. It shows point bottomed rectangular pits with a pair of curved boundaries. Tangents at the mid points of these boundaries are parallel to each other and lie in the direction $[1\bar{1}0]$. The second pair of boundaries are in the direction $[110]$.

These pits are flanked by shallow irregular pits having base (line) in the direction $[1\bar{1}0]$. The pit at the base of a main rectangular pit is a trapezium formed by a pair of base lines (one straight and the other curved black) and two slanting black lines. The base pit is always formed on one side of the centre of the rectangular pit and it is along $[\bar{1}\ \bar{1}\ 0]$. The depth of the pit A is found by light profile to be 9.5 microns. It is known that ionization is very less in the high concentration of acetic acid. Hence such concentrated acetic acid would take more time to produce desirable etch effect. However, this is not true for all organic acids. Further highly concentrated inorganic acids have large ionization i.e. more content of free hydrogen ions, hence they require less time for producing observable etch effect.

Fig. 4.13 (x 170) shows a photomicrograph of a freshly cleaved surface of calcite etched by 95% glacial acetic acid for 6 hours. It exhibits rectangular point bottomed pits showing following characteristics. (1) Rectilinear character of the line PQ on the opposite side of curved boundary. (2) Absence of shallow base pits near PQ. (3) Non-coincidence of the depth point with the geometrical centre of the plane figure. (4) Terraced structure of pits with background etching.

The rectangular character of pits produced on a cleavage surface by concentrated glacial acetic acid is more or less maintained up to a concentration of 92% (i.e. from 98% to 92%). A further decrease in the concentration produces a change in the shape of etch pit. Fig 4.14 (x 170) represents the photomicrograph of the freshly cleaved surface etched by 90% glacial acetic acid for five hours at room temperature. There are remarkable differences in the characteristics of etch figures of fig 4.12 and fig 4.14. The curved line RS (fig 4.12) has shortend and became more rectilinear (fig. 4.14), whereas the lines PR & QS (fig 4.12) has became curved and segmented into two lines giving rise to hexagonal etch pits bound by curved and straight lines. Further depth point has shifted considerably in the direction $[\bar{1}\bar{1}0]$ from the geometrical centre. As a result the steep sloping plane which is shown by dark sloping portion of pit was reduced in size. The black pits A', B' are 7 microns and 5 microns deep respectively. This shape of the pit is maintained up to a concentration of 70% (i.e. from 92% to 70%) of glacial acetic acid. When a freshly cleaved surface of calcite was etched by 60% acetic acid for 7 minutes, etch pits with pentagonal outlines on the surface were produced (fig. 4.15 (x 170)). The point bottomed etch pits are highly asymmetrical around the depth point. Some boundary lines of the pentagonal pit are in crystallographic direction.

It should be noted that the etching time required to produce these pits is a few minutes only, whereas for producing etch pits (figs. 4.12, 4.13 and 4.14) it runs into a few hours. The orientation of the pentagonal figure is positive with respect to percussion mark. The range of concentration of glacial acetic acid producing pit with pentagonal outlines was found to vary from 70% to 35%. Decreasing concentration of acetic acid has noticeably affected the quality of etch patterns on the surface. Fig 4.16a (x 170) shows a photomicrograph of a surface etched by 30% glacial acetic acid for 30 seconds. It is clear from this figure that the shape of etch pit becomes triangular with a general dissolution of the surface. Further the pits are more shallow than those observed in earlier photomicrographs (figs. 4.12 to 4.15). Hence the lateral dissolution rate is much higher than the normal dissolution rate. The lines <u>PB</u> and <u>QC</u> (fig. 4.15) have now completely disappeared and as a result pit shows triangular outlines and is having positive orientation with respect to percussion figure. The boundaries forming triangular etch pit are less clear than the lines joining the vertices and point of maximum depth. A further decrease in concentration of etchant produces more general etching than preferential one. This is shown clearly in the photomicrographs (fig. 4.16b, x 170) of a cleavage face etched by 20% glacial acetic acid for 30 seconds. The

The rate of general (lateral) dissolution is so much that the boundaries of pits could not remain sharp and straight.

The photomicrograph (fig. 4.17a, x 170) was obtained by etching the calcite cleavage by 10% acetic acid for 30 seconds. Although the pit boundary is pentagonal having positive orientation with respect to percussion mark, the quality of these pits is very poor, being less sharp as compared to those pits shown in fig. 4.15. Even the length of the sides and the angles between the boundaries forming these pits are different than those of fig. 4.15. $\angle$QPB and $\angle$PQC (fig. 4.15) are right angles while the corresponding angles for pentagonal pits (fig. 4.17a) are greater than 90°. Further the background etching is more in fig. 4.17a than in fig. 4.15. The background etch effect is reduced with a further decrease of concentration by 6%. Fig. 4.17b (x 170) shows etch pits with quadrilateral outlines on the surface obtained by etching it by 4% glacial acetic acid for 30 seconds. The side PQ along $[1\bar{1}0]$ in fig. 4.17a reduced to a point in fig. 4.17b, thereby increasing the curvature of the slanting sides AC and AB. Further decrease of concentration of this etchant divides the curvilinear sides into two straight parts. Hence the pit shape becomes a hexagon. Fig. 4.18 (x 220) shows irregular asymmetric hexagonal etch pits produced by etching a cleavage surface by 1% glacial acetic acid for 30 seconds.

The boundaries forming these pits are rectilinear with crystallographic directions. Besides, the background etch effect is less in comparison with that found on other photomicrographs (figs. 4.16a, 4.16b, 4.17a and 4.17b). It is found that the sides of a hexagonal pit along [110] decrease with decrease of concentration (from 2% to 0.5% of glacial acetic acid). Fig. 4.19 (x 220) represents a photomicrograph of a freshly cleaved surface etched by 0.45% glacial acetic acid for 30 seconds. It exhibits well defined rhombic pits with sides parallel to ⟨100⟩. The pits are asymmetric about the depth point. Incidently this figure is a cleavage counterpart of figure 4.18. It shows complete correspondence so far as the positions of pits are concerned. Such pits were also produced by 0.1% HCl acid. This is true for concentrations ranging from 0.01% to 0.15% hydrochloric acid. However, the boundaries of these pits (fig. 4.19) are more sharp than those seen in fig. 4.10. This also suggests that the sloping planes of a pit produced by glacial acetic acid are more steep or deep than those of a pit produced by hydrochloric acid. A still lower concentration (0.001%) of glacial acetic acid could etch the cleavage surface when kept in it for a very long time, say 10 hours. This is shown in the photomicrograph (fig. 4.20, x 170) which exhibits the etch pits having triangular boundaries. The isosceles sides of a triangular pit are in

$\langle 001 \rangle$ directions and the tangent at the midpoint of a curved base is parallel to $[1\bar{1}0]$. It is of special interest to note that the orientation of these triangular pits is negative, that is opposite to that of percussion mark. This observation should be compared with that of fig. 4.16a which shows triangular etch pits having positive orientation. Triangular pits are also symmetrical around the $[110]$ line passing through the centre. It should be mentioned that the symmetry of the pit around the $[110]$ line passing through the centre is observed in nearly all the figures (except fig. 4.13) produced by the glacial acetic acid and hydrochloric acid. All these observations are summarized in table 4.3.

The present author has also tried other organic acids such as formic, tartaric etc. as etchants. The etch pits of various shapes could also be produced by using various concentration of formic acid and of propionic acid. However, change in etch pit shape was not observed when cleaved surface of calcite was etched by tartaric acid of various concentrations ranging from 100% to 0.01% of its saturated solution in distilled water. Further for all these concentrations of tartaric acid there is not much difference in etching time required to produce pits of optimum size for studying them under microscope.

