CHAPTER 8

THERMAL ETCHING OF CALCITE CLEAVAGE SURFACES.

8.1 Introduction:

Calcite crystals are widely used for optical work in many precision instruments. Since this crystal decomposes at elevated temperatures (about 850°C) its thermal etching can be studied to find its durability at high temperatures by critically observing the microtopography of thermal etch patterns on the cleavage surfaces. It appears from literature that very little work has been reported on thermal decomposition of calcite with a view to find correlation of thermal etch features with defect structures. Thomas and Renshaw (1966) studied the decomposition phenomenon in single crystals of calcite. From a study of polygonization and linear arrangements of thermal etch pits observed in the initial stages of decomposition at 500°C in vacuum, they suggested these pits

to be at dislocations terminating on the surface. Thermal decomposition of calcite was also studied by Cutler and Kovalenko in the same year. They found strong dependence of the occurrence of thermal nuclei on the pre-history of the specimen surface. They further suggested that the impurity associated with dislocation might be primarily respondible for etch pit nucleation.

In the present account, the author has profusely used the etching technique for studying the defect structure of crystals. In the earlier chapters, some important aspects of chemical and thermal etching have already been given. In this chapter will now be given a detailed systemetic study of thermal etching of calcite cleavage surfaces at high temperatures.

8.2 Experimental procedure:

In the present investigation calcite was etched in the range of 520°C to 560°C in a thermally regulated horizontal rectangular muffle furnace manufactured by Wild Barfield Electric Furnace Ltd., Watford , Herts. This furnace consists of (i) the muffle, with lead outs and connections in the rear, spring-loaded door and protective atmosphere, (ii) temperature regulator, comprising an

energy regulator control unit, (iii) temperature indicator in the form of a thermo-electric pyrometer, (iv) safety devices.

Energy regulator unit (dial) is calibrated in terms of temperatures so that the desired temperature can be obtained and maintained constant. Every time, freshly cleaved sample/s of calcite crystal/s was/were placed in a porcelain crucible at a definite place in the muffle furnace in such a manner that the cleavage surface was always exposed to the atmosphere in the furnace. The accuracy of temperature of the muffle furnace is $\pm$ 10°C for long time period.

The porcelain crucible containing crystal for thermal etching was kept in a muffle furnace and its temperature was slowly raised to desired temperature and maintained fairly constant at this value by the energy regulator. The required temperature(viz. 520°C) was obtained in two hours. After attaining the desired temperature etching time was counted. After thermally etching the crystals for a given time, the furnace was shut off and brought to room temperature. The crystals were then taken out for optical study. When a crystal was suddenly put in the furnace kept at a temp. of 520°C, it

was found that crystal could not maintain its rigidity and got cleaved into several pieces. Hence the earlier procedure mentioned above was invariably followed, for the purpose of thermal etching. It is found from observations that a crystal could tolerate sudden change of temperature of the order of 100°C upto 200°C.

After etching a crystal in the furnace for the required time at a given temperature the cleavage surface was silvered by using thermal evaporation method described in chapter 2. This enabled the author to study crystals under high magnification and resolution and by the use of multiple-beam interferometric technique. The unsilvered thermal etch surfaces were kept in dessicator to avoid the effect of atmosphere.

8.3 Observations and Results:

It is reported in literature that calcite decomposes at 850°C. These crystals were therefore kept well below decomposition temperature, say 650°C, for one hour. When the crystals were taken out from the furnace, surfaces were found covered with a white layer. From the

chemical test it was found that white layer consisted of calcium oxide only. Crystals became so soft that slight force by the forcep can cleave them very easily. Further this surface did not exhibit any meaningful microtopographical features. For all the etching time varied from a few minutes to a few hours this white layer was observed on the cleavage surface kept at this temperature (650°). Etching experiments were therefore carried out at lower temperatures viz. 625°, 600°, 575°, 550° and 495°C.

It was found from the experiments conducted at these temperatures that when the temperature was lower than 560°C visible etching could be observed on the cleavage surface. At the same time, when the temperature was lowered than 520°C practically no etch effect could be found on the specimen observed under very high optical magnification and resolution. When the etching was carried out at a temperature of 540°C for eight hours, the cleavage surface was found to be covered with beautiful regular geometrical figures usually referred to as thermal etch figures. (fig. 8.1, x 90). It is seen from this photomicrograph that the thermal etch figures are of assorted sizes. Besides many large figures are formed on the cleavage line; the figures are also observed at places free from cleavage, slip or twin lines. The figures are having rhombohedral outline with the sloping faces meeting at a point. This point

coincides with the geometrical centre of the rhombic figures. The sides of these pits are parallel to the edges of the crystals i.e. to $\langle 100 \rangle$, whereas the longer and shorter diagonals are parallel to $[1\bar{1}0]$ and $[110]$ respectively. Incidentally in this figure the cleavage lines are parallel to the longer diagonal of the etch figure. However, this is not always the case. Further a short horizontal line CD on the lower left hand side of the figure is observed after thermal etching only. In order to see the inner structure of these figures; another specimen was etched at 540°C for 12 hrs. Fig. 8.2 (x 860) is a photomicrograph of a typical region of this specimen which was observed by using oil immersion objective. The rhombic etch figure is bound by well defined faces, the internal structures of which consist of irregular meshes. It is of interest to note that from the sides of this figure many lines are protuding which appear to be cracks created during thermal etching. Some cracks appear to be crystallographic in nature such as AB along $\langle 100 \rangle$ directions. The figures are symmetrical about the geometrical centre. However the centre is not a point. Thermal etch figures of different geometrical shapes are also observed under certain conditions. Fig. 8.3 (x 270) represents a photomicrograph of a typical region of a freshly cleaved surface thermally etched for 12 hrs. at 520°C exhibiting etch figures with

circular outlines. Internal structures of these etch marks are not clear. The etch figures were formed on cleavage lines and at other points on the surface. This observation is similar to the one described above in the case of rhombic thermal etch figures. It is interesting to note that lines such as CD having crystallographic nature are revealed on thermal etching and appear to be associated with some of these marks. It is found that these lines are in the direction $[1\bar{1}0]$. All the thermal etch figures are not of equal sizes. The average area of circular outline of these figures projected on the cleavage surface is 4×10^{-5} cm^2 while the density of the etch pit is of the order $\sim 10^4/cm^2$.

As the temperature of etching is increased, shape of the etch figure also changes. Fig. 8.4 (x 150) is a light profile photomicrograph of a crystal surface thermally etched at a temperature of 530°C for 12 hours. Instead of circular figures the tendency is to form figures with hexagonal outlines. It is clear from some figures such as A that the transition from circular to hexagonal pit is not abrupt but with intermediate stage which contains boundary of elliptical outlines. The condition for formation of elliptical figures could not be well established due to small change of temperature (i.e. from 520°C to 530°C)

at higher temperature. The internal structure of these figures consists of irregular meshes; [1$\bar{1}$0] line CD which was observed on this surface was not present before thermal etching. These observations suggest that the outlines of thermal etch figures depend on the temperature of thermal etching. Density of these etch figures is of the order of $10^4/cm^2$ while average surface area of these figures is $4 \times 10^{-5} cm^2$.

The thermally etched cleavage surfaces are also affected by atmosphere when exposed for a long period. Fig. 8.5 (x 120) represents a typical light profile photomicrograph of unsilvered freshly cleaved surface thermally etched at 530°C for 8 hours. The thermal etch figures possess elliptical outlines with major axis revealed by a line within them along [110] such as PQ. When this unsilvered crystal surface was exposed to the atmosphere for 12 hours it was found that the major axis of the elliptical figures had disappeared and size of the pit had increased slightly (fig. 8.6, x 120). Further some etch figures such as A, B, C exhibit the production of lines from one end of the major axis. This aging effect due to atmosphere had been found to be common for all thermally etched specimens. Hence enough care was taken to see that the etched surfaces remained unaffected during their preservation and study. When the crystals were etched at

higher temperature ($>560^{\circ}C$) the surface became so delicate that even during careful handling they did not preserve their size and broke into number of small cleavages. When one of these pieces was examined it also exhibited thermal etch figures of rhombic shape. When the crystal surface was kept at a temperature of $540^{\circ}C$ for 12 hrs., the thermal etch figures of different sizes with clear rhombic outline and diagonals are found on the surface (fig. 8.7, x 150). It should be mentioned that the occurrence of rhombic figures with unusually clear diagonals and without any background is rather rare. In most of the cases the thermal etch figures produced at this temperature are of the type shown in fig. 8.8 (x 300). In this photomicrograph, the etch figures have rhombic outline, but the inside structure is not clearly visible except the black spot at the centre in some figures. Further there is white background round these pits and a number of crack lines are protuding from them. Besides many of the pits on cleavage lines have joined together to form bigger pits of unusual size.

