CHAPTER 5

SHAPES OF ETCH PITS UNDER VARYING CONDITIONS OF ETCHING OF CLEAVAGE FACES OF CALCITE BY ETCHANT OF CONSTANT CONCENTRATION.

5.1 Introduction:

In the previous chapter, the effect of concentration on the shapes of etch figures on calcite cleavage surfaces produced by hydrochloric acid or glacial acetic acid of varying concentrations at constant temperature has been reported in detail. Besides concentration of an etchant, the relative motion of etchant with respect to surface placed in the etching solution, the time of etching etc. are also found to be important in developing the shape of an etch pit.

It is observed that different shapes of etch pits are produced by the same concentration of an etchant under different conditions of etching. By condition of etching is meant (1) environmental conditions e.g. atmosphere, presure, humidity etc. and (2) the relative motion of etching solution with respect to crystal surface dipped in the etchant. The effect of the environmental conditions on shapes of etch pits are not studied here. The later condition is referred to as static or dynamic etching of crystals. Static etching is one, where there is no stirring of solution and no motion of crystal surface during the time of etching. This study (static) has already been reported in the previous chapter. The present chapter deals with the changes in the shapes of etch pits due to a uniform relative motion of etchant with respect to a crystal by the magnetic stirrer during the time of etching i.e. due to dynamic etching. These conditions of etching may give rise to different shapes of pits for the same concentration of the etchant and same etching time. Gilman et al, (1958) compared the etch pits produced on lithium fluoride under the above conditions (i.e. static and dynamic conditions). They observed that etch pits produced by dynamic etching are bigger than those produced by static etching under identical conditions. Hanke, (1961) had used dynamic etching to study etch pits produced by acetic acid on calcite cleavages. Dynamic etching facilitates a more rapid reaction between etchant and a crystal surface than the static etching. Different shapes of etch pits produced under different conditions of etching, keeping other factors such as concentration of etchant, etching time and temperature, constant do not appear to have been studied in detail. For the first time this type of study is made on calcite cleavages by using acetic acid and hydrochloric acid as etchants. This study is likely to promote better understanding of the process of dissolution of crystals.

The increase in etching time usually increases the surface area of etch pits formed at defect sites on a crystal surface. If pits are produced at line defects, their depth also increases with the etching time. Ratio of velocity of dissolution parallel to the etched surface (V_s) to velocity of dissolution normal to the etched surface (V_n) i.e. $\frac{V_s}{V_n}$ should be same for different etching periods to preserve same inclination of the planes of a pit with the surface under observation. For a given concentration of glacial acetic acid, Hanke (loc.cit.) observed that for different etching times ratio V_s/V_n was not constant for etch pits produced on calcite cleavages. It was further reported that the directions of V_s usually remained unchanged for different time periods. It will be shown in this chapter that shape of etch pits produced by hydrochloric acid or glacial acetic acid remains same in many cases, though etching time varied from seconds to minutes. An exceptional case will be reported in the present work where the number of sides of the etch pits increase with the change in etching time only.

5.2 Experimental procedure:

The procedure for static etching was the same as mentioned in the earlier chapter. For dynamic etching the solution was stirred at a constant rate by a magnetic stirrer. The rotation of magnet, controlled by a rheostate joined in the main circuit, was increased to a maximum, so that no turbulent flow occurred in the solution. For conducting etching experiments under dynamic condition, a definite amount of etchant, (150 c.c.) was taken in a glass beaker (250 c.c. capacity) so that a constant height of etchant in the beaker was maintained. The maximum speed of stirrer (rotor) was maintained constant for a series of observations reported here. After etching the freshly cleaved crystals under controlled (static or dynamic) conditions for a given time, they were washed in running distilled water and dried by a hot air blower. Every time fresh etching solutions of constant concentration at constant temperature were used for etching work. Aged solution could not yield reproducible observations. The observations were taken on matched cleavage faces, one etched under static condition and counterpart etched under dynamic condition. For enhancing reflectivity the etched surfaces were silvered by thermal evaporation technique and were then optically studied.