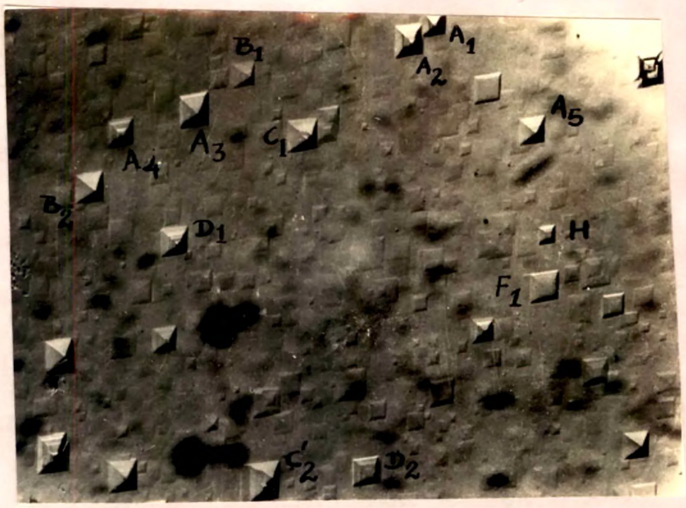

Fig. 4.21a (x220)

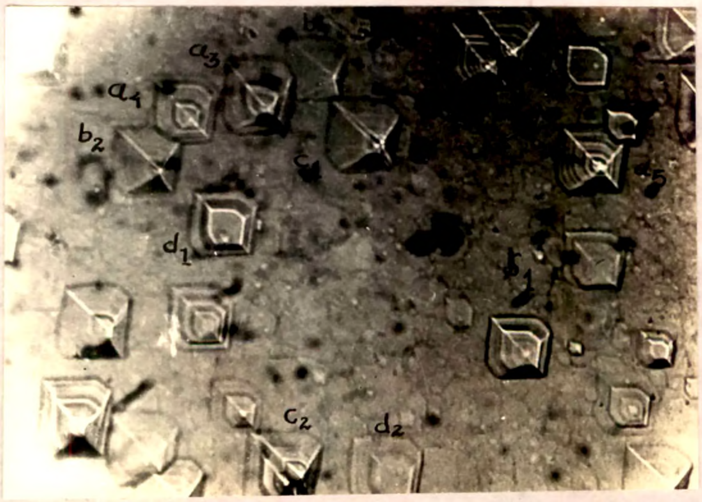

Fig. 4.21b (x220)

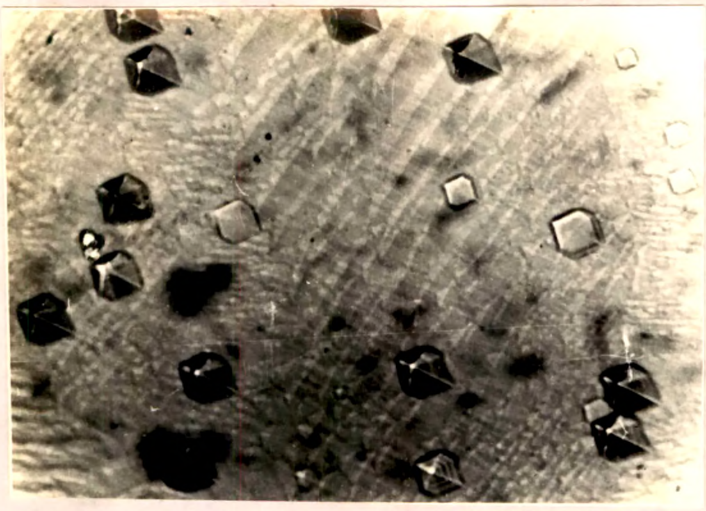

Fig. 4.22a (x220)

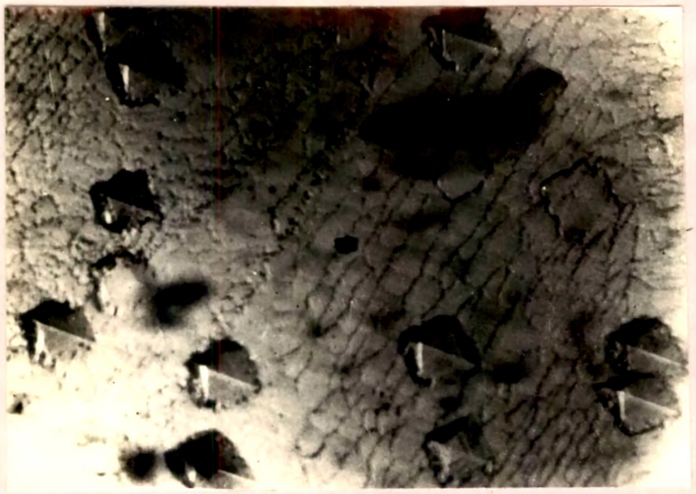

Fig. 4.22b (x220)

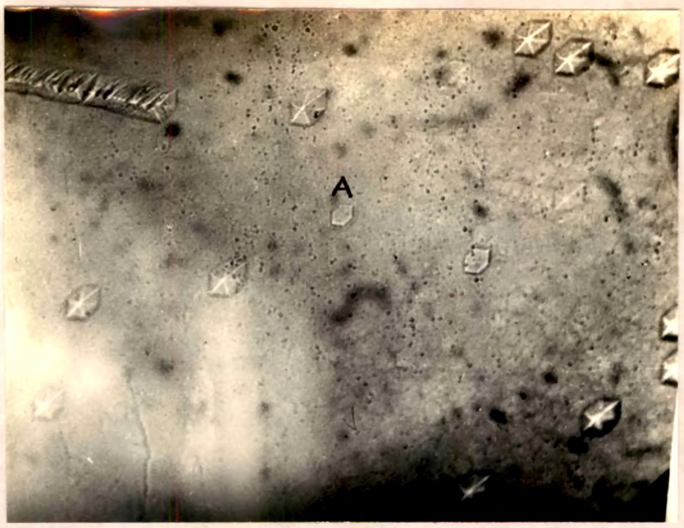

Fig. 4.23a (x220)

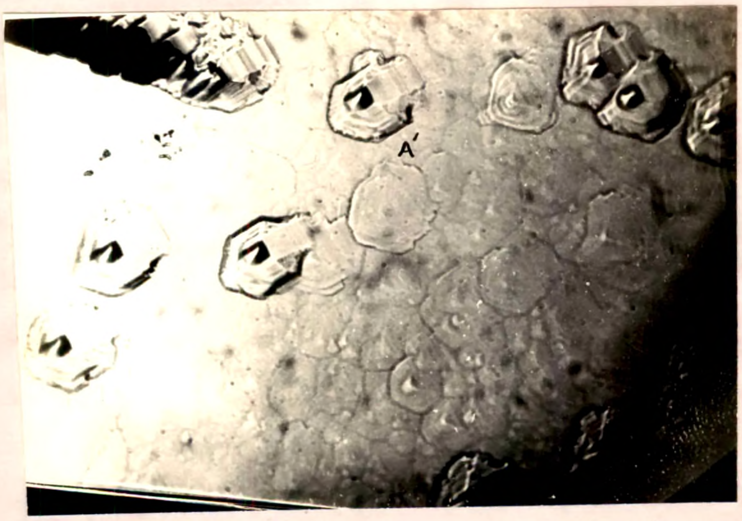

Fig. 4.23b (x220)

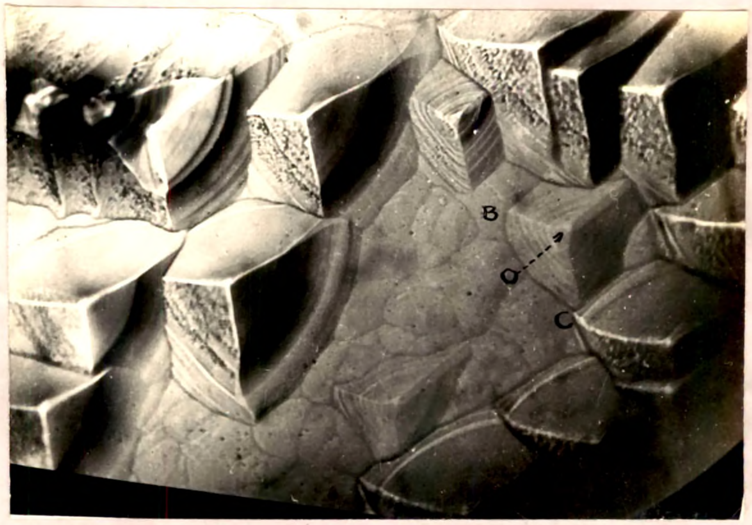

Fig. 4.23c (x220)

Fig. 4.23d (x220)

(c) Multiple etching of isolated cleavage surfaces by different etchants.

It is shown in the earlier sections how the etch pit shape varies with the concentration of an etchant. In this section an attempt is made to study the action of various etchants of different concentrations on the same cleavage surface. This study will be of use in throwing some light on the anisotropic reaction rates and origin of etch pits. Care is taken to select the regions where the density of pits is moderate, so that multiple etching will not lead to advanced and complicated etch patterns. It is further found from etching experiments that a surface can be subjected to etching for two or three times without detoriorating the quality of etch features and the surface. Hence no etching work was carried out on it after this period.

