CHAPTER 4

CALCITE

I

Introduction:

In the entire mineral kingdom, next to quartz, no species are more abundant, wide spread or beautiful than calcite. Owing to its wide dissemination in nature and the unsurpassed beauty of its crystalline form, the calcite has been admired by men since remote antiquity. The mineral by virtue of the size, abundance and perfection of its crystals and its remarkable complexity of habit has attracted the attention of crystallographers and has played a prominent part in the history of mineralogy. The discovery of cleavage in calcite led to the establishment of crystallography as an exact science by Hauy and the discovery of double refraction in calcite led to the development of crystal optics. The invention of nicol prism which is made of calcite, has made possible the identification of fine grained mineral aggregates and rocks.

There is such a vast literature on calcite that it is very difficult to give a brief account of it. However, a humble effort is made on these pages to present briefly information on some of its features. Mellore (1982) and Dana and Ford (1951) have given a nice account of calcium carbonate.

Occurence:

It occurs in nature in several localities and ranges in character from pure transparent single crystals to large conglomerate masses which are quite opaque. It occurs:

(1) as a vein mineral often forming the gaggue of ores,

(2) as travertine, calcareous tufa and cane deposits (stalactites and stalagmites),

(3) as a biogenic mineral forming limestones, organisms, such as molluscas, brachiopads, corals and crinoids, contributing their shells or other hard parts.

(4) as a characteristic mineral in cavities of the basic igneous rocks, especially basalt and often associated with the zeolites. Iceland spar occurs in large cavities in basalt in iceland.

(5) as a prominent mineral in seams and cavities of sedimentary rocks, especially lime stone and also in lesser amounts as cementing material in other sedimentary rocks.

(6) as the principal constituent of metamorphic limestones which were formed from sedimentary limestones by heat and pressure. The metamorphic limestones aften contain other minerals like diopside etc.

(7) as a paramorph after aragonite. Calcite is the stable form of calcium carbonate under ordinary conditions.

Form and Habit:

Calcite is found in well defined crystals (often large in size) in crystalline crusts and druses, in cleavage masses, in various imitative forms, such as stalactitic, pisolitic and oolitic, in granular masses and sometimes in filerous or lamellar forms.

Calcite is the typical example of the hexagonal scalenohedral class of the hexagonal system, embracing some of the finest, largest and most abundant of all crystals. In number of forms and variety of their combinations, calcite is unsurpassed among minerals. Over 300 well-established forms, most of them scalenohedrons, are known, the rhombohedral being very frequently the dominant form in the combinations. Calcite, quartz, apatite, etc., are, among the minerals, most remarkable for their outstanding size. A calcite crystal from Stearling Bush, New York, weighed about 1000 lbs. and measured forty three inches from top to base.

Special names have been given to the more peculiar habits of calcite - for instance there are the so-called dog-tooth spar, nail-head spar, slate spar and satin spar. The latter is a fibrous variety with a silky lustre resembling the satin spar variety of gypsum - the latter is harder than the former. There are several varieties of minor importance which have been named after some admixture or the colour, use of locality, and do not generally indicate important structural or chemical differences. For example, dolomite calcite contains magnesium carbonate, and is known as mangano-calcite; ferro-calcite containing ferrous carbonate and calcite; cobalto-calcite (cobalt carbonate and calcite), zinco-calcite, plumbo-calcite etc.

Cleavage, Gliding and Twinning:

It has a perfect rhombohedral cleavage, a cleavage in three directions at oblique angles (74° 55') to each other, figure 27, and is susceptible to abrasion or scratching. The lines in the figure are the cleavage directions. The crystals cleave so readily that light blows will shatter them into fragments and as they are soft enough to be readily scratched with a knife, extreme care has to be exercised in handling them. There is often parting parallel to $\{0112\}$ and this is sometimes better developed than the cleavage itself. Some specimens of calcite show parting parallel to (0001).

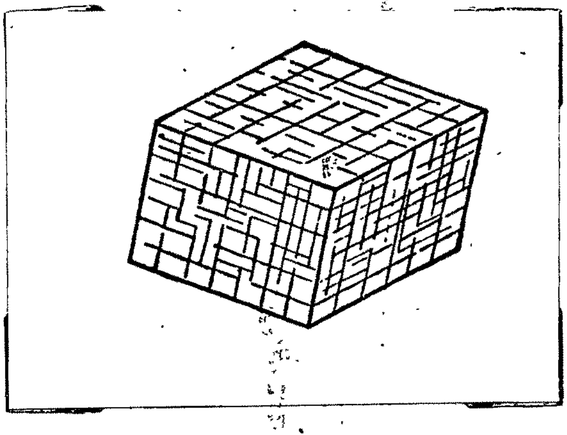


Fig 27

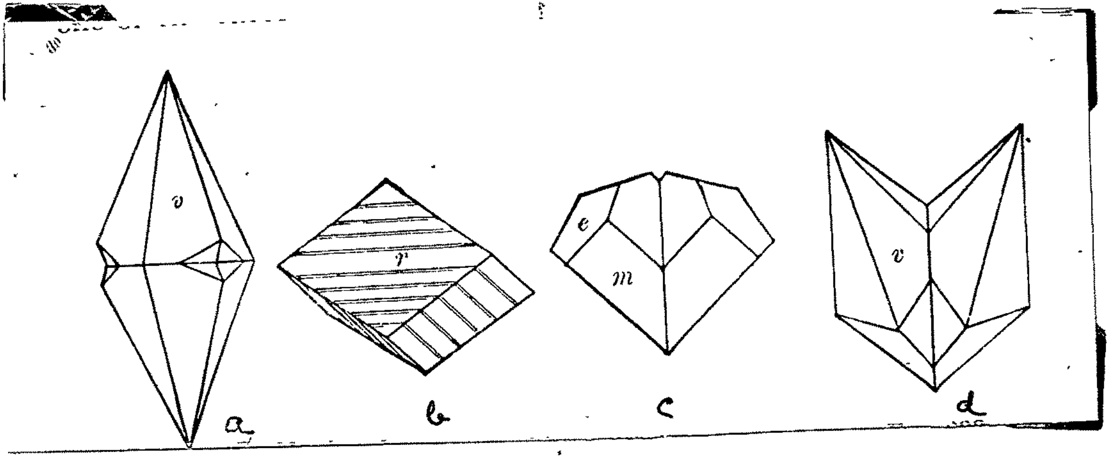


Fig 28

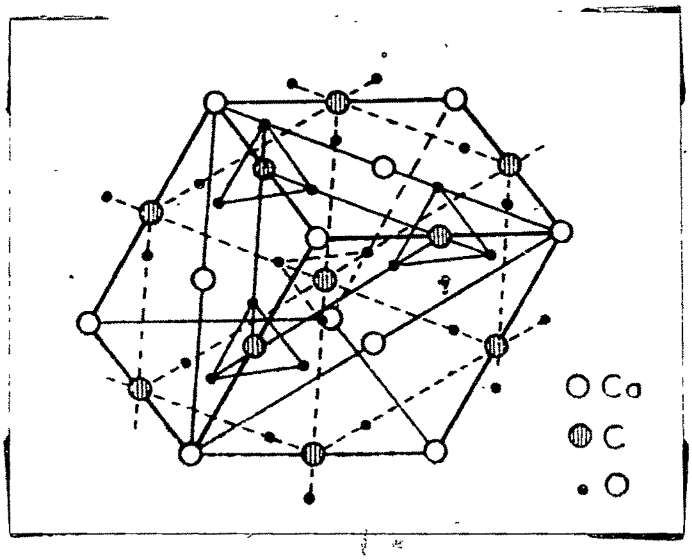


Fig 29

Fracture is conchoidal but difficult to produce, since it is brittle.