It is shown by a number of workers that dislocations are revealed by the etch pits produced chemically on the cleavage surfaces, when there is complete correspondence between the etch pits on oppositely matched cleavage faces (Amelinckx, 1954; Gilman and Johnston, 1956;

Keith and Gilman, 1960, etc.). A few workers have also studied matching of thermally etched cleavage faces (Takeda and Kondoh, 1962). In the present case there is practically very little correspondence between the thermal etch patterns on matched cleavage surfaces of calcite crystals. Figs. 8.9a and 8.9b (x 90) represent the matched cleavage faces simultaneously thermally etched at 520°C for 12 hours. Although the cleavage lines are properly reflected on these surfaces, the thermal etch figures do not show that much correspondence. Even the lines revealed by thermal etching along $[1\bar{1}0]$ are not having correspondence on the matched faces. The density of these marks on both the faces varies from 10^3 to $10^4/cm^2$. Figs. 8.10a and 8.10b, (x 120) show another pair of matched cleavage faces simultaneously thermally etched at 540°C for 12 hrs. The thermal etch figures which have rhombic outlines donot show any correspondence on these faces. The cleavage lines on these counterparts show perfect matching. There are a few common characteristics of the thermal figures on these faces viz. their assorted sizes with identical shapes and white background around most of the etch figures. Again the density of thermal figures vary from 10^3 to 10^4 cm^{-2}.

Many workers have shown from etching study of different crystals that if the pits represent the sites

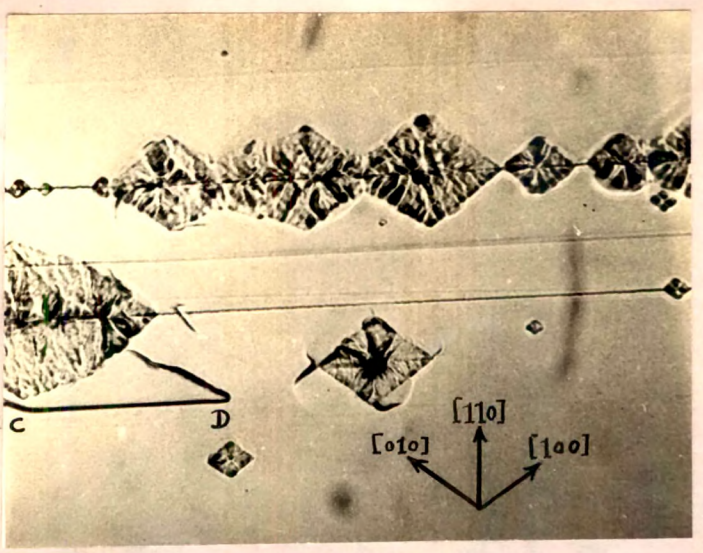

Fig. 8.1 (x90)

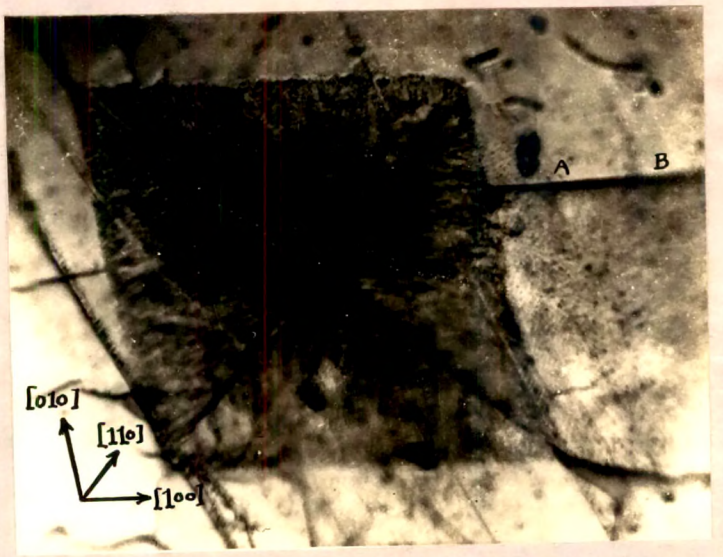

Fig. 8.2 (x860)

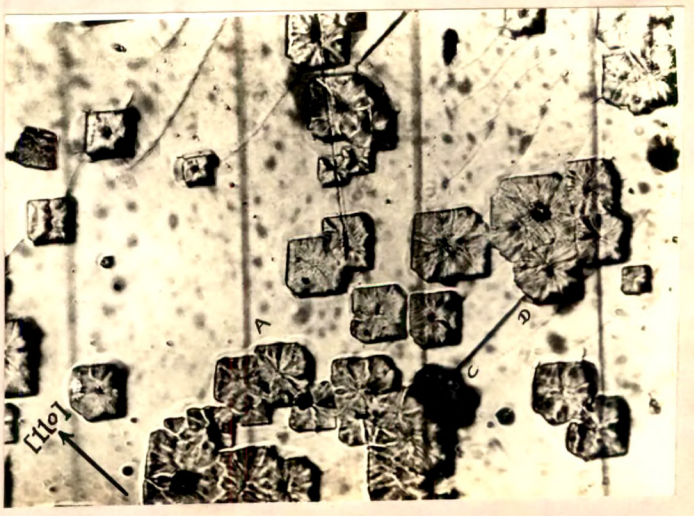

Fig. 8.4 (x150)

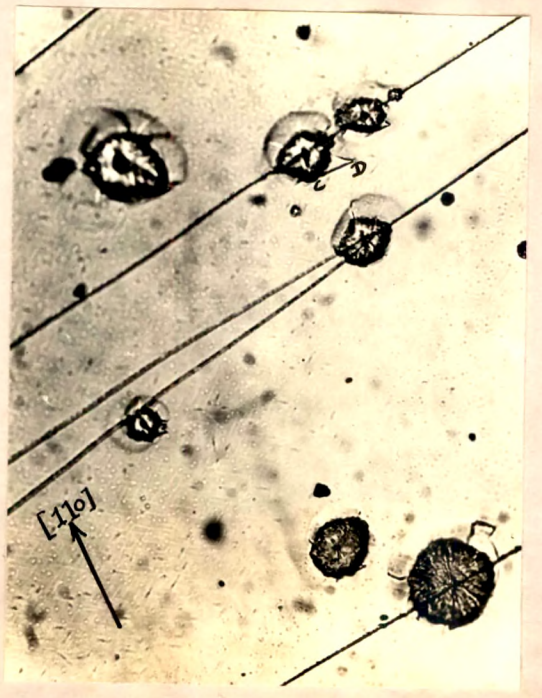

Fig 8.3 (x270)

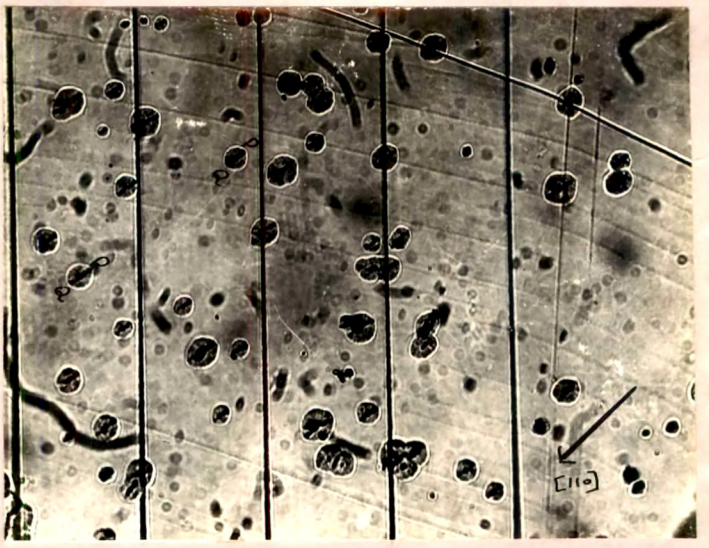

Fig. 8.5 (x120)

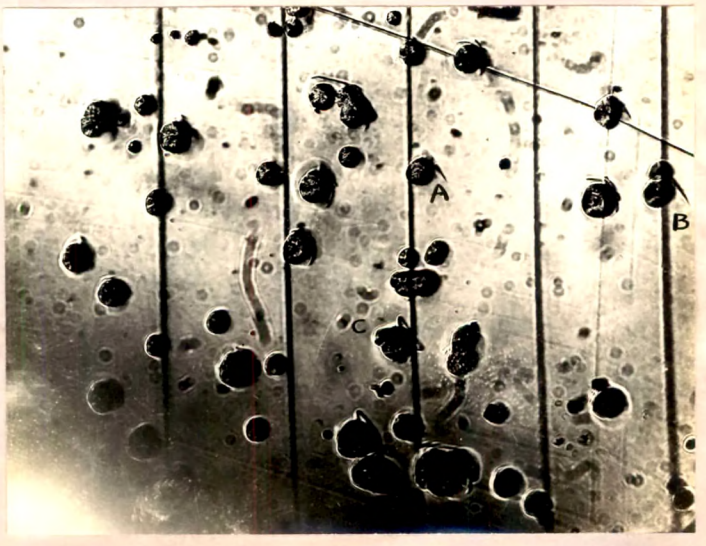

Fig. 8.6 (x120)