Fig. 4.21a (x 220) is a photomicrograph of etched surface obtained by etching a ~~cleavage~~ surface of calcite by 0.3% glacial acetic acid for a period of 40 seconds. It shows a large number of point-bottomed and flat-bottomed rhombic pits with background micropitting. When this etched surface is re-etched by 1% glacial acetic acid for 40 seconds, the etch patterns are shown in fig. 4.21b (x 220). The comparison of these figures brings out the following salient features. (1) Etch pits with hexagonal boundaries (fig.4.21b) are seen at the positions corresponding to rhombohedral etch pits. Identical background effect is also seen in both figures. (2) However, there are certain differences as shown below. (a) Point-bottomed terraced rhombohedral pits A_1 , A_2 -- (fig. 4.21a) correspond with point-bottomed terraced hexagonal pits a_1 , a_2 -- (fig. 4.21b). (b) Point-bottomed rhombic pits B_1 , B_2 (fig. 4.21a) correspond with point-bottomed hexagonal pits b_1 , b_2 (fig. 4.21b). For pit B_1 and corresponding pit b_1 , depth points are slightly shifted from their regular positions in a symmetric pit. (c) Rhombic pit C_1 (fig. 4.21a) has two depth points which have correspondence with those of pit c_1 (two depth point) (fig. 4.21b). (d) Point-bottomed terraced rhombic pits D_1 & D_2 (fig. 4.21a) correspond with flat-bottomed hexagonal pits d_1 & d_2 (fig. 4.21b). (e) Absence of flat-bottomed pit in fig. 4.21a with a corresponding flat-bottomed hexagonal pit f_1 in fig.4.21b and vice versa. (f) Absence of point-bottomed hexagonal pit (fig. 4.21b) corresponding to point-bottomed rhombic pit H (fig. 4.21a).

When the order of etching was reversed i.e. the freshly cleaved surface was etched by 1% glacial acetic acid for 30 seconds (fig. 4.22a, x 220), followed by re-etching the surface by 0.4% glacial acetic acid for 30 seconds, fig. 4.22b (x 220), all the characteristics observed in fig. 4.21a and 4.21b could be reproduced.

The photomicrograph (fig. 4.23a, x 220) is obtained by etching a freshly cleaved surface by 1% glacial acetic acid for 15 seconds. It exhibits scattered point-bottomed hexagonal etch pits. This surface was re-etched by a highly concentrated (about 92%) glacial acetic acid for a period of 3 hours (fig. 4.23b, x 220). Etch pits with octagonal boundaries and having rectangular pits at the centre are found at sites corresponding to those of hexagonal pits (fig. 4.23a). The comparison of etch pits on these figures shows that the point-bottomed pits (fig. 4.23a) usually correspond with the point-bottomed pits (fig. 4.23b). Same is true for flat bottomed etch pits on these figures. Pit marked as A (fig. 4.23a) which is underdeveloped point-bottomed pit becomes flat-bottomed in fig. 4.23b. Fig. 4.23c (x 220) is obtained by re-etching the surface shown in fig. 4.23b by 30% hydrochloric acid for less than a second. It is clear from the comparison of these figures that the point-bottomed octagonal etch pits (fig. 4.23b) correspond with the point-bottomed triangular pits with a large amount of roughening of the triangular plane OBC bound by vertex O (depth point) and curved line BC. Tangent to BC at mid point is along $[1\bar{1}0]$. Further re-etching of this surface (fig. 4.23c) by highly concentrated (94%) glacial acetic acid for 4 hours, reveals clearly the formation of rectangular etch pits at the centres of the triangular etch pits (fig. 4.23d, x 220). A comparison of these pits with those of fig. 4.23b shows a change in orientation of these pits (at the centres) through an angle 90°. However, the preferential sites do not change by successive etching and re-etching by glacial acetic acid and hydrochloric acid of varying concentrations. This therefore clearly suggests that these pits are likely to be the seat of some specific defects within the crystal. Many shallow point-bottomed pits have not significantly changed their positions in the figs. 4.23b, 4.23c and 4.23d.

(d) Matching of cleavage faces successively etched by different concentrations of etchants.

In this section the observations on matched cleavage surfaces are reported. Figs. 4.24a and 4.24b (x 340) are the oppositely matched cleavage counterparts etched by different etchants viz. glacial acetic acid and hydrochloric acid. Fig. 4.24a (x 340) is a photomicrograph obtained by etching the cleavage surface by 0.25% glacial acetic acid for 10 seconds, whereas the photomicrograph (fig.4.24b, x 340) shows the etching of cleavage counterpart by 0.25% hydrochloric acid for 15 seconds. It is clear that there is a good deal of correspondence between the large scattered

Fig. 4.24a (x340)

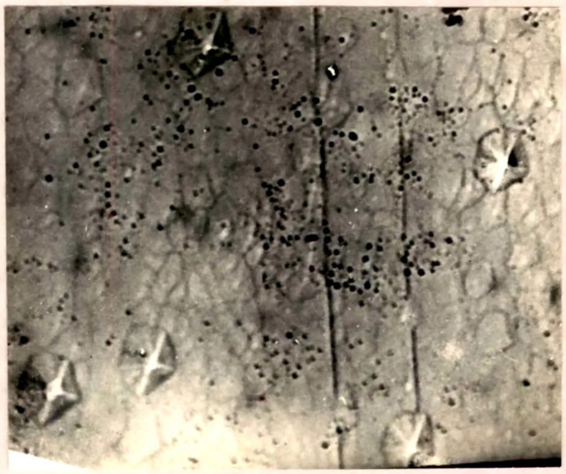

Fig. 4.24b (x340)

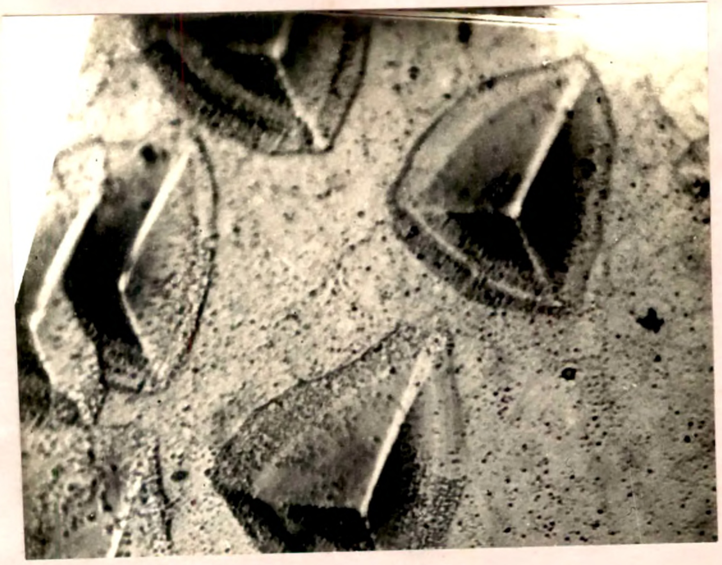

Fig. 4.25a (x340)

Fig 4.25b (x 340)

pits and the cleavage lines; but the background etching is not equally reflected on both faces. There is also a relative shift of cleavage lines on matched faces as observed by Patel and Tolansky, (1959) and Pandya, (1961). The surface shown in fig. 4.24a was re-etched by 30% hydrochloric acid for a second. It is seen that cleavage lines are washed away by etching and the general micropitting of the surface has increased considerably and triangular pits (fig. 4.25a) are observed at the sites of rhombic pits. Fig. 4.25b (x 340) represents a photomicrograph of surface shown in fig. 4.24b which was further re-etched by 0.8% hydrochloric acid for 7 seconds. There is a large amount of general dissolution with disappearence of cleavage lines and preferential etching at those points where large septagonal pits are observed. Fig. 4.25b$_1$ (x 340) shows the effect of further re-etching of surface (fig. 4.25b) by 20% HCl for a second. This has given rise to quadrilateral pits at those sites where pits were formed on earlier etching. The comparison of figs. 4.24a; 4.24b, 4.25a; 4.25b; and 4.25b$_1$ shows that there is almost a complete correspondence between the positions of etch pits on the oppositely matched faces etched by various etchants having different concentrations. However, all the pits are not properly reflected. The terraced point-bottomed pit A (fig. 4.25b$_1$) is not at all reflected in other four figures. It is very likely that during the third etching, the nucleation at this point might have been created