Twin gliding and translation gliding are known in calcite. The lines of intersection of sets of gliding planes may be marked by minute linear cavities - hollow canals and these may give rise to asterism in transmitted light.

Four twin laws are known in calcite. (1) Twin plane {0001} is common, with {0001} as the composition surface. Re-entrant angles are about the equator of the crystal except when bounded laterally by {1010} , the twinning then revealed by cleavage or by the apparent horizontal plane of symmetry. Figure 28a represents a scalenohedron twinned according to this law. (2) Twin plane {0112} is very common, with {0112} as composition face. Sometimes it is repeated and in simple growth twins often accompanied by a distortion through the extension of certain faces. It is also lamellar and produced by pressure either naturally as in marble or artificially. Figure 28b represents the often found polysynthetic twinning with striations parallel to the long diagonal. (3) Twin plane {1011} is uncommon with composition surface {1011} , sometimes repeated and in simple growth twins often heart shaped or accompanied by distortion of shape (which gradually results in suppressing the re-entrant angle). The twinned individuals have their axes nearly at right angles and also have a cleavage plane in common. Figure 28c represents the combination of m {1010} and {0112} twinned according to this law. The vertical axes of the two individuals are almost at right angles (4). Twin plane {0221}, is rare with composition plane {0221}. This is shown in figure 28d.

The crystal structure of calcite, figure 29, one of the earliest to be worked out by X-rays was described by W. L. Bragg in 1914, who later derived (1924) in the first work of its kind, the optical properties of both calcite and its polymorph aragonite in terms of the atomic structure. In the figure 29, are represented the Ca atoms by blank circles, carbon atoms by lined circles and oxygen atoms by black circles. The calcite lattice may be regarded (not quite strictly) as a deformed rock salt lattice. The latter is stood on a diagonal (looked at from above in the figure),all the Na^+ ions replaced by Ca^{++} ions and all the cl^- ions by CO_3^{--} ions (consisting of carbon atoms surrounded by a triangle of oxygen atoms in a plane at right angles to the diagonal, (i.e. the plane of the paper) as shown. Then, on account of the space occupied by these ions, the cube expands in a horizontal direction and forms the cleavage rhombohedral of calcite. Ca and C atoms are spaced at equal intervals along the crystal axes and each carbon is surrounded by three oxygen atoms forming the equilateral triagnle, carbon atom being at the centre of the triangle. In contrast to other XO_3 ions (e.g. ClO_3), the carbonate ion, CO_3^{--} is having a planar structure and the distances between the central carbon atoms and oxygen atoms and also the sides of the equilateral triangle formed by the oxygen atoms are respectively 1.23 A and 2.13 A.

Hardness on Moh's scale is 3 but varying somewhat on different planes and in different directions thereon; relatively soft on $\{0001\}$ and relatively hard on $\{1010\}$, especially in the vertical direction. For pure calcite, specific gravity is 2.7102 ± 0.0002 to 20°, but varies somewhat with the variation in composition. It is usually colourless and transparent or white when pure. The colour varies from white through nearly all colours to black widely with isomorphous substitution or with mechanical admixture. Accordingly, it is transparent, translucent and opaque. Lustre is virtuous, sometimes somewhat pearly indescent on cleavage surfaces or pearly on $\{0001\}$ in white or turbid crystals and tending towards greasy on conchoidal fracture surfaces. Many specimens are fluorescent and often also phosphorescent when excited by U.V. radiation,X-rays,cathode rays or sunlight,often also thermoluminescent. In transmitted light calcite is colourless,uniaxial negative with strong birefringence (0.172). Several workers have determined birefringence of calcite at several visible wavelengths and at different temperature (see for example Smart & Steel 1959). Although, calcite is normally white or colourless, but may have any colour, it is found colourless in thin sections.

Chemical Composition:

Calcite, a carbonate of divalent metal, has a hexagonal scalenohedral symmetry, belonging to the triagonal (or rhombohedral system). Its formula is $CaCO_3$ (CaO, 56 per cent, CO_2, 44.0 per cent). Natural calcite is very nearly pure calcium carbonate but Mn may proxy for Ca to at least about 70 atomic per cent; Pb, Mg or Fe to about 10 or 15 per cent. In rare cases, Zn, CO, Sr, or Ba may be present in small quantities.

Calcite is the thermodynaamically stable form of calcium carbonate at all pressures and temperatures so far investigated. The metastable polymorphs are knownm, aragonite and vaterite (also known as μ - calcite or vaterite-B). These polymorphs change irreversibly to calcite on being heated. A further polymorph of calcium carbonate, α-$CaCO_3$, elatolite, stable at high temps and pressure has been reported, but has not been verified.

Calcite by virtue of its relatively high chemical reactivity and ready solubility in carbonated waters is very commonly found replaced by or altered to other species. That is why it enters into a wide range of compositional variation through the substitution of other divalent cations for calcium. In these instances, the name calcite is applied as the species designation when calcium is the predominant cation in atomic per cent regardless of the total summation of the substituting elements e.g. cobalto-calcite.

The limits of variation in the indices of refraction specific gravity, unit cell dimensions and crystal angles accompanying variation in composition are not fully established, especially in the polycomponent systems.

The solubility of calcite in water is more a chemical property than a physical one. In pure water it is very sparingly soluble, but in water containing CO_2 (Carbonic acid) it dissolves to some extent and appears to form calcium bicarbonate. Its solubility in different solvents has attracted much attention on account of the bearing of the results on geological processes and on the nature of the soil solution.

Calcite and other forms of $CaCO_3$ can always be easily recognized by a hardness of 3 and by their easy solubility with brisk effervescence in cold dil. acids, properties possessed by no other common minerals resembling calcite.

Finest variety of calcite, known as Iceland spar is used in optical apparatus especially for the polarizing prisms of the polarizing microscope. Limestone which is more or less an impure form of calcium carbonate has tremendous industrial uses and surpasses all other minerals in the number and diversity of its uses. It is indispensable in most of the important industries and indeed there is scarcely a single large industry in which limestone or one of its products is not employed, directly or indirectly. An excellent account on calcium carbonate and its multifareous uses is given by Searle (1935) and a physico-chemical survey of high grade Indian limestones is done by Bijawat & Sastry (1957).

Growth of Calcite:

In the literature, are reported a number of methods of preparing calcite crystals in laboratory (see Mellore 1952). In such experiments, crystals composed of unit rhombohedrans $\{1011\}$ are often obtained, although rare in nature, and the habit can be varied by addition of foreign substances to the solution. In the present work, an attempt has been made to prepare crystals of calcite by the following methods.:-

(i) By slow diffusion of a soluble carbonate into a gel containing a calcium salt.

In this method, solutions of sodium carbonate (7 - 10 per cent) were allowed to run gently down the side of the beaker on to 40 - 50 per cent solution of calcium chloride taken in excess. The temperature of the solutions were definite and constant. Owing to the considerable differences of density at low temperatures, the solutions formed two layers, separated at low temperatures by a thin layer of gelatineous calcium carbonate, which served as a diffusion membrane. The diffusion was found to proceed mainly upwards, the calcium carbonate being enveloped by a solution of sodium chloride in a sodium carbonate medium. On carrying out the experiments at temperatures ranging from 20° to 36°C, the diffusion resulted in the formation of less voluminous crystalline product, containing no water of crystallization and giving no reaction with cobalt nitrate (Meigen's reaction) and found to be identical with calcite. Experiments carried out at higher temperatures (40°C and upwards) gave crystalline products, which judging by the gradual increase of (i) their reactivity with cobalt nitrate and (ii) the density, were mixtures ~~with~~ of calcite and aragonite, the proportion of calcite diminishing with rise of temperature.