5.3 Observations and Results:

The inorganic and organic acid etchants viz., hydrochloric and acetic (glacial) acid, of various concentrations which were used earlier to study various shapes of etch pits were also used for the present investigation. The importance of concentration of an etchant for influencing the shape of an etch pit was clearly demonstrated in earlier chapter. It was shown that for a concentration of glacial acetic acid, slightly greater than 0.5%, hexagonal etch pits were produced, whereas the same etchant with concentration less than 0.5% produced rhombic etch pits. In both the cases time of etching was same (figs. 4.18 and 4.19, chapter 4). In order to assess the influence of various factors on shape of etch figures, it is desirable to vary systematically one factor, by keeping all other factors constant.

5.31 Effect of dynamic etching:

In the present work, the effect of dynamic etching on the etch pit shape will be investigated by keeping all other factors including time of etching constant. Fig. 5.1a (x 220) shows a photomicrograph of a freshly cleaved surface etched by 0.45% glacial acetic acid for 30 seconds under static condition at room temperature whereas its counterpart was etched by the same etchant for the same period at room temperature under dynamic condition, [Fig. 5.1b, x 220] . Static etching has produced rhombic pits whereas hexagonal pits were formed by dynamic etching. Besides this change, other equally interesting characteristics are as follows:

(i) The pits with rhombic (fig. 5.1a) and hexagonal (fig. 5.1b) outlines are eccentric since their points of maximum depth do not coincide with their geometrical centres and are a little away from them in the direction , [110] .

(ii) There is a complete correspondence between the deep point-bottomed pits on cleavage counterparts so far their positions on these surfaces are concerned. For some flat-bottomed pits, there is one-to-one matching. However, the background etching in these figures does not seem to be identical. The point-bottomed pits circled in fig.5.1b are relatively shallow and are not reflected on cleavage counterpart (fig. 5.1a).

(iii) The orientations of pits on these figures with respect to any direction on a crystal face, say [110], are identical.

(iv) The cleavage lines PQ and P'Q' have shifted on etching.

(v) It is found from experiments on multiple etching of cleavage surfaces that these pits maintain their shapes.

(vi) Formation of hexagonal pits takes place by the occurrence of lines at the corners producing plane acute angles in the rhombohedral pits. The lengths of those sides developed in dynamic etching producing hexagonal pits are less as compared to those in directions $\langle 100 \rangle$.

(vii) It should be noted that hexagonal etch pits are also produced under static etching when the crystal was etched by glacial acetic acid of concentration greater than 0.45% (e.g. 0.5% to 2.0% of glacial acetic acid see fig. 4.19 of chapter 4).

(viii) Almost all hexagonal pits show terraced structure whereas this is not true in case of all rhombic pits.

These observations have shown that when the crystal cleavages are etched by the same concentration of an etchant viz., glacial acetic acid under different conditions the shapes of pits are different. This is also true for other etchants such as hydrochloric acid. Figures 5.2a and 5.2b (x 220) show photomicrographs of matched cleavage faces etched by 0.8% hydrochloric acid for 5 seconds statically (fig. 5.2a) and for 2 seconds dynamically (fig. 5.2b). The difference in etching time does not change the shape of etch pit. The etch patterns on these figures consist of pits of different shapes. The pits in fig. 5.2a are regular pentagons with a clear point at a centre whereas fig. 5.2b exhibits curvilinear quadrilateral pits with line or point at the centre. Further, pits on both these figures are eccentric, possess identical orientation with respect to any line drawn in the surface and have one to one correspondence with the difference that in a few cases a flat-bottomed pit corresponds with a point-bottomed pit and conversely. The etching of cleavage lines and formation of rows of etch pits in both these photomicrographs exhibit different characteristics. It is of interest to note that the pit marked A_1 is a curvilinear quadrilateral whereas one shown by A_2 is partially developed pentagon etch pit (fig. 5.2a). The centres of maximum depth for these pits A_1 and A_2 (fig. 5.2a) correspond with the line centres of the corresponding pits A_1' and A_2' on the matched cleavage face (fig. 5.2b). The line centre means that all the planes forming a pit meet in a line instead of a point. The line is in the direction $[11\,k]$ whose projection on the observation plane gives line of symmetry. The curvilinear quadrilateral pits can also be produced under static condition on cleavage faces by A.R. quality hydrochloric acid with concentration ranging from 2.0% to 4%. One point which is very clear from all these photomicrographs is that the pits produced under condition of static and dynamic etching are of unequal sizes. The time of etching required under dynamic condition is always less than that required under static etching for obtaining pits of almost equal sizes. This observation is shown very elegantly by photomicrographs (figs. 5.3a and 5.3b, x 220) which were obtained by etching the cleavage counterparts by 1% HCl for 1 second under static and dynamic conditions respectively. The densities of pits on both these figures are almost identical. However, the pits produced by dynamic etching are having larger surface areas than those obtained under static condition.