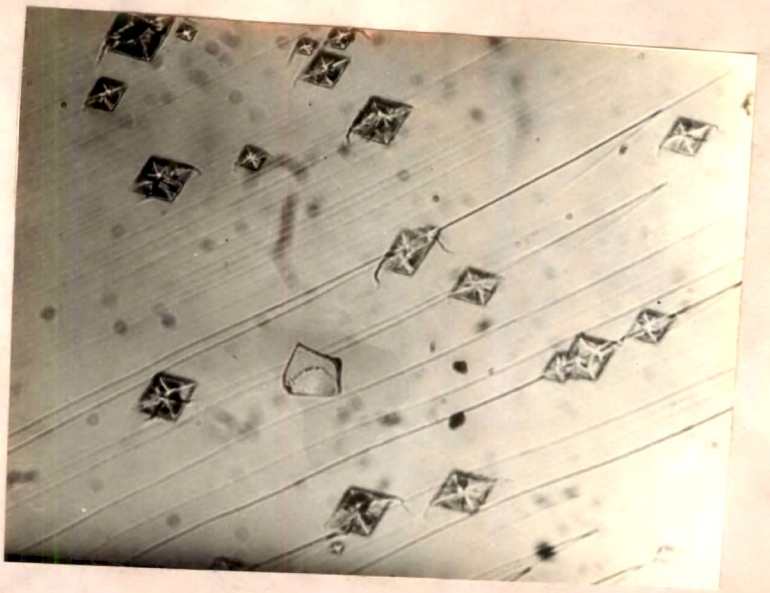

Fig. 8.7 (x150)

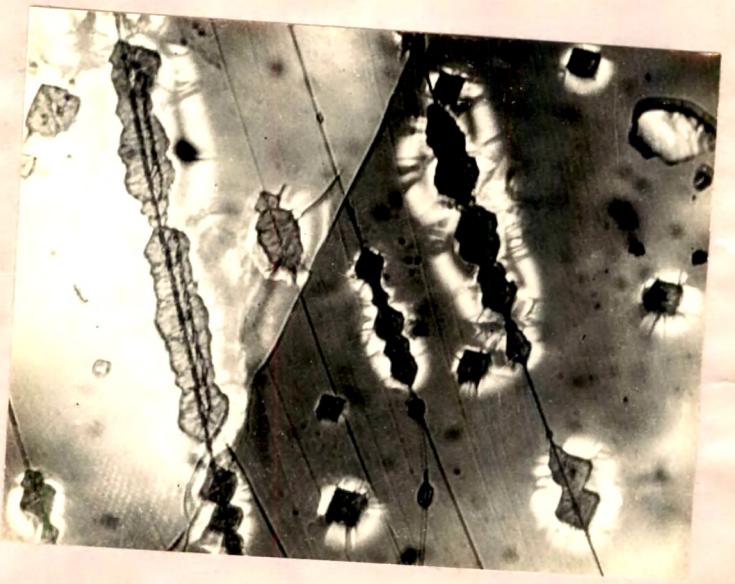

Fig. 8.8 (x90)

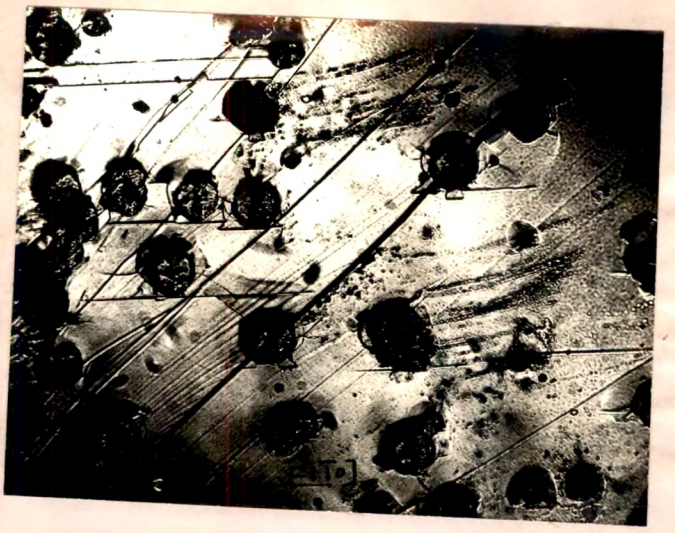

Fig. 8.9a (x90)

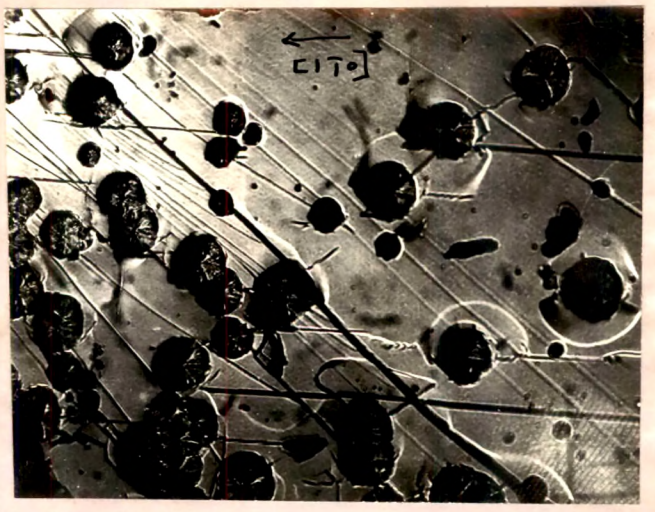

Fig. 8.9b (x90)

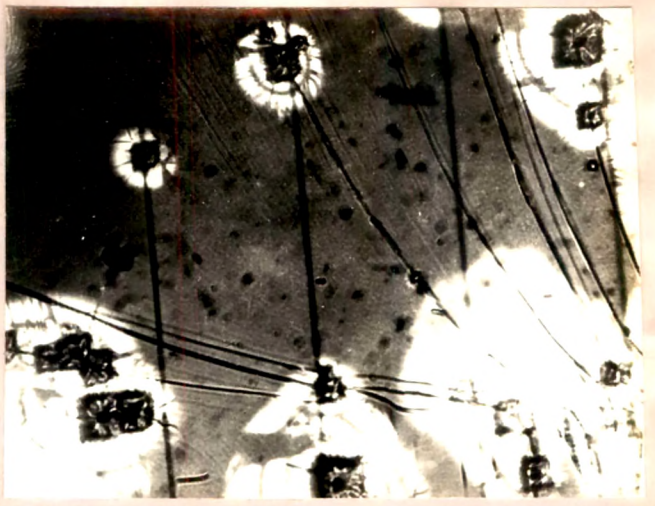

Fig. 8.10 a (x120)

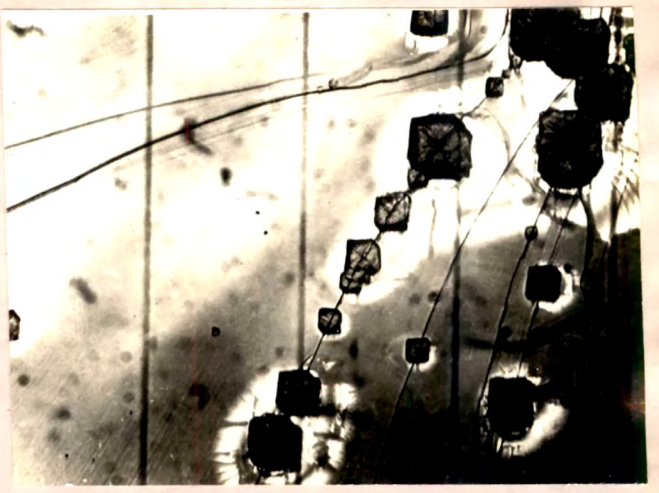

Fig. 8.10 b (x120)

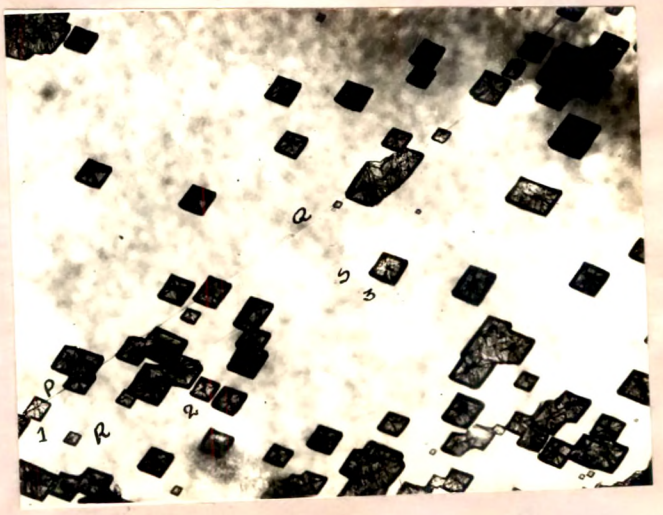

Fig. 8.11a (x90)

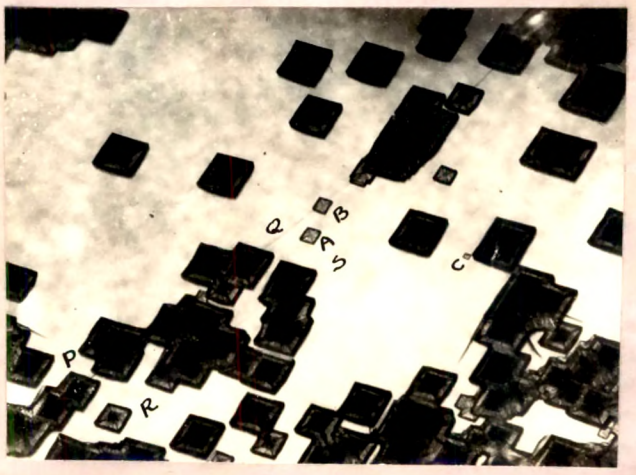

Fig . 8.11b (x90)