On carrying out the experiments at 5° and allowing the diffusion to proceed at this temperature for twenty four hours, the upper layer and partly the lower was found to be filled with a thick growth of well-developed crystals, fairly long pyramidally pointed prisms, which were then examined under a microscope.

Crystals were also prepared by allowing the concentrated solution of calcium chloride to diffuse into a gel (agar - agar gel prepared in water with 0.5, 1, 2 per cent Concn.) containing dilute solution of sodium carbonate (Morse and Donnay, 1931). Calcium carbonate was precipitated, partially as spherules but some as well-formed individual crystals of calcite.

Instead of sodium carbonate solutions, ammonium carbonate solutions at a temperature higher than 40°C was used. The mixture resulted in a voluminous flocullent precipitate which if immediately filtered and dried, appears under the microscope to consist of opaque granules like grains of chalk, but if this same precipitate be left for some time in contact with the liquid from which it has been preci-pitated, it collects into microscopic crystals of calcite.

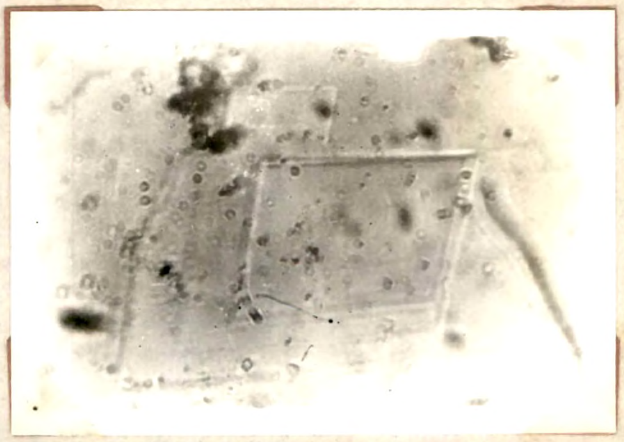
By the above methods, crystals big enough to be handled could not be obtained, but only small crystals were obtained which were studied under a high power microscope.

(ii) Two more methods have been tried to prepare crystals of calcite. In one of the methods, molten mixture of sodium and potassium carbonates (1:1) was prepared, in which a small amount of chalk or powdered calcite is added and kept at the mixture temperature for some time. The mixture is slowly cooled and the cold mass extracted with water. A granular mass is thereby obtained which forms calcite crystals on standing 24 hours in the cold. Similarly fused mixture of sodium and potassium chlorides with varying proportion was used in place of the fused mixture of carbonates. Inspite of the repeated attempts, the methods could not be operated upon with success. The reason for which is not yet quite clear.

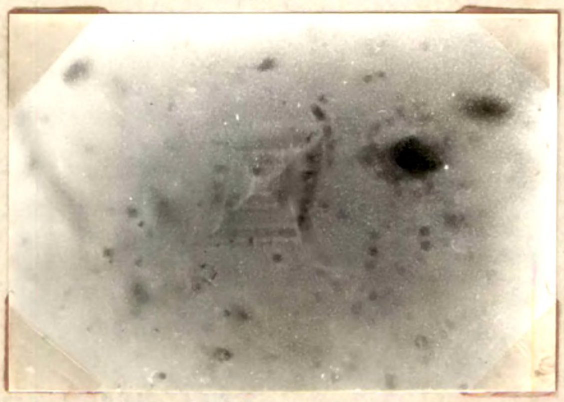
Fig. 30a and 30b (x 700) represent photomicrographs of calcite crystals obtained by the diffusion method. Fig. 30a shows the rhombohedral crystal with some layers, the layers being more visible in figure 30b. From a study of light profile on it, it is evident that the centre is an elevation. Such patterns are observed on most of the crystals and nothing definite can be said from such photomicrographs about the mode of their growth.

<u>Growth Study of Sodium Nitrate Crystals:</u>

Since sodium nitrate is isostructural with calcite and can be obtained easily in the form of crystals in the laboratory, it was decided to study the growth of sodium nitrate crystals from solution. Substances having analogous chemical formulae and atomic arrangement, and being composed of atoms or ions of comparable relative sizes and



(a)



(b)

Fig(30) x 700

polarizability are said to be isomorphous or homeomorphous. A brief glance on the properties of sodium nitrate crystals will show this (see for example Dana and Ford 1951).

In general the nitrates are anisodesmic structures and contains discrete $(NO_3)^-$ groups. These are of the same shape as the $(CO_3)^=$ groups and of only slightly smaller sizes. They are very similar to carbonates although in general less stable due to increased polarization of the coordinated oxygen atoms by the pentavalent Natom. The natural nitrates are few in number, relatively soluble and with the exception of soda niter, are of rare occurrence. Sodium nitrate occurs abundantly in some arid regions as in South America along the Chilean Coastal region. In fact, the extensive nitrate or saltpeter deposits characterized by the hot, dry climates of Chile, India, Peru and Bolivia (and only in regions of very low rainfall) were at one time considered the world's suppliers of sodium nitrate and some potassium nitrate. The sodium nitrate, variously referred to as soda nitre, cubic nitre, nitratine, saltpeter, etc., occurs, mixed with sodium chloride, sulphate etc., in beds up to six feet thick. The sodium nitrate forms 14 to 25 per cent of this caliche, as the material is usually termed. They owe their preservation due to the very dry climate of the area. Chemical composition of sodium nitrate, $NaNO_3$ is Na_2O 36.5 per cent and

NO_2 63.5 per cent.

Sodium nitrate belongs to hexagonal-scalenohedral class of the hexagonal system. Cell contents $Na_2\ (NO_3)_2$ are in the rhombohedtal units. It is structurally similar to calcite.

It crystallizes in the rhombohedrous with almost the same angles as the unit or cleavage rhombohedron of calcite. Variation of habit in artificial crystals was found to be due to impurities in the crystallizing solution. Otherwise, natural crystals are rhombohedra $\{1011\}$, rarely with modifying faces.

Cleavage, Gliding, and Twinning:

Cleavage $\{1011\}$ is perfect. Fracture is conchoidal but seldom observable. Twinning is observed to be (i) on $\{0112\}$ often elongated along the common rhombohedral edge; (ii) on $\{0001\}$ as penetration twins; (iii) on $\{0221\}$, sometimes as aggregates of three or six individuals; (iv) on $\{1011\}$, rare. Also twin gliding is observed as in calcite.

Its specific gravity varies from 2.24 to 2.29, hardness from 1.5 to 2. Optically it is uniaxial negative with birefringence 0.251. It is very deliquescent and is also studied as oriented over-growths upon various crystalline surfaces (see,for example Tscheimark 1882, Miigge 1902, Finch and whitemore 1939 etc.).

It is used extensively as a fertilizer, as the active ingradient of the dynamite "dopes" in commercial black powders and in the manufacture of potassium nitrate. Recent studies indicate that with adequate precautions for preventing its deliquescent property to function, good crystals (which can be prepared with some effort in the laboratory) may be used optically in place of calcite, say for polarizing prisms (Johnson 1943, West 1945, De Log~~e~~nchamp 1947).

Many workers have studied the growth of sodium nitrate crystals. Tilman (1951) studied a number of salts, including sodium nitrate, in the form of dendrites. He noted the increased tendency to dendritic crystallization by addition of gelatin or Agar-Agar. He further observed that dendrites are formed as a result of predominant growth of corners and are favoured by limited supply of the feeding solution. Optical and electron microscopy was used to study the growth of whiskers of sodium nitrate and other inorganic salts (Charsley and Rush 1958). From their study it is concluded that the growth is in two stages:- an initial linear growth and subsequent whisker thickening by two dimensional nucleation. This picture of whisker growth is fitting with the theory proposed by Sears (1957). Electron microscopic observations suggest that the mechanism of whisker thickening is responsible for the known decrease in strength with increasing diameter.