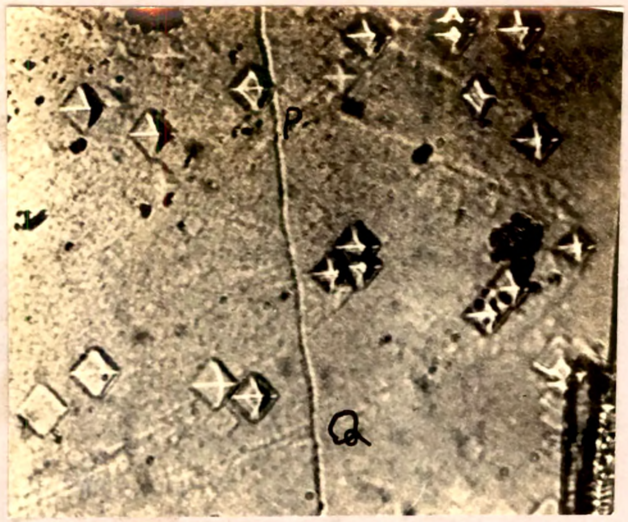

Fig. 5.1a (x 220)

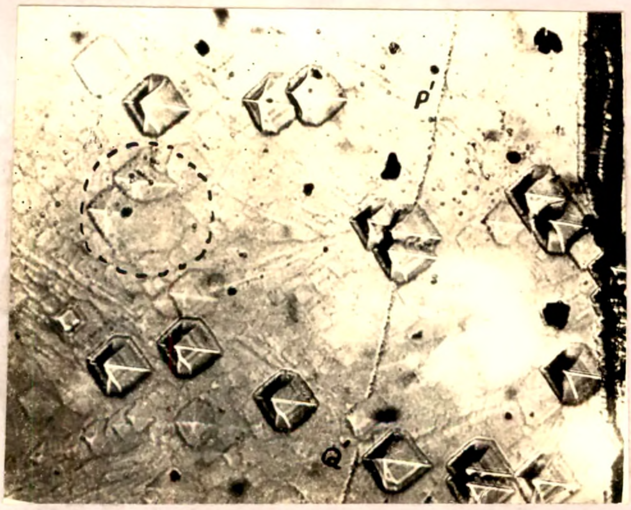

Fig. 5.1b (x220)

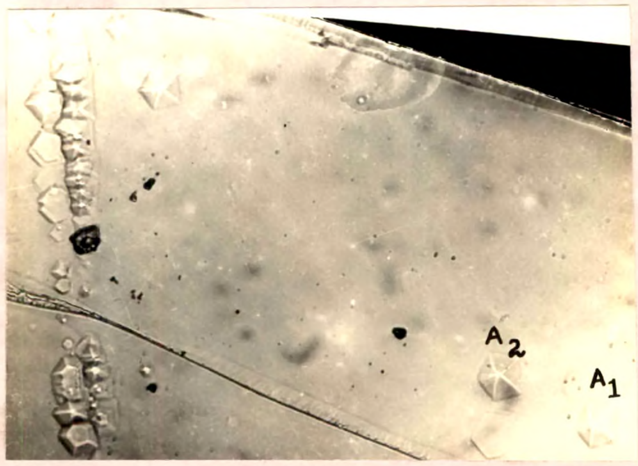

Fig. 5.2a (x220)

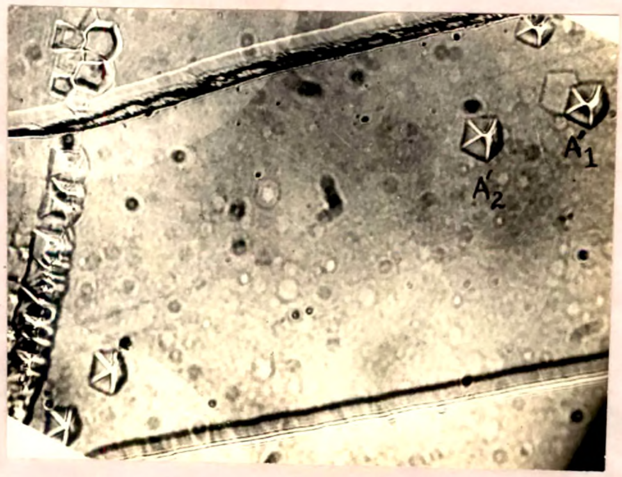

Fig. 5.2b (x220)