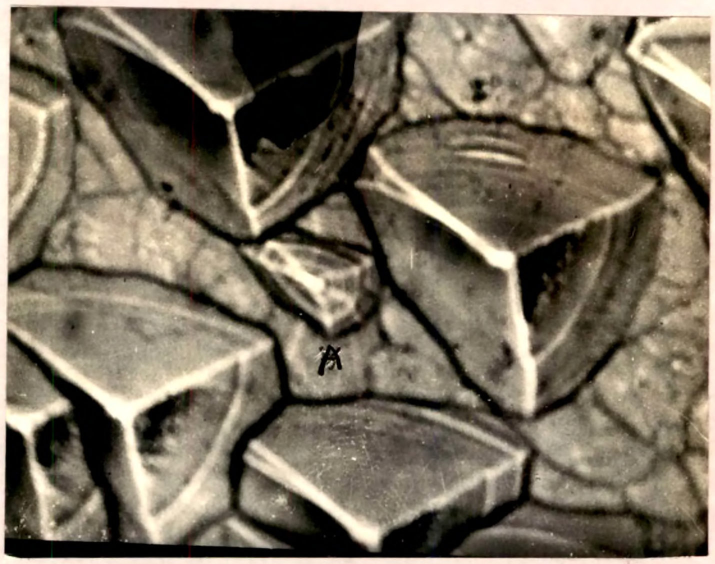

Fig. 4.25b$_1$ (x340)

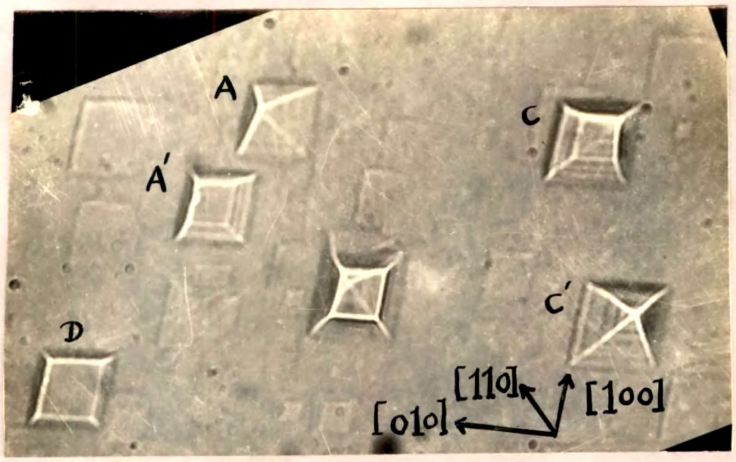

Fig. 4.26a (x170)

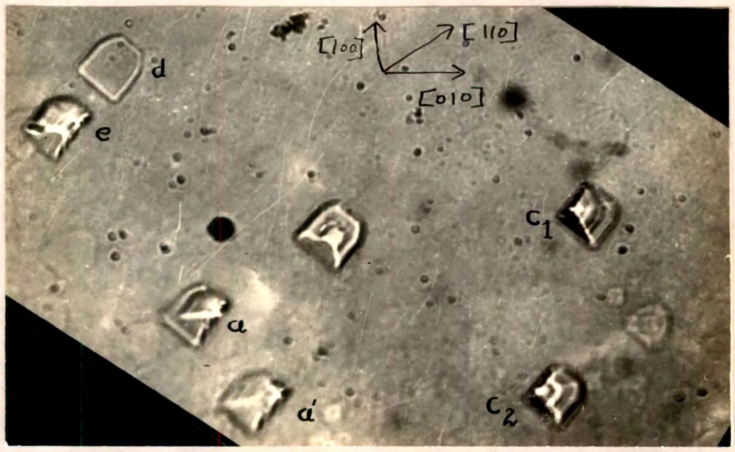

Fig. 4.26b (x170)

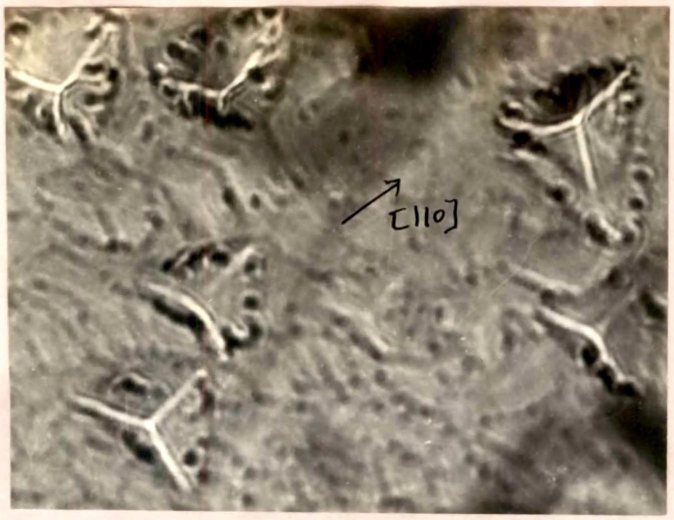

Fig. 4.27a (x200)

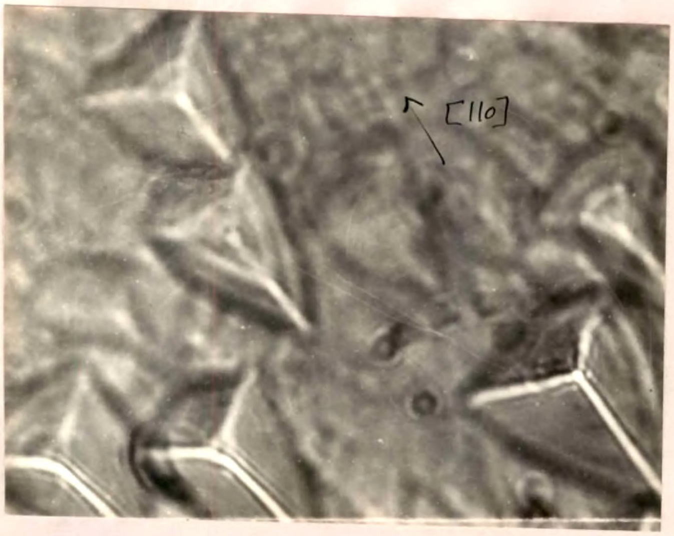

Fig. 4.27b (x200)

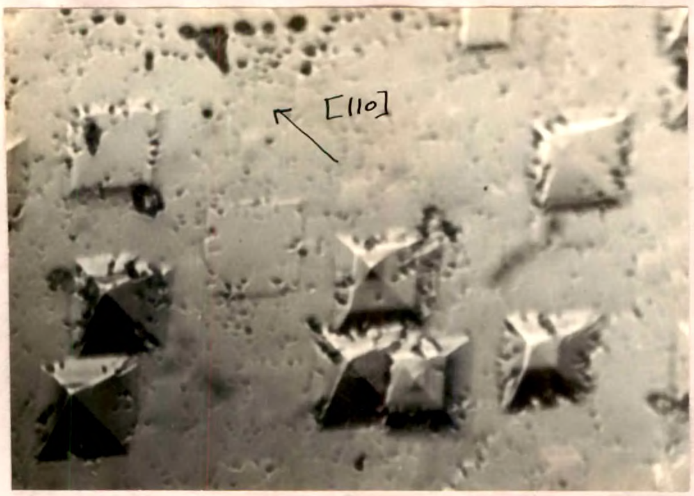

Fig. 4.28a (x170)

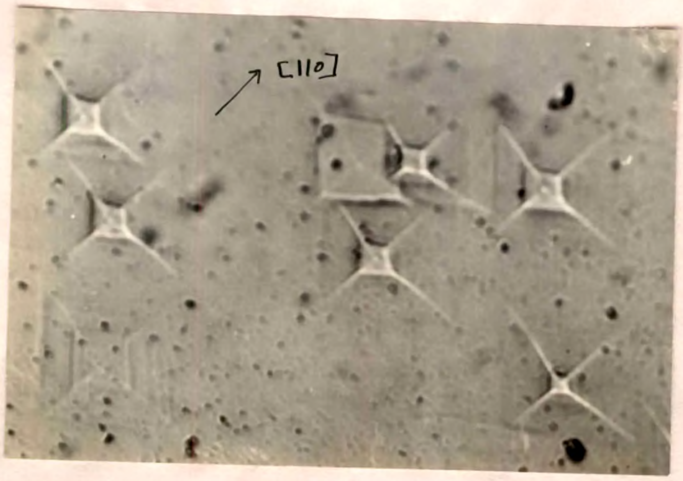

Fig. 4.28b (x170)