In the present work, pure sodium nitrate crystals for studying growth features were prepared by two methods: (i) from aqueous solution of sodium nitrate, and (ii) by cataphoresis (Hirans 1954).

In the first method pure sodium nitrate (BDH product) was dissolved in distilled water and the solutions were prepared with concentrations ranging from a low saturation to about 80 per cent saturations. From such a solution, a drop of it was placed on a pre-silvered microscope cover slip and was kept for drying for about twelve hours. It was then coated with a thinner layer of silver by the thermal evaporation technique described in chapter II and examined under a microscope. Several samples (about 150) obtained from solutions of various concentrations are thoroughly optically examined and representative results are reported below.

In the second method, a supersaturated solution of sodium nitrate at a temperature of about 50°C was prepared and in this solution are placed two platinum electrodes. A battery of storage cells, 4.2 V, a variable resistence and an ammeter are connected in series with the electrodes. A voltmeter is connected across the electrodes to measure the voltage between them. The beaker containing solution and electrodes is placed in a thermostat which was adjusted to a desired temperature; kept constant upto ± 0·1by a thermoregulator. The electrodes are separated by a known distance and at a suitable current density kept constant for a considerable time. A good number of crystals collected at the cathode as compared to those at the anode. The current was stopped and the crystals were carefully detached from the electrode and were fixed on a glass plate by means of Kronig's glass cement and the rhombohedral surfaces were then coated with a thick layer of silver and were observed under a microscope. After some experience it was found convenient to replace platinum electrodes by glass electrodes (of identical size and shape and coated with a silver film on one side only) placed in the solution so as to face each other. This avoids the cumbersome operation of detaching crystals as this had entailed the breaking of so many crystals during that process. By this method, mounting of the crystals on the glass plate was also avoided. The glass plate was silvered and the crystals - which are doubly silvered - could also be used for birefringence study.

By both the methods beautiful rhombohedral crystals were obtained. Microtopographical study of the several

Fig (31) × 360

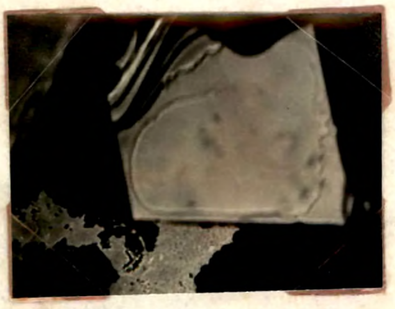


Fig.(32) × 360

Fig (33) × 360

crystal surfaces, thus prepared, are made and the results are reported below.

Figure 31 is a typical photomicrograph of one such crystal observed at high magnification (x 360). It shows a number of complete layers and a light profile on it has indicated that the central portion is the top. With oil immersion objective, it was seen that the central portion was found to be covered with very small shallow dots similar to those of B, C etc. in figure 34. Moreover, all the edges forming the complete layers are not straight but ziggag, indicative of the etching of the layers in the atmosphere. This appears to suggest that the central portion must have been attacked at a faster rate than the surroundings. This may then point to a case of the screw dislocations of opposite sign close to each other and equally developed. The resulting growth pattern will then consist of closed sheets, except at the centre which is fairly eaten away.

Figure 32 (x 360) shows a spiral of only one turn closely similar to that observed on beryl by Griffin (1950). No measurable shift of the light profile was observable. Since it consists of only a single turn, it is difficult to say conclusively to be a growth spiral.

Figure 33 (x 360) represents a photomicrograph of sodium nitrate crystal which consists of a half loop suggesting the existence of the well-known Frank-Read Source (1950). Visual inspection of the high magnification view of the same picture showed that the points A, B, C, D, E, F, themselves consist of a turn with a centre. No clear evidence of the existence of the Frank-Read Source could be obtained.

It should be noted that all the observations were made on dry crystals, the features of the photographs 32 & 33 are usually found when the atmosphere is known to contain a fairly good amount of moisture, while most of the crystals showed the features represented by the photomicrograph 31., When examined in a moderately dry weather. These facts lead to the inference that most of the growth features sought for are associated with the etch features on the crystals. This is supported by the fact that natural crystals are sparingly available and that too only in those regions which are having very dry, hot climate and having very low rainfall.

CLEAVAGE OF CALCITE

II

Introduction:

The cleavage of calcite has been studied by a number of workers (Bergmann 1733, Wulff 1920, Huggins 1923, Sieghbahn 1933). It has been established by multiple-beam-interference methods (Tolansky 1948) that cleavage of mica, calcite, selenite occurs in discrete steps, which are usually simple integral multiples of crystal lattice spacings. Tolansky and Khamsavi (1946a) have also shown from multiple-beam-interferometric studies that the step heights along a cleavage line were constant, and suggested some form of coarse mosaic block structure. Hookyaas (1951a,b) reviewed the theory of crystal cleavages with reference to calcite and other crystals. Pandya (1954) compared the counterparts obtained on cleaving a number of crystals including calcite and showed a perfect matching on the two counterparts. Zapffe and Worden (1949a) from their fractographic studies of metallic and non-metallic crystals have stated that one can find on the cleavage faces a detailed record of (i) the imperfection structure of the crystals (ii) the crystallographic mechanisms involved in deformation and fracture, (iii) the path of the cleavage traverse as influenced by the crystallographic properties subject to imperfection structure and local stress resolution and (iv) other phenomena relating to both intragranular and intergranular characteristics of the grain or crystal. They have defined two fundamental types of patterns on the cleavage surfaces (i) patterns determined by factors within the crystal and (ii) patterns determined by the nature of the stress. The later are the so-called hackle structures and they reveal the existence of a fracturing force as the cleavage traversed the matrix. The former are affected by the structural factors within the crystal and they are, therefore, of paramount importance in studying the crystal imperfection. Hence information regarding the texture (quality)of the crystal can be gained from the studies of type I patterns. In the present work, various methods have been used to produce cleavage surfaces in calcite rhombohedrons and the texture of the resulting cleavage surfaces is studied in detail. Information is thereby gathered regarding the structural factors within the crystal, which has thrown some light on the history of the growth of the crystal. The report is already accepted for publication elsewhere (Pandya & Pandya 1961).

Experimental Procedure:

Natural calcite crystals obtained from Gujarat

(Broach, Pavagarh, Chhota-udepur), Rajasthan and Ward's establishment, New York, were studied in the present investigation. The cleavage faces were produced by a number of different methods. Among them are the following.:-

(1) By the usual way i.e. by giving sharp blow with a hammer on a razor blade kept in contact with the crystal.

(2) By allowing a polished steel ball of known dimensions to fall from a measured height on to the rhombohedron crystal surfaces.

(3) By passing a very high electric discharge through the crystal.

(4) By immersing half the crystal in a solution of HCl and then taking out and very gently tapping on the line of demarcation made by the action of the solution on the crystal.