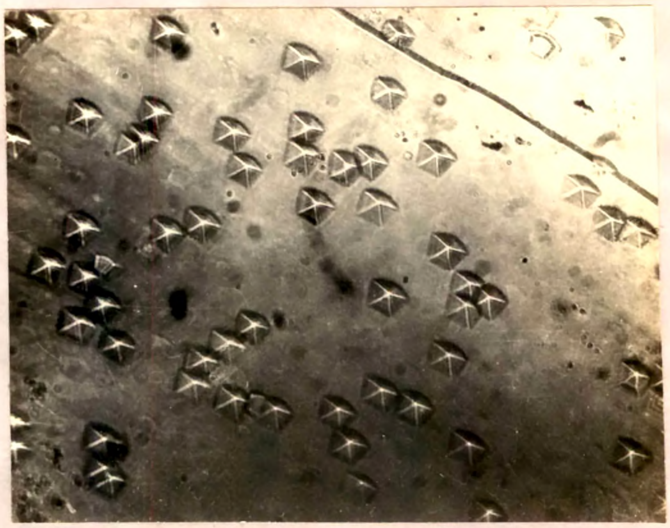

Fig. 5.3a (x220)

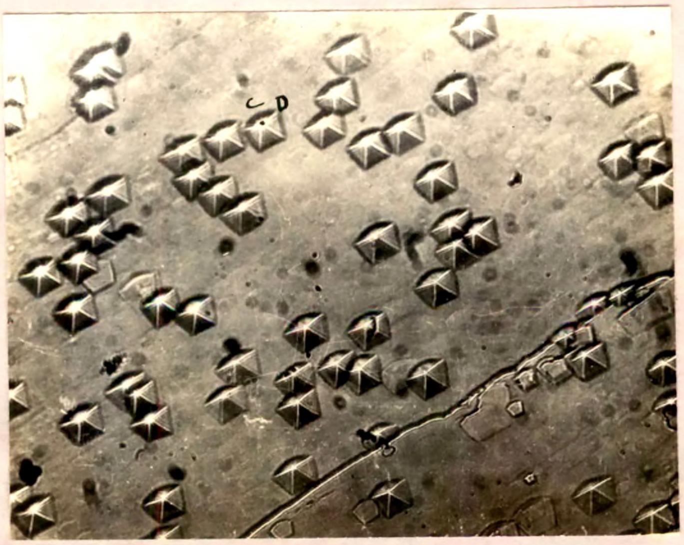

Fig. 5.3b (x220)

Further the positions of points of maximum depths of some pits are changed under both conditions. The depth points are nearer to the curvilinear sides of pits produced by dynamic etching (fig. 5.3b) than those of pits produced by static etching (fig. 5.3a). Besides the lines such as CD, passing through depth points in fig. 5.3b are not single like the corresponding one in fig. 5.3a, but consist of two or more lines. It is thus clear that under dynamic condition the rate of dissolution is not only faster but it also produces a change in the position of depth point with respect to the geometrical centre. The later part of the above statement is shown very beautifully by photomicrographs figs. 5.4a and 5.4b (x 170) which exhibit pits having rhombic outlines on the cleavage faces. These pits are produced by etching the oppositely matched cleavage faces by 0.01% acetic acid for 5 minutes and 1 minute under static and dynamic conditions respectively. Time period does not affect the shape of etch pit at this concentration. The pits on both these figures are identical in all respects except for the positions of points of maximum depths. For pits produced under static condition (fig. 5.4a) depth points from the geometrical centre are pointing to the vertex, which is a meeting place for all three obtuse angles and those obtained under dynamic etching are away from this corner. However, the depth points lie on the symmetrical line with direction [110] .

By changing the concentration of a given etchant and the condition of etching it is possible to obtain pits of identical shapes. Fig. 5.5a (x 170) is a photomicrograph obtained by etching the cleavage surface under static condition by 2% HCl for a period of 5 seconds whereas the matched cleavage face was dynamically etched by 1% HCl for 5 seconds [fig. 5.5b, x 170] . In both these cases the pits possess identical shapes but have different 'shifts' (Separations between geometrical centre and depth point).