Fig. 4.29a (x320)

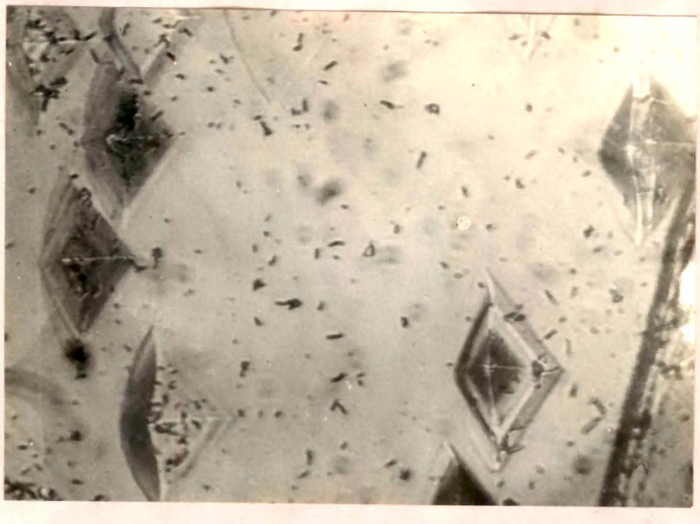

Fig. 4.29b (x320)

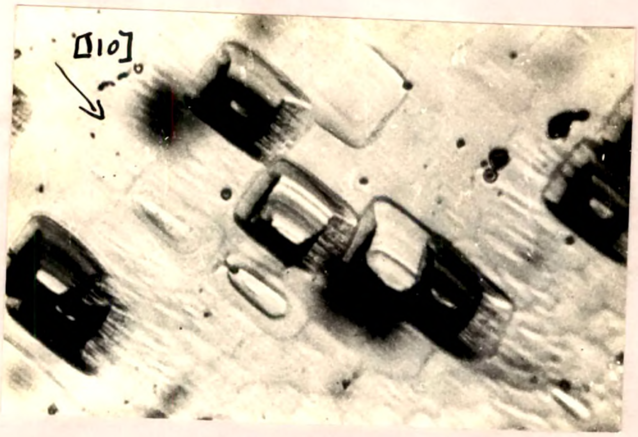

Fig. 4.30 a (x120)

Fig. 4.30 b (x120)

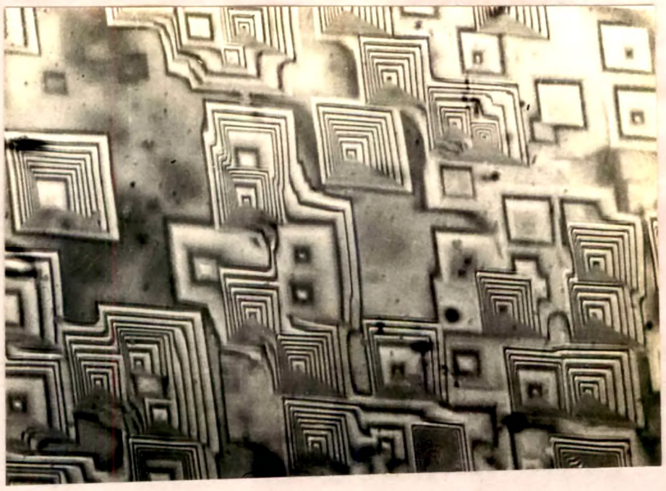

Fig. 4.31a (x120)

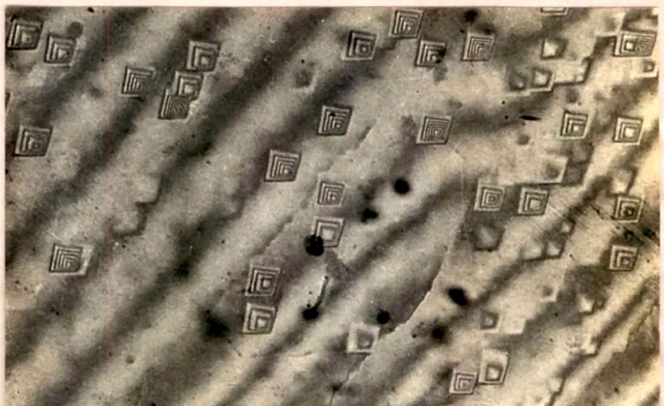

Fig. 4.31b (x 120)

Fig. 4.32 (x120)

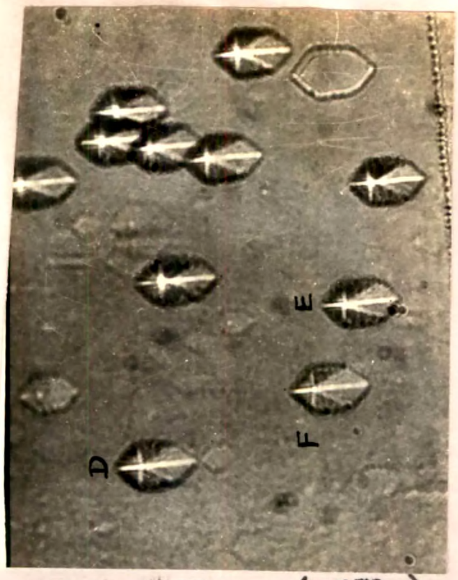

Fig. 4.33a (x170)

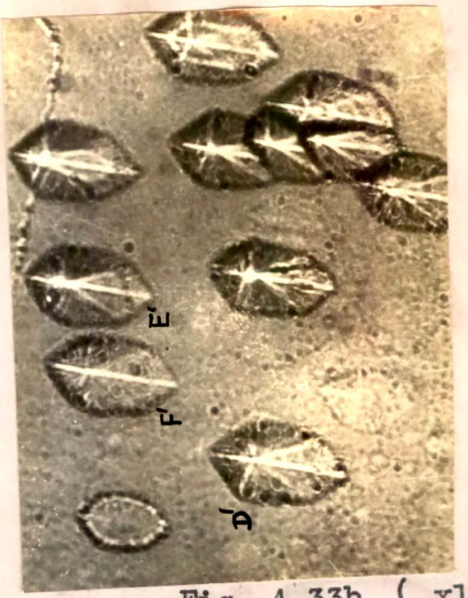

Fig. 4.33b (x170)

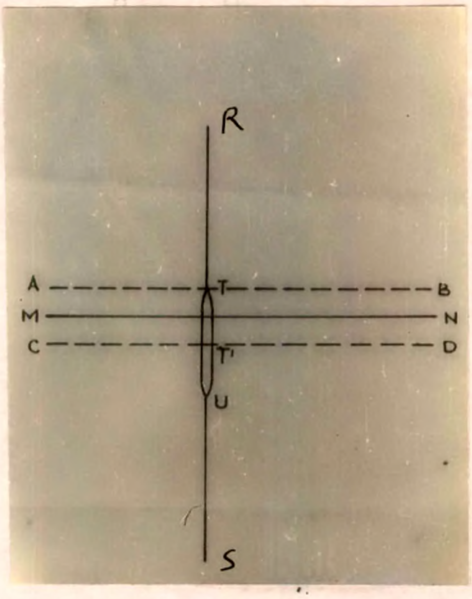

Fig. 4.34

by some unknown condition/s or that it could be due to some defects at a certain depth from the surface of the crystal.

(e) Orientation of etch pits.

The earlier observations on etching of cleavage surfaces by different etchants of various concentrations show very conclusively that the shape of an etch pit on a cleavage surface of calcite is a function of concentration of an etchant, when all other factors are kept constant. The orientation of etch pit on a crystal surface may be associated with the change of etch pit shape. The orientation of an etch pit can be defined with respect to the crystallographic direction or percussion mark on crystal face. It (orientation) can also be defined by considering the position of a depth point with respect to geometrical centre of a plane figure of an etch pit. The observations on the change in orientation of the etch pits, on crystal surfaces have been reported by many workers (Gilman and Jonhston, 1956; Joshi and Ittiyachen, 1967; Haribabu and Bansigir, 1969 etc.). In almost all these cases the outward geometrical shapes of etch figures were considered. It will be clear from the present work that the change in orientation of etch figures is due to amount of diluent used to change the concentration. Further the concentration of an etchant affects the position of depth point with respect to geometrical centre of a pit. Besides the shapes of etch figures whose orientations are changed are usually based on a few known crystallographic directions on crystal cleavages.