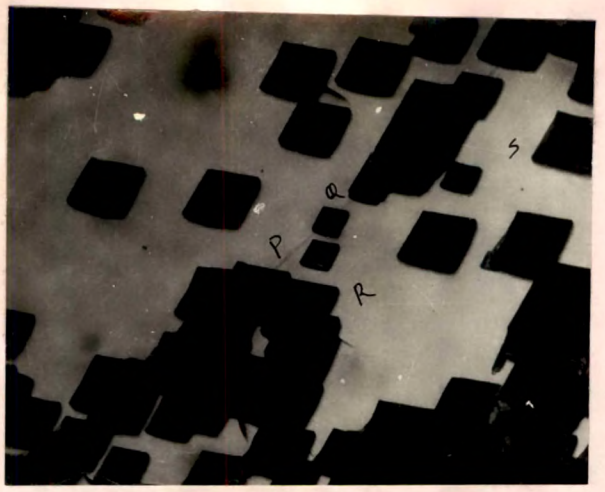

Fig. 8.11c (x90)

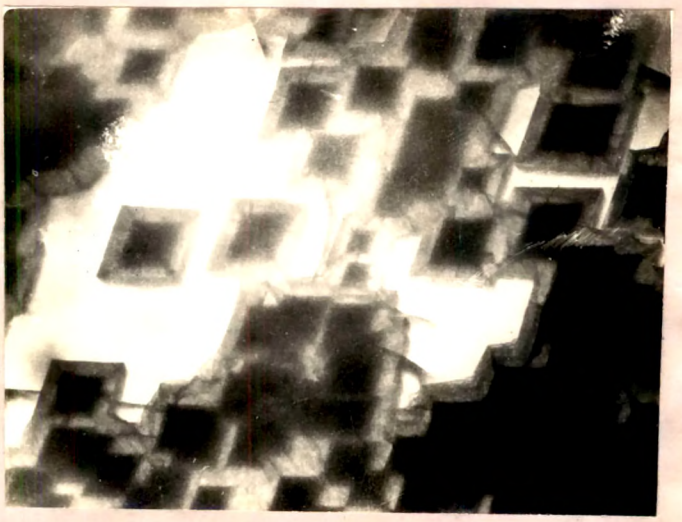

Fig. 8.11d (x90)

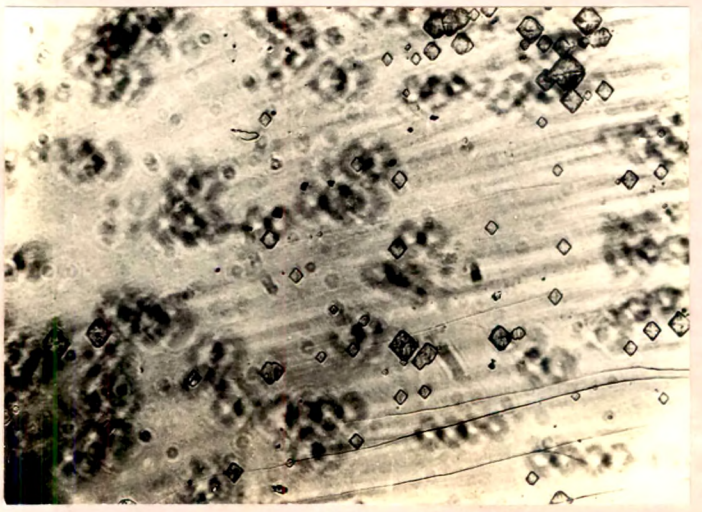

Fig. 8.12a (x120)

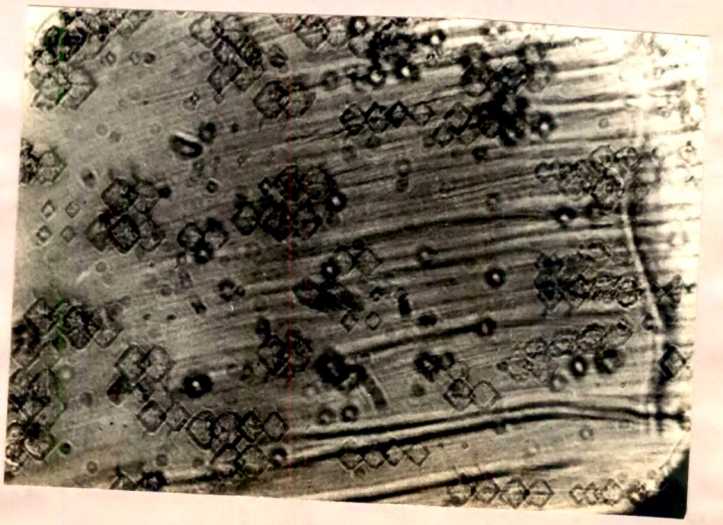

Fig. 8.12b (x120)

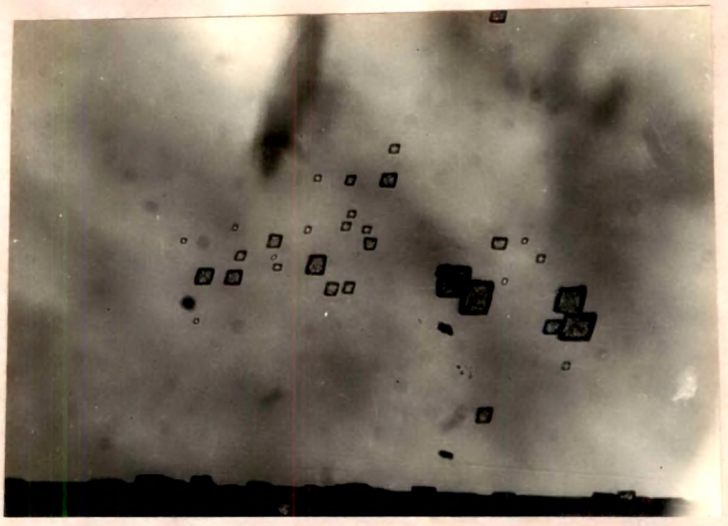

Fig. 8.13a (x90)

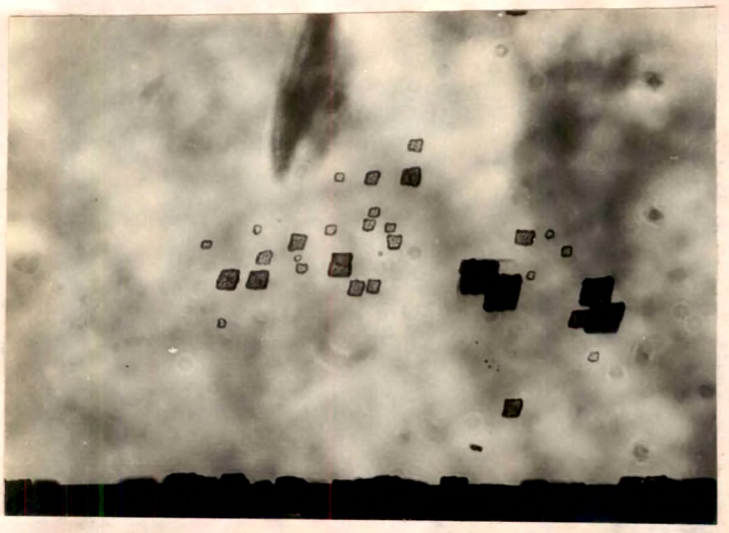

Fig. 8.13b (x90)

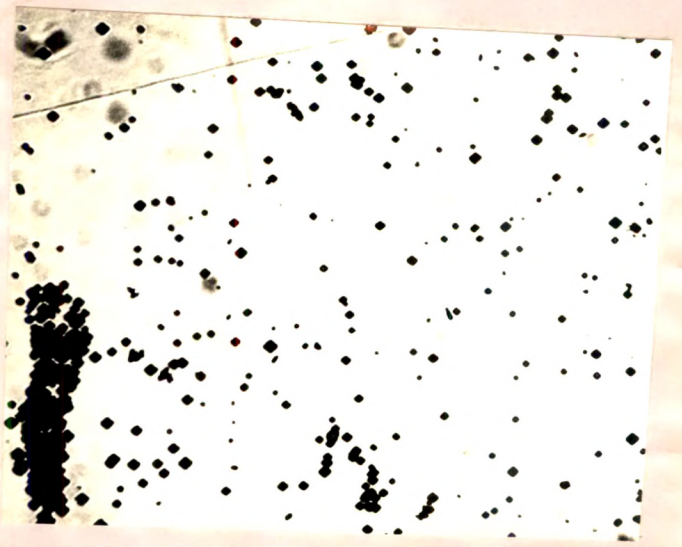

Fig. 8.14 (x120)

Fig. 8.15 (x90)