5.32 Effect of time of etching on shapes of etch figures:

The above observations demonstrated very clearly the influence of condition of etching on the shape of etch figures. Another factor, which governs, to a certain extent, the shape of etch mark is time of etching. It is observed in the following case only. The pits in figs. 5.6a and 5.6b (x 220) are produced by etching the matched cleavages by 1% hydrochloric acid for 3 seconds and 5 seconds respectively under static condition. It is clear that the etching period has a marked effect on the shape of etch pits. The curvilinear quadrilateral pits are observed in figure 5.6a whereas pits have pentagonal outlines (fig. 5.6b)

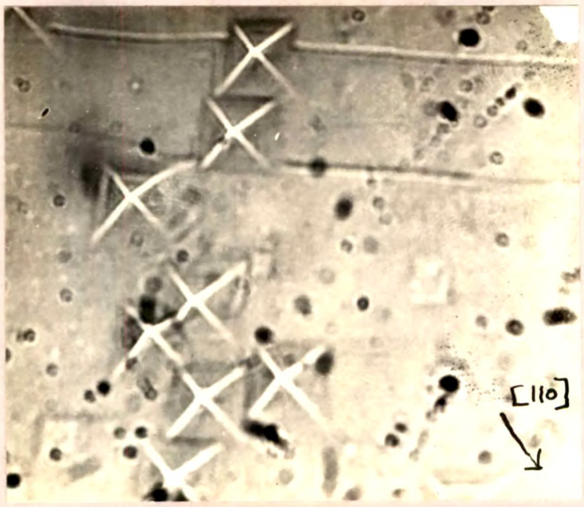

Fig. 5.4a (x170)

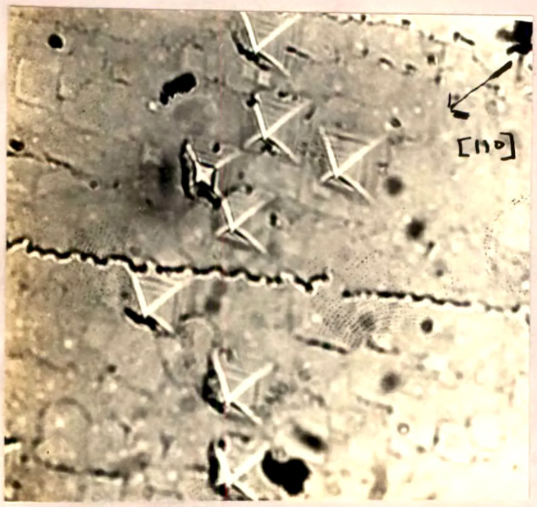

Fig. 5.4b (x170)

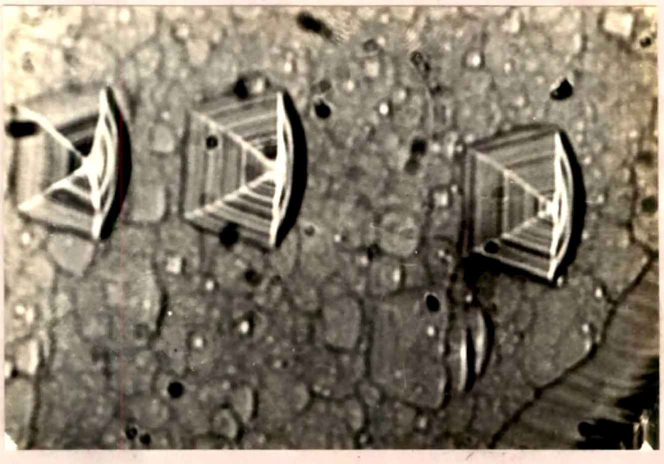

Fig. 5.5a (x170)

Fig. 5.5b (x170)

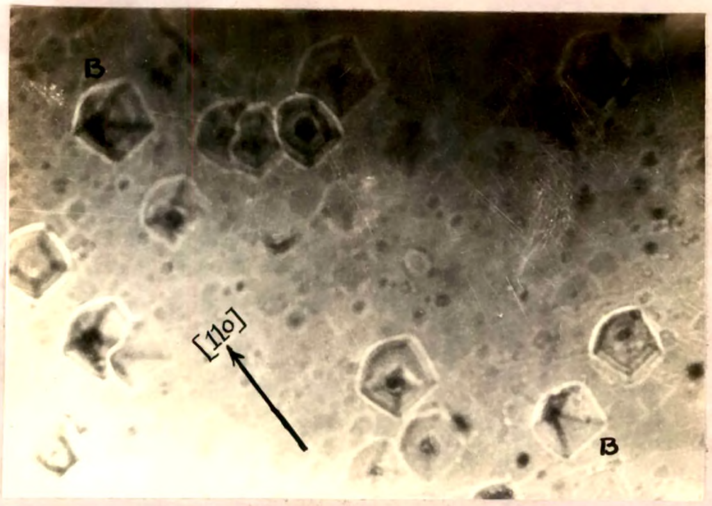

Fig. 5.6a (x220)