Fig. 4.26a (x 170) is a photomicrograph of a cleavage surface etched by 0.45% glacial acetic acid for 25 seconds. The etch pattern consists of point-bottomed and flat-bottomed rhombic pits. Fig. 4.26b (x 170) is a photomicrograph of oppositely matched cleavage surface etched by 94% glacial acetic acid for 4 hours. There appears to be good correspondence between the position of pits on both the cleavage faces. However, there are certain differences. The boundaries and diagonals of rhombic pits (fig. 4.26a) are in the directions $\langle 100 \rangle$ and $\langle 110 \rangle$ respectively. This is not the case for etch pits in fig. 4.26b, where they possess rectangular outlines with sides parallel to $\langle 110 \rangle$. The depth points of pits A and A' (fig. 4.26a) are on the left hand side of the diagonal along $[110]$. Whereas depth points of the corresponding pits a and a' (fig. 4.26b) are on the right hand side of the direction, $[110]$ passing through the midpoint of the plan~~ar~~e figure. For pit ~~A~~C' (fig. 4.26a) and corresponding pit c_1 (fig. 4.26b), the depth points are on opposite sides of the symmetrical line $[110]$. A flat-bottomed pit D (fig. 4.26a) is reflected as pit d (fig. 4.26b) whereas for pit e (fig. 4.26b) there is no corresponding pit on fig. 4.26a. The study of the displacement of the depth point with respect to symmetrical line will be presented in Chapter 6.

Figs. 4.27a and 4.27b (x 200) are photomicrographs of matched surfaces, one etched by 30% HCl for less than a second and the other etched by 30% glacial acetic acid for 30 seconds. Hydrochloric acid has produced isosceles triangular etch pits with well defined boundaries (fig. 4.27a) and are having negative orientation with respect to percussion mark whereas point-bottomed isosceles triangular etch pits with uneven boundaries (fig. 4.27b) produced by 30% glacial acetic acid are in positive orientation with respect to percussion mark. These are more shallow, than the corresponding triangular pits (fig. 4.27a). The nature of micropitting on both these figures is also highly uneven.

The above observations mention the change in orientation of etch figures with respect to percussion mark and/or crystallographic direction i.e. with the crystal face as a whole. It is also observed above that in some cases the point of maximum depth does not coincide with geometrical centre of a plane figure of pit on the observation plane. The position of the depth point appears to be a function of concentration of an etchant when other factors are kept constant. In this case with a change in concentration the regular geometrical outline of a pit on the surface apparently remains unchanged. However, the position of depth point with respect to geometrical centre changes. This gives rise to a change in orientation of etch pit. Figs. 4.28a and 4.28b (x 170) are photomicrographs of matched region etched by 0.05% glacial acetic acid for 2 minutes and by 0.01% glacial acetic acid for 10 minutes respectively. It shows complete matching of rhombic etch pits. Besides, the pits are of nearly identical sizes. It should be noted that depth points of pits lie in the direction $[110]$ from the geometrical centre in fig. 4.28a while the depth points of corresponding pits lie in the opposite direction i.e. $[\bar{1}\bar{1}0]$ from geometrical centre, showing thereby the rotation of etch pits through 180° around the centre.

4.4 Discussion:

All the observations regarding shape of etch pits produced by different concentrations of various etchants are summarized in tables 4.2 and 4.3. It is worthwhile to discuss following characteristic features:

(1) Origin of etch pits.

(2) Observations of fixed shape with certain concentration (range) of an etchant.

(3) Change of shape with change in concentration (range) of an etchant.

(4) Production of identical shapes on a cleavage surface by different etchants.

(5) Different or similar cycles of etch pit shape observed by progressive change in concentration (range) of various etchants.

(6) Change in orientation of etch pits.

4.41 Origin of etch pits:

It was reported by Keith and Gilman (1960) and Bengus et al (1960) that dislocation etch pits were produced by formic and tartaric acid on cleavage faces of calcite. The conclusion of Keith and Gilman was based on the matching of etch pits on cleavage faces and by the movement of dislocation etch pits produced by formic acid. They also suggested revealation of dislocations by etch pits produced by other etchants such as acetic acid, lactic acid, propionic acid etc. From the observations on complete matching of etch pits on cleavage counterparts and constant density of pits on successive etching, Bengus et al suggested tartaric acid as a dislocation etchant. Pandya and Pandya (1961) have shown, from the study of successive etching, of matched (etched) cleavage counterparts of linear arrays of etch pits, T and L shaped etched boundaries and movement of dislocations, that the pits are formed at dislocations. They had used various etchants such as NH_4Cl, NH_4I, HNO_3, HF of appropriate concentrations, suggesting that all were equally suitable for revealing dislocations. Keith and Gilman found deterioration of the quality of pits when produced by an etchant where its dilution reached beyond a certain concentration (e.g. 10% for propionic acid). The present observations have shown very clearly that it is possible to obtain fairly sharp pits by etching the crystal by glacial acetic acid or hydrochloric acid of very low concentration. Figs. 4.29a and 4.29b (x 320) show the photomicrographs of matched regions of cleavage counterparts etched by 0.001 % of glacial acetic acid for 10 hours. The isolated sharp etch pits with triangular outlines have fairly good correspondence on cleavage counterparts. The rate of attack on the crystal surface is found to be less in very low as well as very high concentration (more than 95%) of glacial acetic acid. Hanke (1961) had studied the etching behaviour of calcite by different concentration of glacial acetic acid and conjectured that the origin of etch pits to be at some impurity centres which might occur in process of natural growth. Figs. 4.30a and 4.30b (x 120) show the photomicrographs of the matched areas on the counterparts, one etched by concentrated formic acid for 40 seconds and other by 95% glacial acetic acid for 2 hours respectively.

Nearly complete correspondence of the etch patterns are observed on counterparts. These observations along with no increase in etch pit density [refer to 4.3 (c), (d)] on multiple etching show that all the concentrations of hydrochloric acid and of glacial acetic acid are capable of revealing dislocations intersecting the surface.

If pits are produced at the sites of dislocations, depths of pits should increase with etching time. It is reported by Hanke (loc. cit.) that depth of point-bottomed etch pits produced by lower concentration of glacial acetic acid is not more than 2 to 3 microns. Further, after some depth pit becomes flat-bottomed. It is observed that depth of the point-bottomed pits produced by different concentration of etchants (HCl or $\overline{HAC}$) can be increased to more than 5 microns if etching is prolonged. Fig. 4.31a (x 120) is an interferogram taken over the surface etched by 0.22% glacial acetic acid for 3 minutes. It is seen very clearly that depth of pits are more than 3 microns which is determined by counting the number of fringes and multiplying it by $\lambda/_2$ where $\lambda = 5461^\circ$ A. The exact correspondence of etch pits on matched surface (fig. 4.31b, X 120) can also be seen very clearly. Fig. 4.32 (x 120) shows another interferogram taken over the cleavage surface etched by 50% HCl for a second. Triangular etch pits are observed. Average depth of triangular pits are more than 7 microns.

However, it should be noted that all etch pits are not of equal depths.

When the faces forming a pit are very steep, the pits are very deep. In this case, it is not possible to determine their depths by multiple beam interferometry. This is found to be the case for pits produced by acetic acid of high concentration (> 50 %). In such cases light profile microscopy ~~has~~ is used to determine their depths (fig. 4.12).