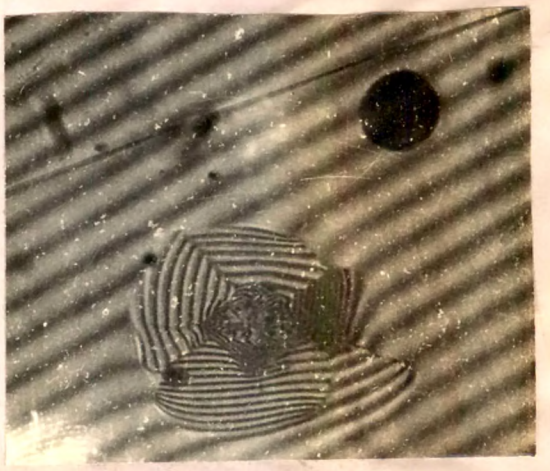

Fig. 8.16 (x150)

Fig. 8.17a (x90)

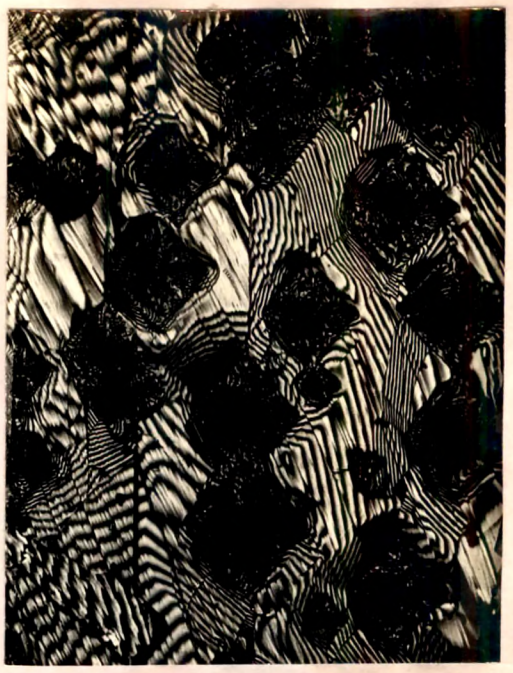

Fig. 8.17b (x90)

Fig. 8.17c (x90)

of line defects, the repeated etching of these crystals surfaces should not show any change in the number, position and orientation of these pits. Figs. 8.11(a,b,c,d) (x 90) represent photomicrographs of a freshly cleaved surface successively thermally etched at 540°C for 12 hrs., 26 hrs., 40 hrs., and 54 hrs. respectively. It is unusually clear from all these figures that although these etch marks which are of different sizes increase in dimensions with the increase of etching period, yet a few new etch figures are found in the second stage of etching such as A B C. The density of thermal figures on this surface is practically constant (10^4 cm^{-2}). The cleavage lines PQ and RS are unaffected by thermal etching and do not shift from their position as is usually found, in the case of chemical etching (Tolansky and Patel, 1959; Pandya J. R., 1961). The neighbouring pits enlarge on repeated etching and coalesce to form bigger pits of varying sizes. The internal structure of these figures also change with repeated etching. Thus in fig. 8.11(a) the internal structure of the figures such as 1,2,3, ... consists of a few zigzag lines giving rise to irregular cellular structure with central portion black in many pits, whereas in fig. 8.11b, these lines have disappeared with the centres seen as black dots. However the number of cracks propagating from the thermal etch figures increases with the time of etching. In figure 8.11 d, the diagonals

of the rhombic etch figures are clearly seen with the central rhombic figures more black. In the [illegible] fig. 8.11d the cleavage line is not clearly seen [illegible] because the marks are found all along it. Upto fig. 8.11c the cleavage line is clearly visible.

It is well known from the properties of dislocations that they should end on the surface of a crystal or should form a closed loop within the crystal. Hence if a straight dislocation or a loop possesses sufficient length it must be found on either side of a thin flake of the crystal. In the present case thermal etching was carried out on a number of thin flakes of calcite cleavages with thicknesses varying from 700μ to 1200μ. Figs. 8.12a and 8.12b (x 120) show photomicrographs of a thin flake with thickness 700μ etched at 540^{o}C for 12 hrs. It is crystal clear from the study of the front and rear surfaces of thin flake that there is very little correspondence between the thermal etch figures on them. The density of thermal etch figures on these surfaces are also slightly unequal and are of the order of 10^{4} cm^{-2}.

When a crystal is cleaved by the usual method, i.e. by putting a sharp end of the blade along a chosen direction on a crystal surface and giving a gentle blow

to it, it is found that comparatively more distortion or damage occurs at the edge from which the crack has propagated in the crystal. As a result, the preferential attack on this strained region is likely to be more than elsewhere. Hence when such a crystal is thermally etched at 540°C for eight hours and regions near this edge are examined, it is observed that there are a few thermal etch figures of different sizes (fig. 8.13a; x 90). When the same was re-etched for four hours more, these regions did not disclose more marks (fig. 8.13b; x 90) but the dimensions of existing thermal figures increased. This observation should be compared with the observations (figs. 8.11a, b, c, d) on successive thermal etching of cleavage face. When the crystals obtained from different localities were studied, it was found that the density of thermal etch figures are different and in some cases, some changes in the structure of figures are also observed. Fig. 8.14(x 120) represents a typical photomicrograph of a cleavage surface etched at 540°C for 12 hours. The etch figures are having rhombic outlines and their density is 5×10^4 cm^{-2}. Fig. 8.15 (x 90) is a photomicrograph of a cleavage surface of a crystal of different lot, thermally etched at 540°C for 12 hrs. It is clear from these two figures (figs. 8.14 and 8.15) that although the conditions of etching are identical in both the cases, the dimensions and density of thermal figures are different. The etch marks shown in

fig. 8.15 are slightly different from those observed earlier. Although the basic shape is rhombohedric yet the area round these marks consists of a number of wings stopped by a line whose direction is found to be [1$\bar{1}$0] and which occurs on only one side of these marks. The density of these figures is 10^3 cm^{-2}. The interferogram taken over one of these figures is shown in fig. 8.16 (x 150). The wings are elegantly revealed along with the straight line fringes nearly parallel to each other round the etch mark thereby showing that region on its either side is fairly smooth. It is also clear from the pattern of fringes on wing around thermal etch figures that there is an abrupt change in direction of fringes as they cross the wings. This shows that wings are inclined with respect to one another. In order to find the structure of these etch marks, multiple beam interferogram (fig. 8.17b, x 90) is taken over a region shown in fig. 8.17a, (x 90) which is a photomicrograph of a cleavage surface of calcite thermally etched at 540°C for 18 hrs. It is evident from the fringe pattern that the internal structure of these marks is very complicated due to the occurrence of a large number of fringes in an irregular manner around them and is without the usual orderly arrangement of terraces and/or sloping faces within them. The fringes round these figures also change their directions

number of times due to the lines along [1$\bar{1}$0] revealed by thermal etching at 540°C for 18 hrs. and found on one side of these figures. Fig. 8.17c (x 90) is a multiple beam interferogram over the cleavage surface which was first thermally etched and then chemically etched. This figure shows very clearly the contrast between the nature and quality of these two types of pits. All these different characteristics are summarized in table 8.1.

8.4 Discussion:

The above observations clearly indicate that the thermal etch patterns on calcite cleavages possess characteristics which are somewhat different from those of chemical etch figures. The first point that one would like to decide is their relation with respect to the surface i.e. whether they are hillocks or depressions. This was studied by taking a light profile over one of the etch figures. A very mild thin scratch (fig. 8.18, x 150) is drawn below this figure. The direction of motion of the profile over the etch figure and the scratch clearly showed that these figures were depressions. This has been confirmed by finding profile over almost all these figures and by using fine focussing arrangement for observing the pattern and scratch. The depth of the etch pit A shown in

fig. 8.18 is 1.5 microns. It is now necessary to find the origin of thermal etch pits. Since these pits exhibit different characteristics, it is worthwhile to compare them with those produced by chemical etching. For this purpose a series of experiments were performed. They will now be discussed. Fig. 8.19 (x 90) shows a photomicrograph of a freshly cleaved surface thermally etched at 540°C for 12 hrs. The region of this figure was selected with the intention of having isolated clear thermal rhombic etch pits. This surface was chemically etched by 0.2% glacial acetic acid for 10 seconds. (fig. 8.20, x 90). The pits produced by chemical etching possess the same outline as those of thermal etch pits but are produced at places free from thermal pits. Further the inner structure of thermal pits is affected by chemical etching and the thermal pits become darker showing thereby that they are too deep to be resolved by microscope. The chemical etch pits are also produced on the crystallographic line [1$\bar{1}$0] near or coming from the thermal pits. This is seen more elegantly in fig. 8.21 (x 120), which is obtained by etching the thermally etched surface by 0.4% glacial acetic acid for 40 seconds. It should be remarked in passing that in the case of thermal pits, the point of maximum depth coincides with the geometrical centre of the rhombic pit, i.e. the eccentricity as defined in chapter 6 is zero; whereas the chemical etch pits are usually

eccentric. Apart from the isolated chemical pits and the clustering round the thermal pits the surface does not exhibit any micropitting i.e. the rest of the surface is highly resistant. The environment (white background) round the thermal pits is quite sensitive to the concentration of acetic acid. Thus fig. 8.22 (x 100) shows the thermally etched surface chemically etched by 94% glacial acetic acid for 12 hrs. at room temperature. The usual background round the thermal pits has completely disappeared and instead a black octagonal outline is formed round the thermal etch pits which have become shallow. The effect of concentration of etchant on the shape of chemical etch pits is obvious by comparing them with those of fig. 8.21. The chemical etch pits in fig. 8.22 are having rectangular outlines whereas those of fig. 8.21 possess rhombic outlines; the diagonals of rhombic pits are parallel to the sides of rectangular pits i.e. the orientations of these pits have changed. When a thermally etched surface was chemically etched by a saturated solution of sodium hydroxide in distilled water for ~~2.1/2~~ 2.5 hours the thermal etch pits show hexagonal outlines (fig. 8.23; x 90). The rhombic (thermal) outline is combined with the boat shaped chemical pits in such a manner that appearence becomes hexagonal (fig. 8.24). In all these cases it is observed that the chemical pits are produced at places free from thermal pits. However, the type of attack on thermal pits is dependent upon the nature

and concentration of an etchant.