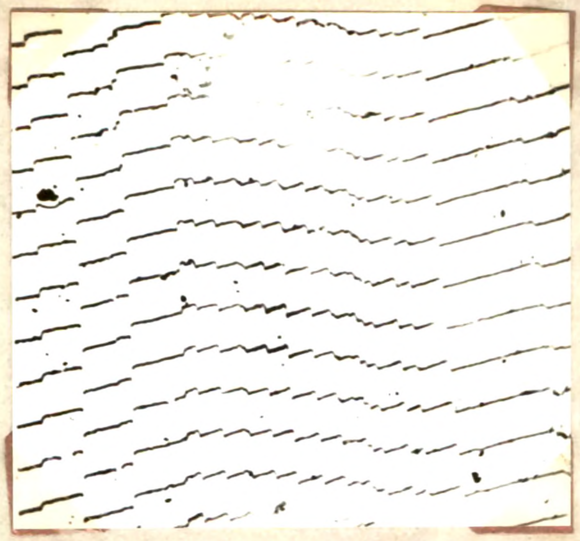
(5) By compressing the crystal between two firm supports.

All these methods gave rise to cleavage faces with a high degree of natural polish. In order to study the surfaces so obtained, under high powered microscope objectives such as oil immersion or 4 mm., a good deal of contrast is required. This ~~x~~ is achieved by coating the freshly cleaved surfaces with a thin layer of silver film, some 500A thick by vacuum deposition. It has been established that such a film perfectly contours the microstructure and of itself introduces no falsification. (Tolansky 1948, 1957). The cleavage surfaces thus prepared were examined by the techniques described in chapter 2.

Observations:

In all observations reported in this work, crystals were cleaved by any of the methods stated above and the two faces obtained by cleaving were silvered and observed under the microscope. Although, a number of crystals obtained from different localities have been studied the observations on only a few representative selections are reported. The crystals do not make an exhaustive collection from all over the world, but whatever were easily available have been investigated. A preliminary survey soon showed that the crystals could be grouped according to the texture of the cleavage faces. Crystals obtained from Chhota-Udepur (Gujarat State), Rajasthan and Ward's establishment, N.Y., fall in one group, hereafter named A, whereas those from Pavagarh and Broach (both Gujarat State) fall in the other group named B.

Irrespective of the method of producing cleavage



Fig(34) x30

Fig(35) x170

Fig(36) x170

all the crystals showed the following features.

Familiar cleavage lines distributed in direction starting from the edge where cleavage begins with steps of widths varying from 0.005 to 0.01 mm and with step heights upto 1600 A. The areas between the cleavage lines are molecularly flat as seen from multiple beam Fizean fringes Step heights along a cleavage line usually remain constant (Fig. 34x70). Some cleavage lines are straight, some curved and some converging in pairs. One important point in the case of V-shaped cleavage lines terminating in surface is that the steps at the elevated and depressed regions between the lines are not always identical and such lines are not as frequent as curved or straight cleavage lines. These lines may be due to differential gliding in the act of cleavage as suggested by Pandya (1954).

Figure(36) x 170 represents a photomicrograph of an isolated cleavage surface obtained by the usual way. It resembles the river systems characteristic of both amorphous and crystalline substances (Zapffe & Wordan 1949a, Keis et al 1950). It is found that the pattern on the counterpart (not shown) is identical with the above pattern fig.36, thereby showing the exact matching.

Figure 36 x 170 shows a cleavage system obtained by cleaving the crystal by the method (2). It shows cleavage steps with a number of parallel cleavage lines, revealing the mosaic character of the crystal since each element of the mosaic appears to cleave along its own (100). Observation of the corresponding pattern on the counterpart shows the exact matching.

Figure (37) x 170 represents a photomicrograph of a cleavage pattern observed on a cleavage surface produced by the method (3). The surface is covered by a number of cleavage lines which are approximately parallel. The photomicrographs suggest the lamellar structure of calcite, the lines being traces of the planes dividing lamellae of more perfect crystals. Molecularly flat area over a cleavage face shows the existence of perfect crystal block in that part of the crystal.

Figures (38,39) x 170 shows the matched areas on cleavage faces produced by the method (5). A system of river lines from one side breaks out from a line boundary and subsequently coalesces into a fewer number of more prominent cleavage lines. These patterns appear to have close resemblance to cleavage systems observed by Zapffe and worden (1949b) in ammonium dihydrogen phosphate. Several workers (Fisher 1954, Pratt 1954, Gilman 1955 and Hirsch 1956) suggested that such groups of river lines might be associated with the presence of a twist boundary between adjacent sub-grains of the crystal, each line being initiated by a screw dislocation emerging in the surface. Figures (40a, b) x 170 shows another matched pair. It is therefore clear from ~~all these observations~~ [illegible] all these observations that there is a perfect correspondence between the cleavage patterns observed on both the matched surfaces.

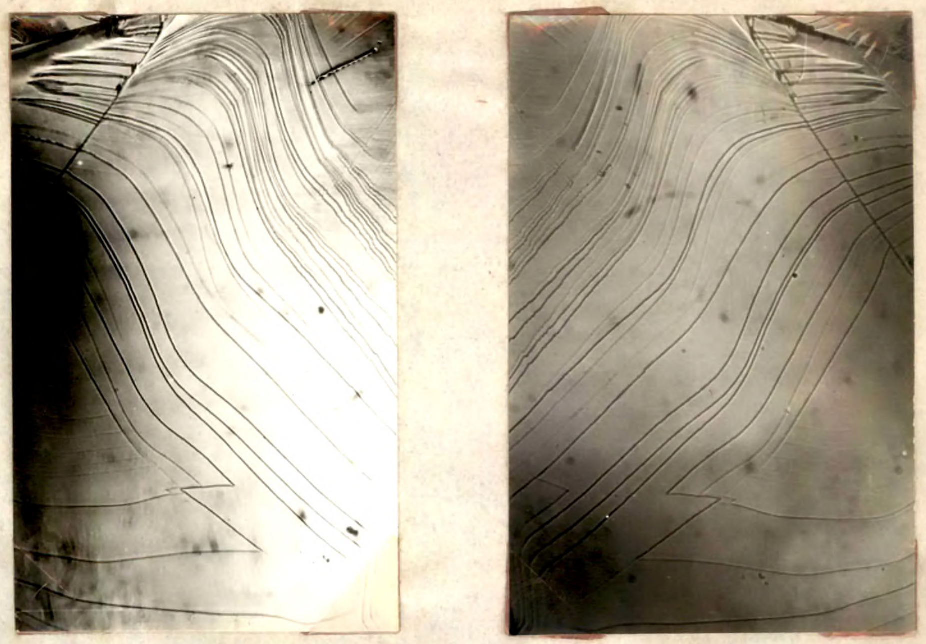
The cleavage faces produced by compression showed an entirely rare feature which is related to the fracturing force. The cleavage faces of all the crystals showed a number of lines parallel to the longer diagonal of the rhombic face figure (41) x 12. The observations with a light profile indicate that running of the profile over this striated face is sharp with a rise, but not zig-zag. These lines have crystallographic directions $\{110\}$. This is determined with reference to the percussion figure on the cleavage rhombohedron surface of calcite.

Since the percussion mark is an important characteristic of the crystal face on which it is produced, a brief description of it will not be out of place here. A sharp, quick, blow with a dull conical point on a crystal face develops a figure which is a characteristic property of

Fig (37) X 170

Fig (38) X 170

Fig (39) X 170



(a) (b)

Fig (40) ×170

Fig (42) ×12

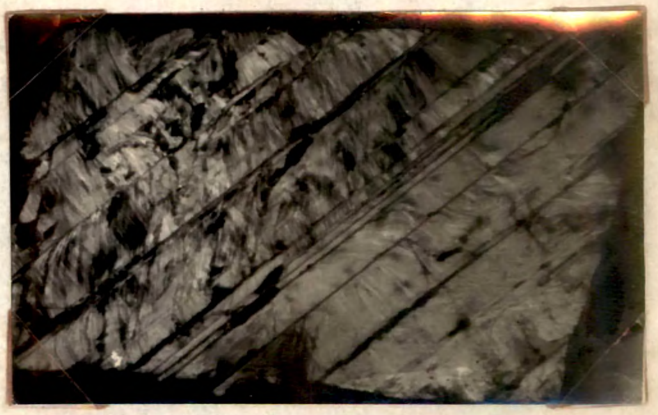


Fig (41) ×12

the crystal itself and is related both to the structure of the crystal and to the orientation of the face with respect to the impact point. The figure so produced is called the percussion figure and is of much help in determining the orientation of the crystal. By employing two beam interferometry, Raman (1959) made an optical study of the percussion figure on various crystals.