It is desirable to estimate the angles made by various planes forming a pit with the observation plane. This is done by using light profile and multiple beam interferometric technique (for determining depths) and filar micrometerr eyepiece (for measuring linear distances on the surface). It is found that these angles vary between 2^{o} and 4^{o}; this shows that these planes are slightly deviated from the cleavage plane. Hence they must be vicinal faces, i.e. faces having high Miller indices. This view is supported by the fact that when surface, etched by an etchant of a given concentration, say 0.25% glacial acetic acid, to produce rhombic pits, is re-etched by the same (or different) etchant of different concentration, say 0.6% glacial acetic acid, to produce hexagonal etch pits at the same unchanged locations, the variation in angles made by the faces forming these pits is not quite significant and that the cleavage plane and the faces forming these pits are almost equally attacked by both the etchants. It is also found that sometimes those faces forming a pit do not meet at a point (which is the point of maximum depth of the pit), but meet in a straight line. This line is usually found to be parallel to direction [110] . Figs. 4.33a and 4.33b (x 170) represent the matched areas of the cleavage faces, one etched by 1.5% glacial acetic acid for 45 seconds and the other etched by 1% glacial acetic acid for 30 seconds respectively. In addition to exact matching of point-bottomed hexagonal etch pits on the counterparts, the following features are interesting. (1) Pits marked as D , F in fig. 4.33a and corresponding pits D′, F′ in fig. 4.33b are point-bottomed. (2) Point-bottomed pit marked as E in fig. 4.33a has corresponding pit E′ in fig. 4.33b having line at the centre. The occurrence of line in direction [110] at the centre may be due to small dislocation loop in the {110} plane. Matching of point-bottomed pits with pits having 'line-centre' can be explained by the schematic diagram (fig. 4.34). RS is a dislocation line passing through the {110} plane of a crystal. Suppose a close loop of very small width is formed with end points T and U on this line. Now if this crystal is cleaved along the direction

MN, and the resulting match cleavage faces were etched for a certain period, new faces with traces AB and CD in fig. 4.34 are developed and that the point at which the dislocation intersects the traces, viz. T and T' are preferentially attacked with the formation of point-bottomed pit at T and a corresponding line-bottomed pit at T'. It can be explained by the above diagrams that line-bottomed pits may coincide with line-bottomed etch pits.

4.42 Shapes of etch figures:

Different shapes of etch figures are produced due to different chemical reaction rates along various directions on a crystal surface. Chemical reaction rates may change their magnitude or directions or both due to different concentration of the etchant and anisotropic character of crystal. It is very difficult to say which reaction rates are prominent at particular concentration of an etchant. The change in magnitude of reaction rates does not change the shape of etch pits. Within certain concentration range energy of etchant is such that it does not produce any change in the direction of reaction rates i.e. no change in shape of etch pit is produced. If the energy is more to produce change in the directions of etch rates, etch pits with different shapes are observed. From the whole spectrum of etch pit shapes it is clear that pits are usually bound by directions of low indices. Geometrical outlines of etch pits having more than seven sides are not observed on the crystal surface. Since the shape of etch pits remains nearly same, when they are produced at line defects or point defects, the normal rate of dissolution for these pits does not affect the shape noticeably. The factor governing the shape of etch pits is the lateral rate of dissolution, V_s, along different directions on the surface. From the study of change of shapes of pits with progressive change in the concentration of an etchant, it can be conjectured that there is a systematic change in the direction of reaction rates on the surface. This in turn suggests creation of new directions of reaction rates and elimination or modification of old directions. This view is supported by the fact that when the pit shape changes from a triangular outline to a quadrilateral one, produced by a change of one concentration range (90% to 25%) to another concentration range (25% to 15%) of an etchant HCl, a fourth direction of reaction rate has developed in addition to the reaction rates along these directions (table 4.2) for triangular pits,, and has consequently given rise to a small plane OPQ and a quadrilateral outline on the surface. The area of this plane increases with the progressive decrease in the concentration of hydrochloric acid. Similarly septagon etch pits change into pits with pentagonal outlines by the elimination of sides along [$\bar{5}\bar{3}0$] and [350] . This means that reaction rates along [$3\bar{7}0$] , [$\bar{7}30$] are reduced to zero. It should be noted that directions of reaction rates which are making equal angles with the line of symmetry [110] are simultaneously eliminated or produced by a systematic change in the concentration of an etchant (tables 4.2 and 4.3). Due to production or anhilation of pairs of reaction rates around [110] , the pyramidal pit or flat bottomed pit with any geometrical outline on the surface remains symmetrical about the line of symmetry of a crystal face,[110] .

4.43 Identical shapes of etch pits produced by various etchants of different concentrations:

Identical shapes are also produced by different concentrations of various etchants. Rectangular etch pits whose sides are parallel to $\langle 110 \rangle$ are formed by highly concentrated formic, glacial acetic and propionic acids. The rate of reaction of glacial acetic acid is less than that of formic acid but is greater than that of propionic acid. These are true for acids of high concentration only. If the chemical structure of these acids is taken into account, it can be said from the above observation that greater is the length of carbon chain in the structure of an acid less is its reactivity on the cleavage surface of calcite. Keith and Gilman (loc. cit.) had observed change in orientation of the pit boundary when concentrated glacial acetic acid is used as an etchant instead of concentrated formic acid. This observation is at variance with the one described here. Rhombic etch pits obtained by them on the cleavage surface of calcite by highly concentrated HAC should be actually due to low concentration of glacial acetic acid. It is very likely that these pits are produced during rinsing of the crystal after etching. In the present work it is shown above (fig. 4.19) that such pits can be produced by etching the crystal cleavages by concentrations ranging from 0.005% to 0.5% of glacial acetic acid for a few seconds. This shows that the directions of reaction rates are identical for highly concentrated monocarboxylic acids used for etching calcite surfaces. Equal decrease in concentration of all these acids, produce different cycles of etch pit shapes.

Identical shapes of etch pits are also obtained by using glacial acetic acid and hydrochloric acid in appropriate concentration range. The irregular pentagon etch pits of almost equal sizes are produced by etching cleavage surfaces by 10% HCl and by 10% HAC for one second and 30 seconds respectively. This suggests that directions of reaction rates are similar for both concentration of acids but their magnitudes is much more for hydrochloric acid than for glacial acetic acid. Rhombic etch pits are produced by both etchants HCl(0.01% to 0.15%) and HAC (0.005% to 0.5%) . Rhombic etch pits are also obtained by using low concentration of propionic acid and NH_4Cl solution. The reaction rates along $\langle 150 \rangle$ only produce rhombic etch pits on the rhombohedral cleavage surface of calcite. The change in magnitude of reaction rates along $\langle 150 \rangle$ shifts the depth point from geometrical centre and both types of (+ve and -ve) eccentricity can be observed in all the etch pits produced by appropriate concentration of HCl, HAC, NH_4Cl and propionic acid.

It is possible to ~~c~~conjecture from a study of the bonding energy between different atoms on a cleavage face of calcite that due to minimum amount of bonding energy $\{100\}$ perfect cleavages are obtainable. Hence directions perpendicular to $\langle 100 \rangle$ will be easy direction of propagation for lateral dissolution of crystal surface. If the concentration of an etchant is progressively reduced, the geometrical shape, an etch pit assumes on the surface, should be a rhombic pyramidal or flat-bottomed pit with sides along $\langle 100 \rangle$. However, this is at variance with the observation where an etchant of extremely low concentration (0.0001% $H\overline{AC}$ and 0.0001% HCl) produces triangular etch pit with negative orientation on the cleavage surface. It should further be noted that etch pits with triangular outlines and having negative orientations are also produced by inorganic acids (such as H_2SO_4, HNO_3) of high concentration (figs.4.1, 4.2 and 4.3).

4.44 Cycles of etch pit shapes produced by progressive changes in concentration of various acids:

It is mentioned above that irregular pentagon and rhombic pits are formed by different concentrations of both acids i.e. hydrochloric and glacial acetic acid. The cycles of etch pit shapes varying from pentagon to rhombic outlines on a cleavage surface produced by hydrochloric and by glacial acetic acids with concentrations changed in a systematic manner are different.

(1) The cycles of etch pit shapes produced by HCl successively diluted are as follows:

a) For a concentration ranging from 15% to 5%, the pits with irregular pentagonal outlines are produced. The pentagon is bound by sides with direction $[\bar{5}\bar{3}0]$ $[1\bar{1}0]$ $[350]$ $[100]$ and $[0\bar{1}0]$. The concentration decides the lengths of the sides.

b) By using concentration ranging from 5% to 1.5% of HCl the quadrilateral pits are obtained. They are bound by $[\bar{5}\bar{3}0]$ $[1\bar{1}0]$ $[350]$ and a curved line produced by removing the intersection point of lines with direction $[100]$ and $[0\bar{1}0]$.

c) The pits with regular pentagonal outlines and side with directions shown in a) are produced by hydrochloric acid with concentration ranging from 1.5% to 0.5% HCl.

d) Use of concentration range (0.5% to 0.2%) of HCl produces pits with septagonal outlines whose sides are parallel to $[\bar{5}\bar{3}0]$ $[\bar{1}00]$ $[1\bar{1}0]$ $[010]$ $[350]$ $[100]$ & $[0\bar{1}0]$. The lengths along $[\bar{5}\bar{3}0]$ and $[350]$ diminish with the regular decrease in concentration of the acid.

e) The pits with pentagonal outlines are produced by HCl and with concentrations ranging from 0.2% to 0.15%. The sides along $[\bar{5}\bar{3}0]$ and $[350]$ are eliminated and the pentagons are bound by sides parallel to $[\bar{1}00]$ $[1\bar{1}0]$ $[010]$ $[100]$ and $[0\bar{1}0]$ i.e. by $\langle 100 \rangle$ and $[1\bar{1}0]$.

f) The etchant with concentration range (0.15% to 0.001% of HCl) produces pits with rhombic outlines and having boundaries along directions $< 100>$.

g) Hydrochloric acid of concentration less than 0.001% produces pits with triangular outlines bound by the straight lines with directions $[\bar{1}00]$ and $[010]$ and a curved line.