A second series of experiments were carried out. In these experiments the freshly cleaved surface of calcite was chemically etched and then placed for thermal etching. Figs. 8.25a and 8.25b (x 90) show the chemically etched matched surfaces thermally etched at 540°C for 12 hrs. The photomicrographs show scattered chemical pits with micropitting due to thermal etching. This is rather unusual in the sense that when the virgin surface was first thermally etched under identical conditions of etching it exhibited large thermal etch pits. Subsequent chemical etching did not exhibit features of the type shown in figs. 8.25a and 8.25b. This suggests that chemical etching produces some unknown effect on the cleavage surface. As a result when the surface was thermally etched, instead of a few isolated big thermal pits a large number of thermal pits were produced.

Figs. 8.26a and 8.26b (x 110) are the photomicrographs of freshly cleaved matched surfaces, one is thermally etched (fig. 8.26a) at 540°C for 12 hrs. and other is chemically etched (fig. 8.26b) by 0.2% glacial acetic acid for 30 seconds at room temperature. Fig. 8.26c (x110) is a composite picture obtained by superposing these

oppositely matched etched faces. It is very clear from these photomicrographs that there is very little correspondence between the thermal and chemical pits. Although the sides of these pits are parallel to one another, one type (chemical pits) is asymmetrical whereas the other is symmetrical with respect to their centres. Further the point of maximum depth can be clearly recognised in case of chemical pits whereas this is not the case for thermal pits. Besides background micropitting is found for chemically etched surface only. Fig. 8.27b (x 90) shows a cleavage surface chemically etched by 1% HCl acid for 5 seconds at room temperature whereas its counterpart (fig. 8.27a; x 90) is a light profile picture obtained by thermally etching it at 520°C for 12 hrs. Fig. 8.27C, (x 90) is the composite picture of these oppositely matched faces. A group of circular pits such as A' on fig. 8.27a shows some correspondence with a group A of pentagonal pits. (fig. 8.27b) Except these pits the other features are not properly reflected on these etched surfaces. The photomicrographs [figs. 8.28a and 8.28b (x 180)] are oppositely matched faces simultaneously first thermally etched at 540°C for 12 hrs.; and then chemically etched by 0.4% glacial acetic acid for 30 seconds at room temperature. The thermal pits are bigger comparatively and more black than the chemical pits. The outer boundary of the thermal pits is created due to chemical etching. The figures exhibit

excellent correspondence for chemical, but a very poor correspondence for thermal, pits. Similarly there is no correspondence between the thermal and chemical pits on these figures. This is also shown clearly by the composite picture (fig. 8.28C, x 180) of these figures.

These observations suggest that the origin of thermal pits is different from that of chemical pits. In order to bring out subtle differences between these two types, localized plastic deformation was produced by percussion or indentation on the cleavage surfaces. They were then subsequently subjected to chemical and/or thermal etching. Figs. 8.29a and 8.29b (x 150) are the photomicrographs of cleavage surfaces indented by a diamond pyramidal indenter by identical load of 20 gms. and thermally and chemically etched respectively. The thermal etching has affected the indentation mark and the surrounding region consists of wings inclined with one another by producing pits, whereas the chemical etching produced by glacial acetic acid has revealed lines along which etch pits are formed. However the area surrounding this mark has remained practically unaffected.

It is clear from the above observations and comparison between chemical and thermal etching that thermal

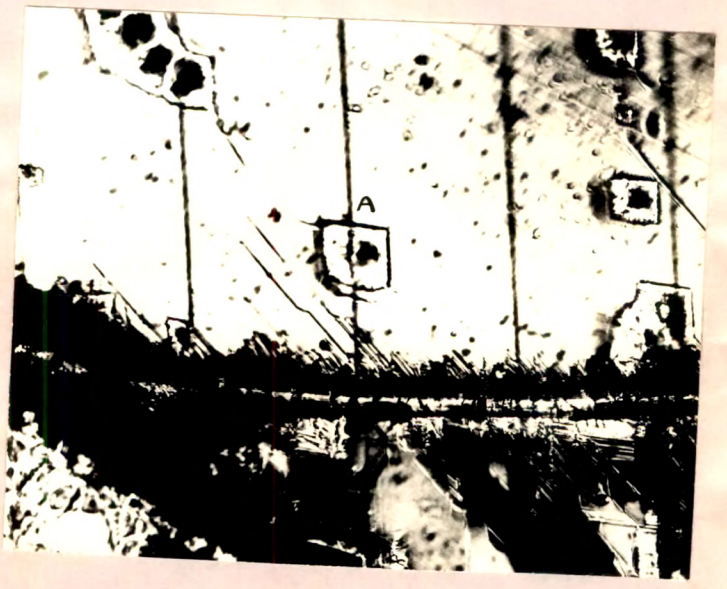

Fig. 8.18 (x150)

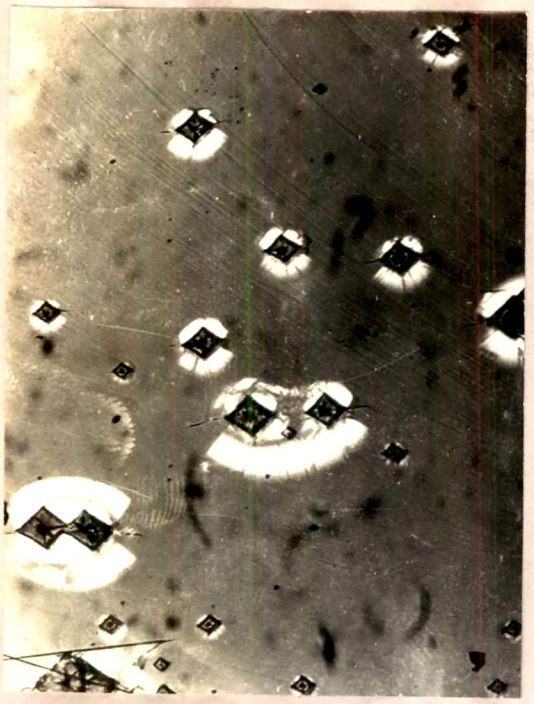

Fig. 8.19 (x90)

Fig. 8.20 (x90)

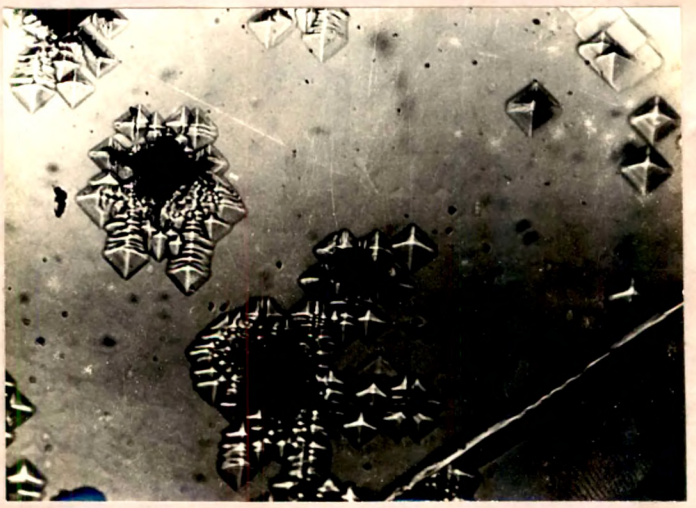

Fig. 8.21 (x120)

Fig. 8.22 (x100)

Fig. 8.23 (x 90)

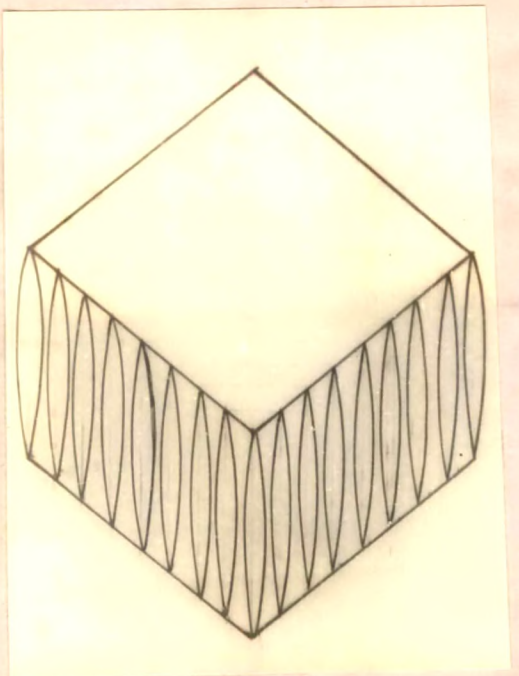

Fig. 8.24

Fig. 8.25a (x90)