On a freshly cleaved surface of calcite is produced the percussion figure by the above method, figure (42) x 12. It can also be produced either by allowing a polished steel ball of appropriately chosen size to fall from a known height or by passing heavy spark from an induction coil, on to the crystal face. In the latter case etching is necessary to reveal the figure.

An examination of the percussion figure reveals that the characteristic cleavages of calcite play an important role in determining the result of impact. It is observed that on either side of the area of contact between the points of impact and the crystal face, two cleavages making an acute angle with each other develop and extend outwards from the edges of that area. These cleavages are clearly visible on the face of the crystal and they sharply limit the area within which the fracture develops and spreads inwards. The spreading of the shock wave generated by the impact of the polished steel ball is clearly visible in figure (42a) x 170. Another interesting feature is the appearance of a whole series of parallel lines outside the region of contact and only on one side of it. These lines are equally inclined to the two sets of cleavages and are parallel to the longer diagonal of the surface. They may be explained as being due to glide occuring within the crystal along the direction of rhombohedral edge. These lines are also parallel to the lines observed on the cleavage surfaces produced by compression and to those observed on the cleavage surfaces of crystals (Pavagarh and Broach) produced by any of the first four methods mentioned above. This is shown in Figure (42b) x 170. Furthermore, on some crystals from Pavagarh, a number of lines are revealed by etching, one set of which is parallel to the series of lines observed in the percussion figure. The lines AB observed on cleaved crystals from Pavagarh & Broach are parallel to the series of lines generated by the percussion. The lines AB are identified in the present investigation to be the twin lines as they are found all over the crystal and moreover they always reappear on etching the mechanically polished cleavage surface whereas the lines produced by the percussion disappear on mechanically polishing the specimen and are never observed on subsequent etching.

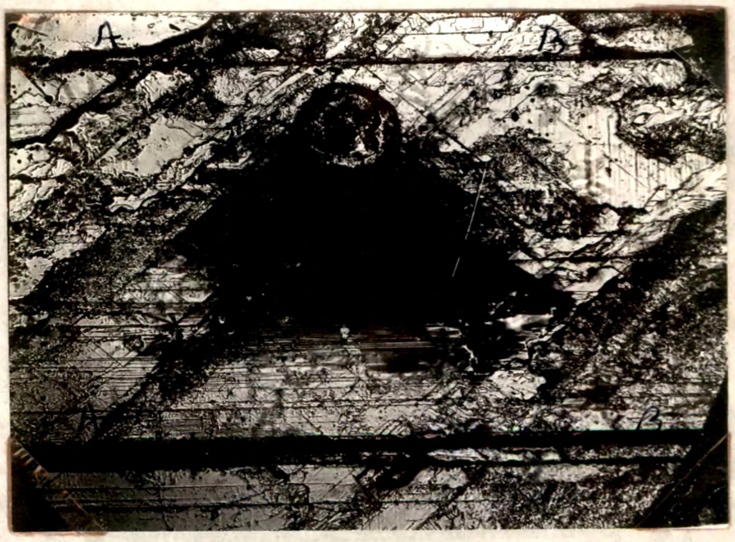
The whole percussion figure with the point of impact as the vertex of the triangle formed by the two cleavages and the series of lines is oriented oppositely with respect to the corner of the crystal where the three obtuse angles meet. Figure 42 x 12 shows the figure with the whole crystal, A is the point where the three edges meet making obtuse angles. Figure 43 x 170 shows the percussion figure which is lightly etched by a concentrated solution of sodium sulfate. This should be compared with figure 42a or b On the unetched virgin surface lines have not come out clearly whereas the light etching brings out the glide lines very nicely.

The study of crystals belonging to group B showed features which have not been reported before. On cleaving the crystals by any of the methods described above, the lines mentioned above were obtained on both the counterparts and in addition a number of lines parallel to the edges of the crystal also appear. These lines, parallel to the edges of the crystals, correspond to cleavage directions of the crystal. A typical photomicrograph is shown in figure 44 x 170. There is complete correspondence in the occurence of the lines on the matched faces and these lines also run continuous on all the faces of the crystal. It can be reasonably argued, therefore, that they are not due to the fracturing force used in the act of cleavage described by Zapffe and Worden (1949a).

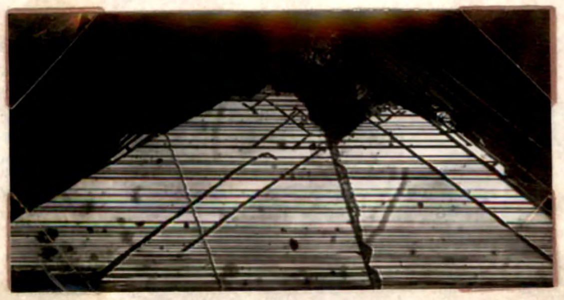
To study the effect of deformation, the crystal was sheared and then cleaved, the resulting cleavage patterns were then studied in detail. This pattern and the one observed on cleavage surfaces produced by compression have close resemblance in that both produce twins. Figure (45a, b) x 360 show phase contrast photomicrographs of a matched region of the sheared crystal cleaved by any of the first ~~form~~ four methods mentioned above. A line boundary cutting across the river system is seen very clearly. The line has been identified as a twin line. Moreover, the matching of the counterparts is also exact, which is also of some significance. Only at those places near the tapped point from where the cleavage proceeds, the matching is not very exact, but at all other places the matching is perfect suggesting that plastic deformation has not occurred at these places.

One more typical phase contrast picture of the cleaved crystal previously treated as mentioned above, is represented in figure (46) x 360. The black, horizontal and somewhat thick line is a twin line and the markings below it are parallel to the edges of the crystal. It should be noted that this is a pattern typical of the cleaage