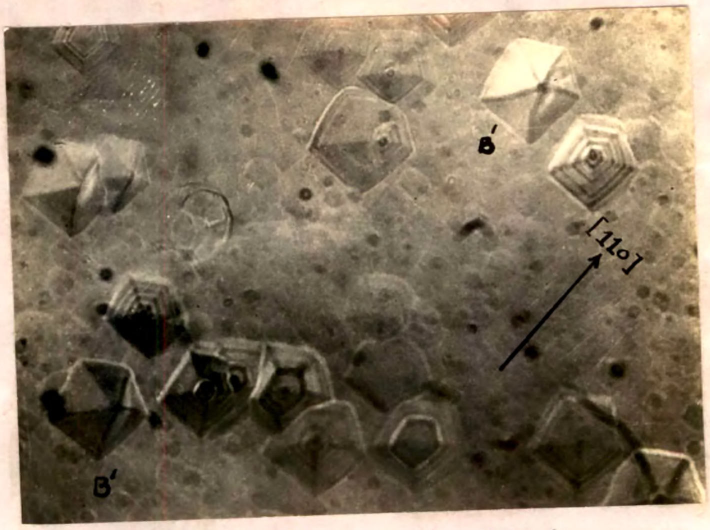

Fig. 5.6b (x220)

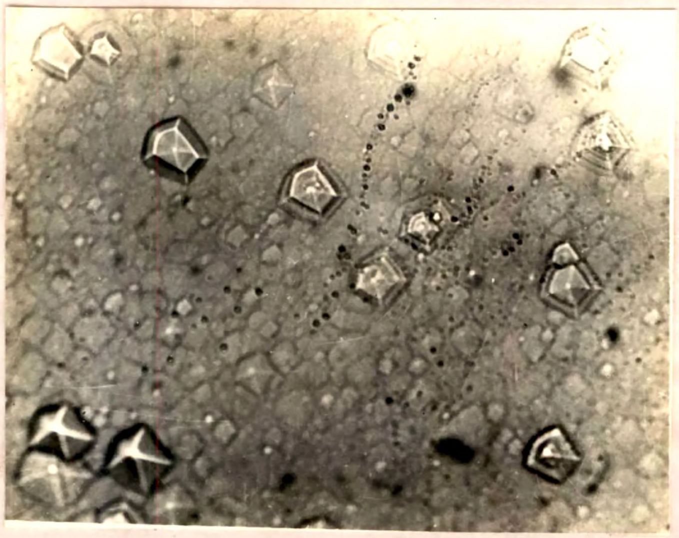

Fig. 5.7a (x220)

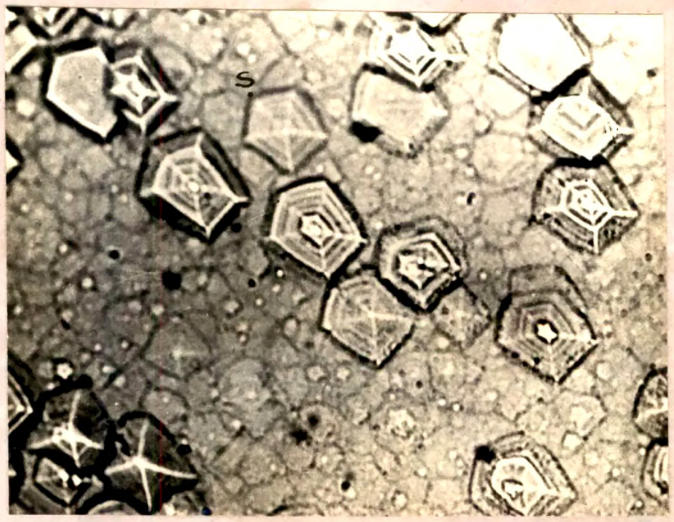

Fig. 5.7b (x220)