In all these cases it is observed that the lengths of the boundaries of a pit depend on the value of the concentration within a given range produces a displacement of the point of maximum depth from the geometrical centre of the regular outline of the pit.

(2) The cycles of etch pit shapes produced by glacial acetic acid successively diluted are as follows:

a) Etch pits with irregular pentagon outlines are produced by acetic acid with concentrations ranging from 15% to 6%. The boundaries of this pentagon are essentialy the same as those produced by HCl and mentioned in a) of (1).

b) Use of concentration of range from 6% to 2% of acetic acid produces quadrilateral pits bound by sides parallel to $[\bar{5}\bar{3}0]$, $[350]$, $[100]$ and $[0\bar{1}0]$. It should be noted that for quadrilateral pits produced by HCl and mentioned in b) of (1), the curved side is formed by removing the intersecting point of $[100]$ and $[0\bar{1}0]$, whereas in the present case the line $[1\bar{1}0]$ of irregular pentagon pit mentioned above in a) has disappeared, thereby giving rise to quadrilateral pit.

c) When the concentration range of acid was changed to 2% to 0.5% the hexagonal pits are produced. For forming this pit, the sides of quadrilateral pit, viz. $[\bar{5}\bar{3}0]$ and $[350]$ are segmented into two parts with direction $[\bar{1}\bar{1}0]$, $[\bar{1}00]$ and $[010]$, $[110]$. This change of shape from quadrilateral to hexagon pit by a change of concentration range from (6% to 2%) to (2% to 0.5%) of acetic acid should be compared with the change of shape from quadrilateral to regular pentagon etch pits produced by a change in concentration range (5% to 1.5%) to (1.5% to 0.5%) of hydrochloric acid.

d) Etch pits with rhombic outlines on cleavage surface are produced by acetic acid whose concentration varies from 0.5% to 0.005%. The etch pit is formed by sides parallel to $\langle 100 \rangle$. This shows that $\langle 110 \rangle$ boundaries of hexagonal pit have disappeared. For the formation of rhombic pit by HCl acid (concentration range - 0.001% to 0.15%) the side of a pentagon pit parallel to $[1\bar{1}0]$ is reduced to zero.

e) By using acetic acid of concentration less than 0.005% triangular etch pits with boundaries parallel to $[\bar{1}00]$ and $[010]$ and a curved line are obtained. This is identical with the triangular pit produced by HCl acid having concentration less than 0.001%.

Again in all these cases the length of the boundaries of a pit depend upon the concentration chosen, whereas the point of maximum depth is displaced from the geometrical centre by using a concentration within a given range. It is clear from the above discussion that the shape-cycles of pits produced by HCl and $\mathrm{H\overline{AC}}$ having concentration changed in a systematic manner are different and that in some cases the formation of pits take place by a different mechanism which is a characteristic of the etchant used. From the observations at very low concentrations (0.15% HCl and 0.5% $\mathrm{H\overline{AC}}$) it can be conjectured that same mechanism operates for the formation of etch pits of identical shapes. Looking to the complicated motion of steps induced by an etchant on the surface, it is rather difficult to give a complete theoretical explanation for the formation of different shapes observed on the cleavage surface of calcite.

4.45 Change in orientation of etch pits:

The different shapes of etch pits produced by various etchants of different concentrations bring to the forefront the change in orientation of etch pits with respect to a line on a cleavage plane. This actually happens for the etch pits produced by 92% acetic acid (fig. 4.26a) and 0.4% acetic acid (fig. 4.26b). The boundaries of pits produced by 92% acetic acid are in the directions < 110> , while for pits produced by 0.4% acetic acid the directions of boundaries and diagonals of etch pits are < 100> and < 110 > respectively. This can be explained by the change in direction of reaction rates due to change in concentration of an etchant. The reaction rates are only along < 110> for rectangular pits while for rhombic pits reaction rates are along < 150> . The change from a rectangular pit to a rhombic etch pit consists of long cycle as shown in table 4.3, This type of orientation change can also be observed using propionic acid of varying concentrations. In the present case of the change in orientation of etch pits, the directions of boundaries and diagonals can be interchanged. Since the geometrical outline is a rhombus, the change has given rise to a rectangular pit from a rhombic one.

30% HCl produces triangular etch pits with negative orientation, whereas 30% HAC produces triangular etch pits in positive orientation with respect to a percussion mark on the cleavage surface. The directions of boundaries of the positively oriented pits and negatively oriented pits are same and reaction rates are in the same line but in opposite directions for both types of etch pits. This shows that action of 30% acetic acid and 30% HCl acid is different and they act in opposite directions. The magnitudes of reaction rates are also different for these acids because large time is required for formation of etch pits by glacial acetic acid. Triangular pits are also produced by HCl acid and by glacial acetic acid of very low concentrations. In this case the pits have identical boundaries and identical orientation (negative) with respect to percussion mark. However, direction of boundaries of etch pits in these cases are different than those of triangular pits produced by 30% HCl or 30% HAC.

It is possible to consider the orientation of etch pits with respect to position of depth point from the geometrical centre of the plane figure of an etch pit. This change is brought about by a change in the concentration within a given range of concentrations of an etchant. This study is made for the first time by the present author. The distance between depth point and geometrical centre of a plane figure of an etch pit is called shift, which is related with the rate of lateral dissolution, V_s , on a crystal surface. For an etch pit with rhombic outline on a cleavage surface, it can be shown that the lateral dissolution rates are along [150] [510] $[1\bar{5}0]$ and $[\bar{5}\bar{1}0]$. Reaction rates along [510] and [150] ; and $[\bar{1}\bar{5}0]$ and $[\bar{5}\bar{1}0]$ is same for preserving symmetrical nature of etch pit about [110] . If the reaction rates along [150] and $[\bar{5}\bar{1}0]$ are same, symmetrical pit arises where depth point coincides with geometrical centre giving a zero shift. If reaction rates along [150] are more than those along $[\bar{5}\bar{1}0]$ negative shift results and vice versa. The values of V_s along [150] and $[\bar{5}\bar{1}0]$ depend~~s~~ upon the concentration of an etchant. Higher concentration of etchant produces a larger value of V_s along $[\bar{5}\bar{1}0]$ than along [150] while for lower concentration of the same etchant produces larger V_s along [150] than along $[\bar{5}\bar{1}0]$. The shift of depth point from geometrical centre is observed in both directions [110] and $[\bar{1}\bar{1}0]$, for rhombic etch pits. Hence orientation of etch pits with respect to depth point through an angle of 180° can be obtained. This type of orientation change is also observed for pits produced by HCl of appropriate concentration.

4.5 Conclusions:

(1) Etch pits produced by different concentrations of various etchants (such as HCl, HĀC ...) on cleavage faces of calcite are at dislocation sites.

(2) The shapes of etch pits depend on the concentration of an etchant. The change in the shape of an etch pit is due to different reaction rates along different directions for various concentration ranges. However, for a given range of concentration of an etchant (HCl or HĀC) unequal rates of reaction along one/or more directions do not produce a change in the shape of etch pits.

(3) The two ~~p~~types of orientation of etch pits viz. a) the rotation of an etch pit with respect to a crystal face and b) the shift of the point of maximum depth in an etch pit of constant shape, are found to be due to different reaction rates along different directions.

(4) Similar etch pit shapes may be observed on calcite cleavages by different concentrations of various etchants. Similar shape-cycles are not observed for systematic change of concentrations of various etchants. However, for very low range of concentration of etchants (HCl or HĀC), similar shape-cycles of etch pits on rhombohedral

cleavage faces of calcite are observed.

(5) The pyramidal or trunctated planes forming etch pits on a calcite cleavage surface are vicinal faces.