Fig(42a) x170

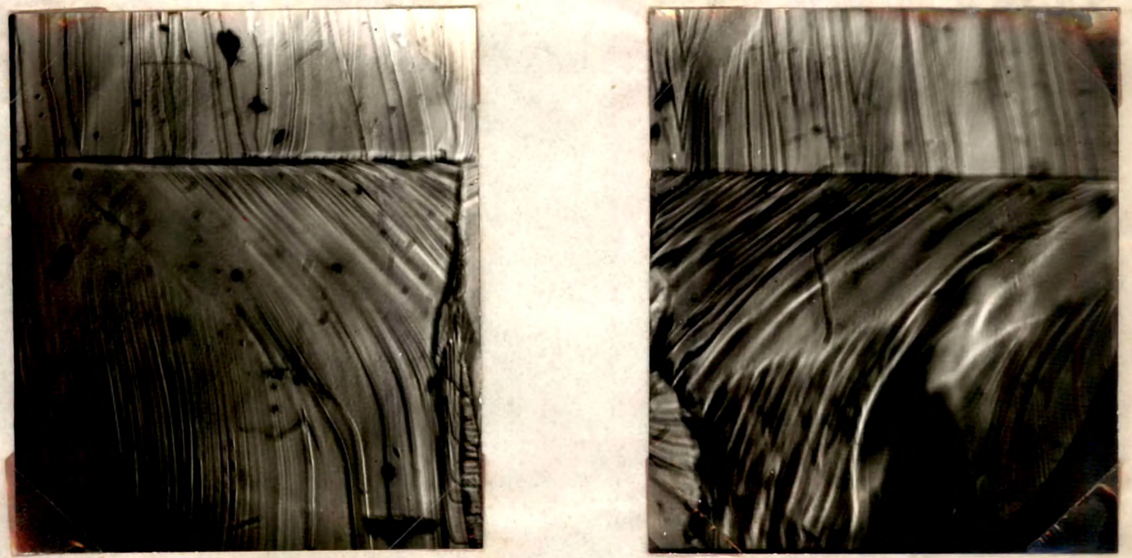


Fig(42b) x170



Fig(43) x170

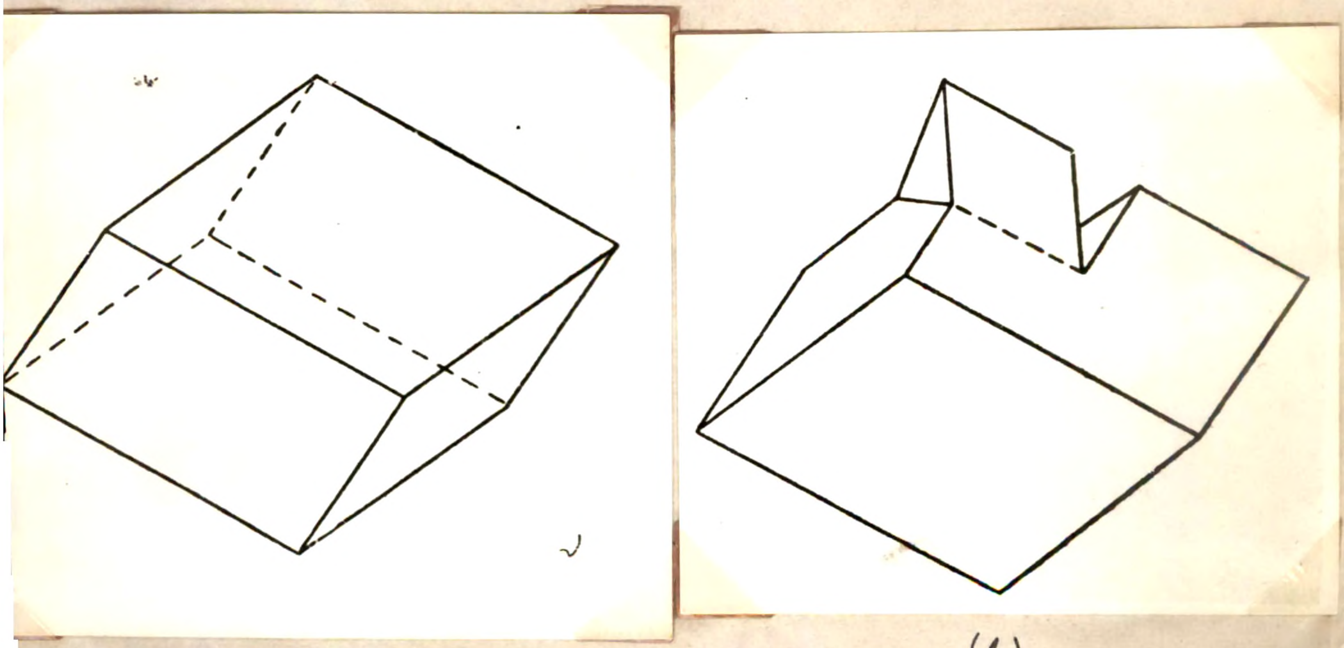
Fig (44) ×170



(a) (b)

Fig (45) ×360

Fig (46) × 360



(a) (b)

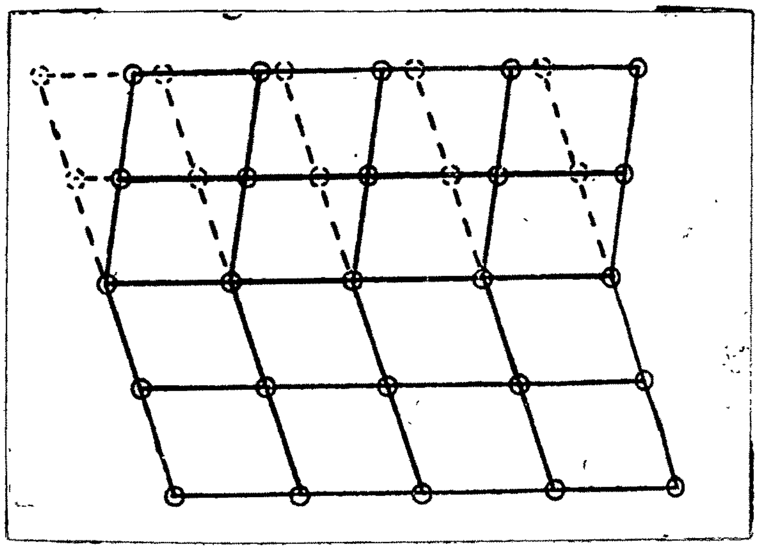
Fig 47

surface of sheared crystals. Such patterns are not usually and distinctly observed on the crystals which were cleaved by any of the first four methods listed above.

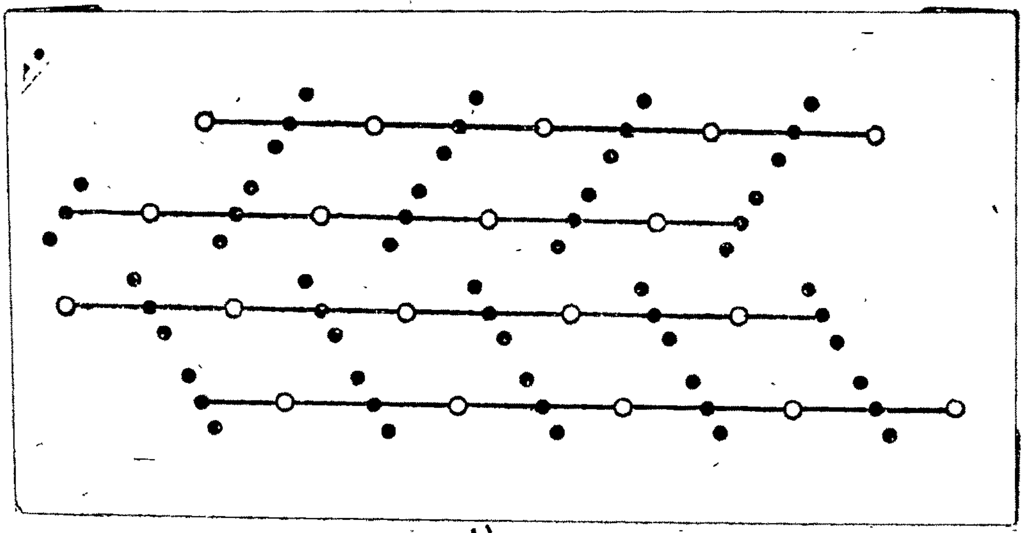
Discussion and Results:

The features described on crystals belonging to group A indicate that most of the features are due to the nature of the fracturing stress and the compression method of cleavage clearly shows that the characteristic pattern is due to the nature of force. The lines or striations that are observed parallel to the longer diagonal in case of crystal cleavages obtained by compression method are only superficial. They are the well-known glide-twinning striations in calcite described in text-book on mineralogy (Rogers 1937).