on the surface. The depth points of eccentric pits are usually found to lie on the median with direction [110] . The pit marked B' in fig. 5.6b is of interest. Its depth point has shifted towards the right from median while for the corresponding pit in figure 5.6a it is shifted towards the left of the median. This point is of particular interest so far as the internal structure of pit is concerned. However, it will be discussed in the next chapter on the eccentricity of etch pits. If the surface shown in fig. 5.6a was etched for a further period of 2 seconds by the etchant under static condition, curvilinear quadrilateral outlines of pits become pentagonal, similar to those shown in fig. 5.6b. Figures 5.7a and 5.7b (x 220) are the photomicrographs of a freshly cleaved surface subjected to multiple etching under static condition for 2 seconds and for a further period of 3 seconds by 1% hydrochloric acid respectively. Fig. 5.7b clearly exhibits the formation of fully developed pentagonal pits. Once one corner, 'S' giving rise to formation of pentagonal pit from a quadrilateral pit, is formed the shape of the etch pits remains unchanged for all subsequent period of etching. Besides, this corner is invariably formed on etching the cleavage surface by hydrochloric acid with concentration ranging from 0.01% to 1% only. During this range of concentrations the shapes of the pits do change, but the curvature or the sides of pits other than those corresponding to pentagon pits will not be formed at this corner, i.e. the angle made by the sides of pentagon pits at this corner remains almost constant.

The influence of the time of etching on changing the shape of etch pits is shown by etchants for a certain narrow range of concentration and within a definite period of etching. The pyramidal pits with rhombic outlines produced by 0.45% acetic acid maintain their outlines for all periods of etching, this is also true for pits having hexagonal outlines.

5.4 Discussion:

The following interesting features are brought out clearly by comparing the etch patterns produced by using the same etchant for identical periods of etching under dynamic and static conditions of etching.

(1) Etch pits produced by dynamic etching are larger in size than those produced by static etching.

(2) Displacements of depth points from the geometrical centres of etch pits are unequal under dynamic and static conditions of etching.

(3) The shape, an etch pit assumes on a cleavage surface of calcite under dynamic etching is usually maintained when the cleavage surface was statically etched by the same etchant of higher concentration.

(4) Under dynamic and static etching the pits are formed at the unchanged locations.

Patel and Goswami, (1962B) had used dynamic etching for calcite cleavages. They had observed that etch pits produced by citric acid under dynamic etching are formed at sites of dislocations. They did not observe any change in shape of etch pit though they found unequal changes in breadth and length of etch pits produced statically and dynamically by using same concentration of citric acid. As opposed to static etching, the dynamic etching takes place due to a large uniform relative motion between crystal and an etchant at the time of etching. This relative motion may influence the shape and other characteristics of etch pits due to following reasons: (1) It helps to remove molecules of etchant and reaction products quickly and the etching solution acting at a given point on the surface is constantly replenished due to this uniform motion. It is known that etching is a continuous process. Hence reaction product/s and etchant may mix with each other if etching is slow. As a result local dilution of etchant or arrest of etching action on or near pits takes place. This shows that local dilution occurs under static condition whereas it is almost absent under dynamic condition of etching. (2) There is a large amount of uniform relative motion of etchant with respect to crystal. Hence in addition to chemical energy the etching solution possesses mechanical energy.

These observations are helpful in understanding the formation of different shapes of etch pits on a cleavage surface produced under different conditions. In case of chemical reaction of glacial acetic acid (or of HCl) with calcite, the reaction products are calcium acetate (or $CaCl_2$), water and carbon dioxide. The later goes to the atmosphare whereas the former remains in the solution. When a cleavage surface of calcite was statically etched by 0.45% glacial acetic acid, rhombic pits were produced (fig. 5.1a). However, for the same period of etching if a cleavage surface was dynamically etched by 0.45% glacial acetic acid, hexagonal etch pits are formed (fig. 5.1b). These pits are also produced if the cleavage surface was statically etched by 0.5% glacial acetic acid. This shows that dynamic etching by 0.45% glacial acetic acid is equivalent to static etching of calcite cleavages by 0.5% glacial acetic acid. Hence under static condition of etching local dilution of about 10% at defect points has taken place. Similarly the rhombic pits are produced when a cleavage surface was dynamically etched by 0.4% acetic acid. Again in this case 10% local dilution at the pits is observed. It will be shown a bit later that this local dilution at a defect point depends on the concentration of an etchant.