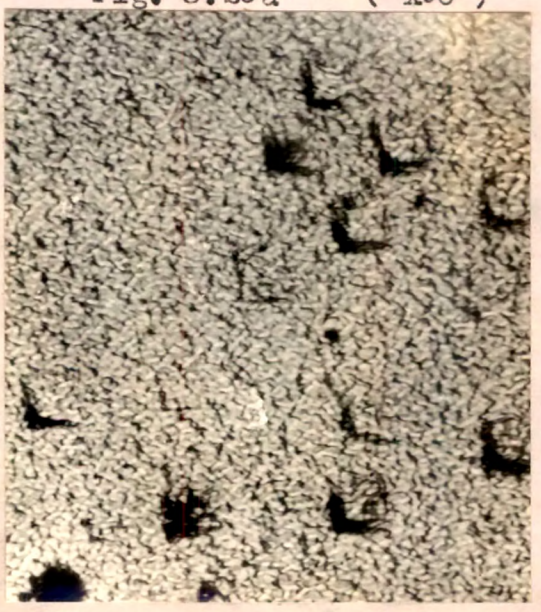

Fig. 8.25b (x90)

Fig. 8.26a (x110)

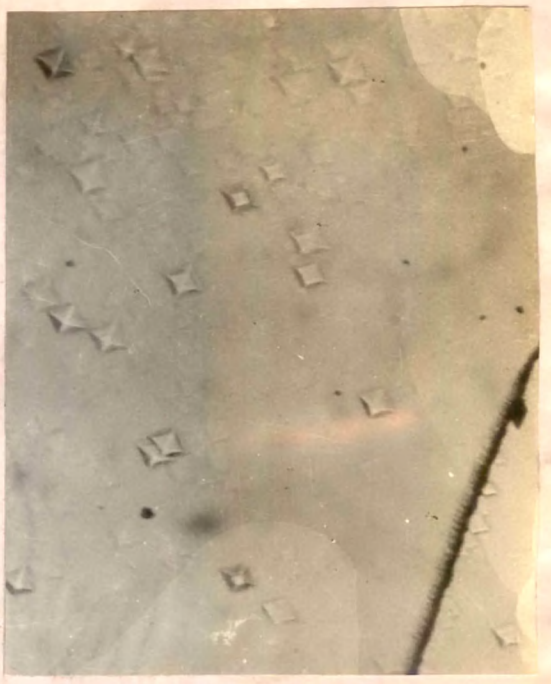

Fig. 8.26b (x110)

Fig. 8.26c (x110)

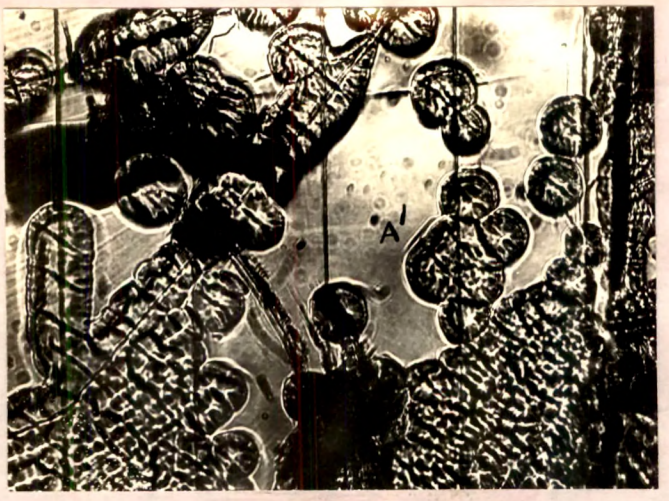

Fig. 8.27a (x 90)

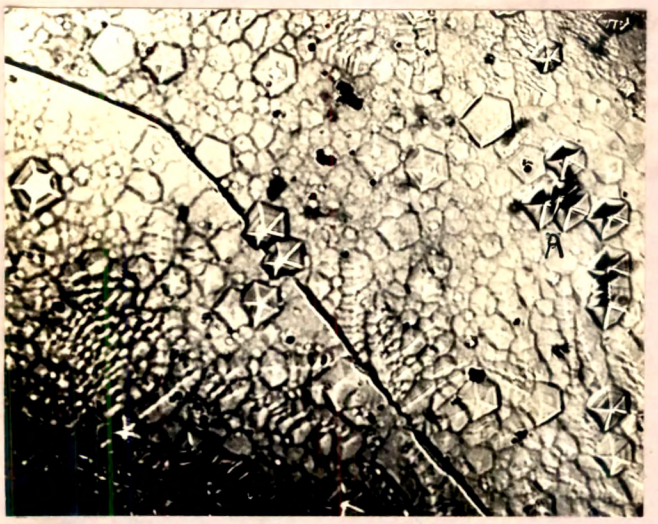

Fig. 8.27b (x 90)

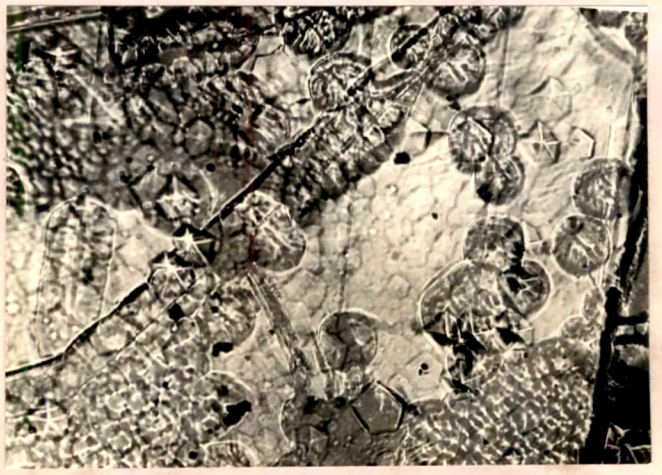

Fig. 8.27c (x90)

Fig. 8.28a (x180)

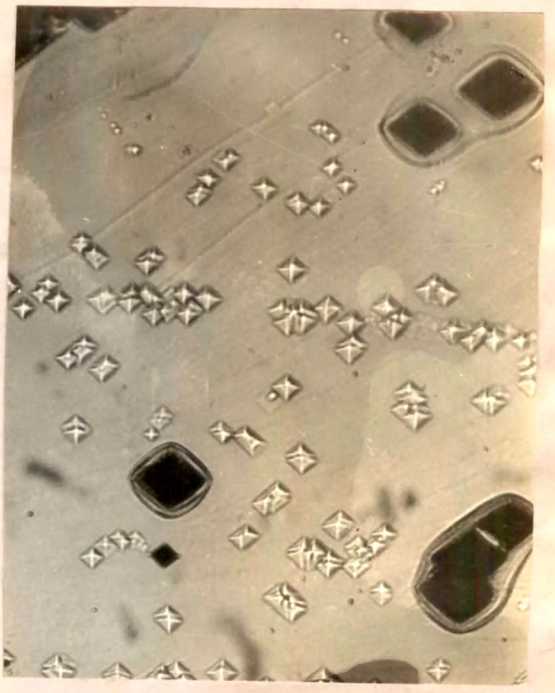

Fig. 8.28b (x180)

Fig. 8.28c (x 180)

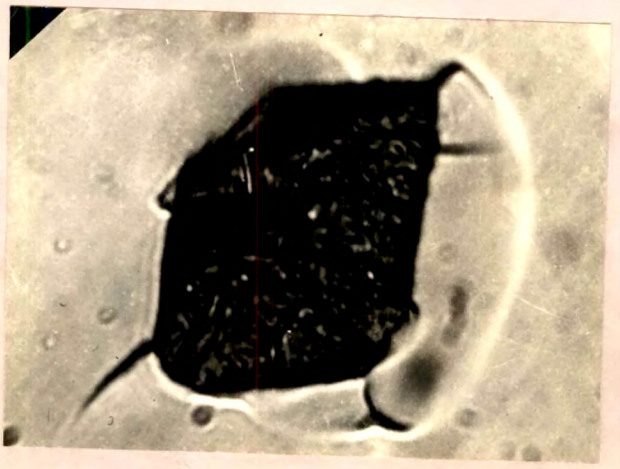

Fig. 8.29a (x150)

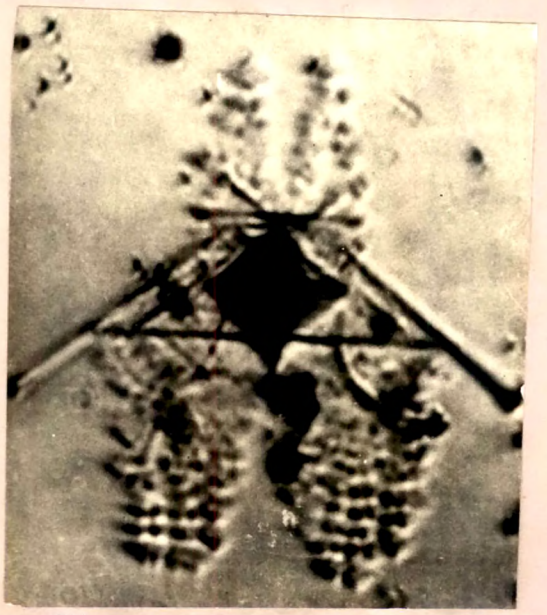

Fig. 8.29b (x150)

etch pits are different from chemical etch pits. There is one fundamental difference between thermal and chemical etching. The chemical etching is carried out at room temperature ($\sim 300^{\circ}K$) whereas the thermal etching takes place at a temperature of $\sim 800^{\circ}$ K. There is thus a very large significant difference between temperatures at which these processes are carried out. This difference directly affects the lattice points and imperfections in the crystal structure. The mobility of most of the imperfections changes with temperature.