In the earlier chapter, shape-cycles of etch pits produced statically by HCl and H$\overline{AC}$ of different concentrations are reported. The same shape-cycle can almost be repeated if a crystal was successively etched under static and dynamic conditions for a given period of etching. This cycle for two shapes viz. hexagon and rhombic outlines is mentioned above for dynamic etching by glacial acetic acid of 0.45% and 0.4% respectively. This should be compared with the static etching by glacial acetic acid of 0.5% and 0.45% for producing pits with hexagonal and rhombic outlines respectively.

In order to ascertain the effect of dynamic energy of the etchant on the etching characteristics, an experiment was conducted, where the cleavage surfaces were separately subjected to dynamic etching by 0.03% HCl and 0.45% acetic acid. Under static condition these etchants produce pits with rhombic outlines (fig. 4.10 and 4.11). Under dynamic condition, these same etchants produce pentagonal and hexagonal etch pits respectively. In both the cases the amount of dynamic energy of an etchant is the same. Even then the pit shapes are in accordance with shape-cycles mentioned in chapter 4. This shows that dynamic energy does not change the chemical energy of an etchant. It simply retards or annuls the local dilution at a preferential point on a crystal surface. On the basis of local dilution on or near pit on a crystal surface it is possible to explain the change in shapes of etch pits produced by hydrochloric acid of varying concentration [figs, 5.2a and 5.2b] (and possibly for any other etchant) on a cleavage surface of calcite.

It is shown in previous chapter that etch pit shape remains identical for definite concentration range of etchants but depth point relative to geometrical centre changes. If there is local dilution of the etchant in static etching, change of depth point with respect to geometrical centre of an etch pit produced by same concentration of etchant under dynamic and static condition should be observed. Actually this has happend as observed in figs. 5.4a and 5.4b.. The static etching produces etch pits with negative shift while dynamic etching produces etch pits with positive shift. Positive shift of depth point of a pit is observed in high concentration range ($0.02 < c < 0.45\%$) of glacial acetic acid. The local dilution of etchant in this case is more than 50%. Alongwith the earlier observation, this shows that greater is the concentration of etchant, less is a local dilution at a given point on crystal surfaces. It is mentioned above that time of etching is also less for producing etch pits of similar sizes under dynamic etching than that under static etching. This can be explained by considering: (1) occurrence of local dilution of concentration in static etching, (2) fast rate of etching due to easy movement of etchant on crystal surfaces and (3) availability of a large amount of free hydrogen ions.

It should be remarked here that etch pits produced under static or dynamic conditions on a cleavage surface of calcite by hydrochloric acid and glacial acetic acid, reveal dislocations, because good matching of etch pits is observed on matched counterparts and no change of density of etch pits on successive (dynamic or static) etching.

In one typical observation, it is found that the geometrical outline of an etch pit depends upon the time of etching. Thus when a cleavage surface was etched by 1% HCl for 3 seconds, etch pits with curvilinear quadrilateral outlines (fig. 5.6a) were observed. If this, surface was re-etched by the same etchant for a further period of

3 seconds or more, the pits with pentagonal outlines were obtained. It is difficult to explain how this change of shape takes place with a little change in etching period. The dynamic etching usually produces pits with terraced structure. It is hard to explain this structure on the basis of the existence of impurity (Gilman, 1960) at defect sites. The present author feels that there are other unknown factors contributing towards the formation of this structure.

5.5 Conclusions:

(1) Irrespective of conditions (static or dynamic) of etching the pit, produced by HCl or H$\bar{AC}$ are at dislocations terminating on the cleavage surface of calcite.

(2) Within a given range of concentration of an etchant (HCl or H$\bar{AC}$) different amounts of local dilution at or near etch pits are produced under static condition of etching.

(3) Etch pits which are produced by a given concentration of an etchant under static condition can also be formed at a little lower concentration of the same etchant under dynamic condition of etching.

(4) Similar etch pit shapes can be observed by changing the condition of etching and concentration of an etchant.

(5) The shapes and/or eccentricity are different for etch pits produced by a given etchant under dynamic and static condition of etching.

(6) The change in time of etching can also produce a change in the shape of etch pits obtained by etching a cleavage surface of calcite by a given concentration of etchant under favourable condition of etching.