When the crystal is kept at a constant higher temperature for a definite time, a momentary equilibrium is attained and the etching action preferentially starts at those defect points where the imperfections have diffused. As a result etch figures are produced. It is therefore evident that matching of thermally and chemically etched cleavage counterparts, is not likely to occur (figs.8.26a and 8.26b; 8.27a and 8.27b). Even the matching of thermally etched cleavage counterparts (figs. 8.9a and 8.9b; 8.10a and 8.10b) for this crystal is a remote possibility because it (crystal) is very soft and brittle and during the act of the cleavage and propagation of stress wave, uneven strained is likely to be created on the oppositely matched cleavage faces. This energy due to plastic deformation is locked at room temperature and is mostly released

at high temperatures. Since this is a statistical process, the matching of thermal etch figures will not take place. However, the successive etching of a cleavage surface under identical conditions of etching will produce thermal etch pits at unchanged locations on the surface. Hence the pit density will almost remain constant. (figs. 8.11a, 8.11b, 8.11c and 8.11d; 8.13a and 8.13b). It is also shown above that the density of thermal etch pits is always less than that of chemical etch pits. It is usually less by a factor of ten. This is also easy to understand because due to increased mobility of imperfedtions at high temperatures, some of them are likely to anneal out and/or annihilate at certain points, with a consequent reduction in the pit density.

It is observed that at a temperature of 793° K, the shape of thermal etch figure is circular and it progressively changes to elliptical and then rhombic outlines as the temperature for producing thermal etching is increased. This means that at lower temperature 793° K, the propagation of steps along different directions is completely isotropic. When the thermal energy is increased, the step propagation becomes anisotropic except for some prominent and important directions such as $[110]$, $[1\bar{1}0]$ and $\langle 100 \rangle$. Hence the pits with elliptical and rhombic

outlines are symmetrical about these directions. These are summarised below:-

VARIOUS SHAPES OF THERMAL ETCH PITS OBSERVED IN CALCITE CLEAVAGES.

Shape of etch pits	Temp. °C	Time of etching
Circular	520°	8 hrs.
Elliptical or hexagonal	530°	8 hrs.
Rhombic	540° to 560°	8 hrs.

Rhombic shape possesses the symmetry of the crystal surface. It is shown in the study of chemical etching of calcite cleavages that such shapes are produced by a particular range of concentration of an etchant (0.15 to 0.001 % for HCl and 0.5% to 0.005% for the $H\bar{A}C$). If the range is changed the pit shape changes. In the present work on thermal etching it should be possible to produce pits of different eccentricities and of different shapes also. However, the practical consideration precludes this observation, since thermal etching at temperatures higher than 813°K produces a large amount of dissociation of $CaCO_3$ with the formation of a thick layer of CaO on the surface which completely hinders its

microtopographical study. Similarly with the rhombic outline it is very difficult to determine the eccentricity by locating the position of the point of maximum depth because of the deposition of CaO within the thermal etch figures. This CaO can be removed to a certain extent by immersing the thermally etched crystal in water or by keeping it exposed to the atmosphere for a sufficiently long time. This partial removal is likely to reveal the pyramidal and flat bottomed character of the etch figure (figs. 8.5 and 8.6).

It is also reported that below certain thermal etch figures, lines with direction $[1\bar{1}0]$ are observed. This is rather unusual as compared to the chemical etch pits. However, it is possible to understand the production of these lines by considering the process of thermal etching. It is well known that when $CaCO_3$ (chemical formula for calcite) is raised to a high temperature, chemical dissociation takes place and as a result two products viz. CaO and CO_2 are formed. In the present case when the crystal is raised to a temperature of about 800°K, the thermal energy is sufficient at some places to break the bounds between CaO and CO_2 and release them to the atmosphere. However, in this process, if only one CO_2 molecule is involved, it will produce a unit pit too small

to be observed by an optical microscope, or even by an electron microscope. Hence, it is the cumulative effect of CO_2 molecules moving at the localized points producing impacts on them and trying to leave the surface, which will produce visible pits. Due to statistical distribution of energy at different points within a crystal at higher temperatures and due to continuous random and oscillatory motion of CO_2 molecules within localized points, a very mild percussion or indentation at these points will take place. Slip lines are usually formed when a percussion or indent mark is mechanically made on a cleavage face of calcite crystal. Slip lines should be produced in a similar way below some of the thermal etch figures. This is why a line with direction $[1\bar{1}0]$ is produced below thermal etch figures. However, below all thermal etch figures, such lines are not observed. This can be easily understood if one considers the dependence of production of slip lines on load when cleavage surface is indented. It is found from the study of microhardness that indentation marks with production of slip lines are obtained at a minimum load of about 5 gms, (see chapter 11). It is possible to correlate the energy corresponding to this value with the thermal energy. Assuming the motion of CO_2 molecules within localized points, to be random, the distribution of thermal energy would be radial. Hence the thermal energy per degree of freedom in a direction normal to the cleavage surface is $1/2\ KT$ where K

is Boltzmann's constant (1.38×10^{-16} erg/^{o}K) and T^{o}K is the temperature of the system. For a temperature of about 800^{o} K this energy is 0.5×10^{-13} ergs. The average surface area of thermal etch figures giving a line below them corresponding to this temperature is about 4×10^{-5} cm^2 and assuming a depth of one micron, the number of CO_2 molecules within this volume will be about 10^{13}. Hence the thermal energy for these molecules will be $\sim$ 0.5 ergs. For a 5 gm. load producing an indent mark with a depth of about one micron, the energy given to the surface is $5 \times 980 \times 10^{-4} \simeq$ 0.5 erg. This calculation suggests very clearly that the CO_2 molecules should generate enough pressure due to their collisions with the localized regions before leaving the surface. This produces a very mild percussion on the surface. This also shows that only those places where the pressure of CO_2 molecules is enough would be able to exhibit lines below the etch figures. Even with less pressure, percussion is produced on the cleavage surface but is not visible. However, it can be made visible by chemically etching the thermally etched cleavage surfaces (figs. 8.20 and 8.21). These figures show very clearly the formation of the tips of etch pits along direction [110] . Chemical etching of indent mark also produces such etch rows along [110] . Further the geometrical centre of thermal etch figures is not clearly visible because of the formation of CaO and the continuous random and oscillatory

motion of CO_2 molecules within the pits before leaving the surface. Further the impact of CO_2 molecules within the localized region generates transient short lived shock waves within the crystal and produces dislocations which are not thermally affected, when the same surface was thermally etched but were revealed on chemical etching. Incidently this also explains the constant density of thermal etch figures on multiple thermal etching. The generation of dislocations within the localized region after first etching makes this region highly susceptible to repeated thermal etching as compared to other regions on the surface. Hence the pit density almost remains constant. This also suggests that the thermal etch pits are not produced at dislocations meeting the surface.

This speculation is further strengthend by the fact that cleavage lines are not displaced during thermal etching. The controlled chemical dissolution of a crystal surface produces uniform etching of kinks and cleavage steps, thereby producing a displacement of the cleavage line parallel to itself. The thermal etching of calcite at higher temperature is unable to induce dissolution at every point on a cleavage step. However, it does induce enough mobility to a few atoms on the surface which migrate in a random way towards prominent positions (such as kinks) on the cleavage steps, which act as barriers for

them. Similarly there will also be a motion of a few atoms on the cleavage line towards the other parts of the surface at higher temperatures. This motion will be arrested by obstacles on the surface. As a result all these positions become amenable for easy thermal attack at higher temperatures with a consequent production of thermal etch figures. These obstacles are likely to be the impurity centres on the crystal surface. Thus the thermal etching of the cleavage surface of calcite in all probability produces etch pits at the impurity centres.

8.5 Conclusions:

(1) Thermal etch pits are formed in the short range of temperature from 520°C to 560°C.

(2) The shapes of thermal etch pits depend only upon the temperature at which the thermal etching is carried out.

(3) The cleavage lines donot shift on thermal etching of calcite cleavages.

(4) Thermal etch figures are characterised by (i) undefined centres, (ii) formation of minute network within them, (iii) protuding crack lines (sometimes) and (iv) formation of slip lines (sometimes). They are also

accompanied by the localized deformation as shown by the production of characteristic lines below them, air gaps near the pits and etch rows of chemical etch pits along definite crystallographic directions when the thermally etched crystal was chemically etched. These characteristics are not shown by chemical etch pits produced on a cleavage surface of calcite.

(5) The thermal etch figures are most likely to be at the impurity centres on the cleavage surfaces of calcite.