The phenomenon of twin-gl~~i~~iding of pressure gliding was first recognised by Brewster in 1815 in calcite, and the glide was first experimentally affected by Reusch in 1867 in the same species. This phenomenon - the glide twinning of calcite by mechanical stress - was investigated by many workers (see for example Reusch 1867, Baumhauer 1879, Johnsen 1902, Yakutovich and Yakovleva 1935; Stepanev 1947, etc.). Figure 47a shows the sketch of the rhombohedron crystal of calcite. If such a rhomb is pressed with a sharp knife (fig.47b) on the polar edge, the crystal divides, one part



(c)



(d)

Fig 47

turning out at an opposite angle, but still remaining attached, and giving rise to the formation of twin. The generative process is clearly a glide of definite amount, with the glide plane horizontal and the glide direction the rhombohedral edge. The phenomenon is often called "shift" since it differs from 'glide' or 'slip' in taking place discontinuously to a limited extent, it being supposed that the displacement between neighbouring lattice planes is less than the lattice period (figure 47c). It does not occur with such crystals as rocksalt, which undergo continuous deformation. Calcite and rocksalt have the same structure, so far one can compare the cl' of the NaCl with the radical CO_3 in calcite, $CaCO_3$. The shift has been explained (Ewald, Posch and Prandtl, Physics of Solids and Fluids, 1930, 145) as due to the interlocking, in one or other of two extreme positions, of the lattice planes of the calcite owing to the extended nature of the CO_3 group (figure 47d), whereas in rocksalt the spherical cl ions offer no positions for such interlock. Frank and Van der Merwe (1949) has also given an explanation of this phenomenon on the dislocation theory.

A quick and simple method of distinguishing twinned crystals from untwinned one is given by La~~y~~doo and Myers (1951). If the crystals show repeated twinning, the bands of bright rainbow colours appear when it is viewed by transmitted light at an oblique angle. Such bands may also be due to air films in incipient fractures. In some twinned crystals, these colour effects may not be evident. In such cases the presence of defects due to twinning may be readily tested. If a small clearly defined dot is placed on a piece of white paper and a cleavage fragment of calcite placed over the dot, two dots will ordinarily appear a short distance apart due to double refraction. If, however, the crystal is moved slowly back and forth and the dots observed closely, additional indistinct dots may also appear in certain positions. Such a phenomenon is an indication of twinning and crystal fragments that exhibit it are defective for optical purposes, unless the pieces ~~that constitute the pieces~~ which constitute the twinned form are large enough so that optical parts may be cut from them without passing beyond the plane along which such pieces are united. In searching for any such evidence of twinning observations should not be confined to one direction but should be made in the three principal directions through the three opposite pairs of parallel faces.

Gilman (1957) and Forty (1957) have shown that the stress around the tip of a cleavage crack in crystalline materials may initiate plastic flow and produce dislocations. From the present work, it appears very unlikely that the act of cleavage has introduced into the crystal any plastic -

deformation. Hence the surface pattern will be determined by the defects and dislocations already present in the crystal prior to cleavage.

The markings on the opposite cleavage faces of zinc single crystals are not completely reflected, and this is usually taken as evidence that plastic deformation has occured after cleavage (Pratt 1953). The present study, however, has demonstrated the complete matching of the counterparts, so that no plastic deformation has occured after cleavage. During the process of cleavage, the faster elements - the cleavage cracks - shoot ahead and stop the slower ones. This may ~~a~~ then account for the appearance of river patterns on the cleaved surfaces.

The crystallographic nature of the lines observed on the crystals of group B suggest that they are due to texture within the crystal and may be perhaps related in some way to the history of the growth of the crystal. These lines always appear on repeated cleaving of the crystal. The lines are exactly similar to these obtained in group A by compression only, viz., parallel to the longer diagonal which may be due to twinning during the growth. If the lines are removed by polishing, they reappear on subsequent etching. The V.shaped lines terminating in the surface are probably due to dislocations introduced on cleaving. The lines parallel to the edges of the crystal face are also supporting the view that small blocks are stacked one over the other in all the three dimensions with some misorientation giving the lines, and mosaic block structure (Tolansky 1946) can thus be explained. Pandya and Pandya (1960) also point to the mosaic block structure of crystals supporting the conclusions drawn from this study.

Regarding the origin of twin lines observed on the cleaved crystals of group B, one must consider the following points.:-

(i) When crystals capable of twinning separate from a solution or magma, supersaturation favours the deposition of twins as opposed to single crystals (Johnsen 1907, Buerger 1945, Deicha 1949).

(ii) According to Scacchi (quoted by Johnsen 1907) substances which do not by themselves readily form twins can sometimes be made to do so by adding specific impurities, and a twinned nuclei, once established grow faster than do single crystal nuclei.

(iii) Experiments on polycrystalline calcite deformed at 10000 atmospheric pressures (Griggs and Miller 1951) indicate that application of high pressure facilitates more twinning. Turner et al (1954) have shown from compression tests on calcite that twin-gliding on $\{0112\}$ is the dominant mechanism of deformation at all temperatures where orientation permits.

(iv) Powerful concentration of stress can create a twin. Pile-up of slip dislocations can produce the required stress concentration (Bilbey and Enthwisle 1954).

It is clear from all these observations that lamellar (or polysynthetic) twins must have been formed either at the beginning of the growth of the crystal or somewhat at a later stage probably due to unequal development of stress during crystallization. Mugge (1888) has supposed that all such twins are mechanical in origin, even though many of these twin lines cannot be produced by artificial mechanical means. On the other hand Deicha's observations on barium chloride crystals (1949) show that lamellar twins can be made in the laboratory by separation from supersaturated solutions. Equally true is the fact that this crystal can twin mechanically also. It is, therefore, difficult to understand why mechanical twins of appreciable size should be formed under such peaceful conditions of crystallization. It was suggested (Prof. A.R. Verma, Private Discussion) that the polysynthetic twins observed in the present work might be Neumann bands, which are now known (Kelly 1953, Paxton 1953) to be mechanical twins.

Inspite of the successful development of the theory of crystal growth by spiral mechanism and its ability to predict numerous observed features of crystal topography (Frank 1949, Verma 1953), it does not appear to have been extended to a consideration of the growth of twinned crystals, nor have growth spirals been searched for on twinned crystals. Very few observations appear to have been reported on growth of twinned crystals from the above point of view. Rae and Robinson (1954) have studied growth twins in lithium sulphate, and found that growth spirals sometimes extended from the tip of a thin twin lamellar, the lamella and the spiral had associated growth steps of the same height. Many more observations are needed before coming to a final conclusion.

It is with this idea that the present author had tried to grow single crystals of calcite in the laboratory by various methods, but inspite of repeated attempts, the author could not obtain macroscopic crystals big enough to handle them for performing experiments to decide the origin of the polysynthetic twinning. It is also known that heat and pressure are considered to be important factors in the growth of calcite crystals. This observation coupled with the failure to obtain big crystals comparable to those found in nature tends to suggest that the polysynthetic twins observed on cleaved crystals of group B might be probably mechanical in origin.

ETCHING OF CALCITE

III

Introduction:

Since calcite is one of the commonest and most widely distributed of all minerals, many workers have reported the etching of calcite crystals. It is, therefore, worthwhile to review briefly the earlier work on etching of calcite. Many authors studied the etching of calcite from the crystallographic point of view. (Ichikowa 1916, Honess 1918, Goldschmidt and Porter 1924, Himmel and Kleber 1937, Bods 1943). Goldschmidt and Porter (1924), reported the etching of calcite spheres by dilute hydrochloric acid. For producing etch figures, Himmel and Kleber (1937) used organic acids as etchants, Boos etched the crystals by HNO_3, H_2SO_4, dl-, d- and l- tartaric acids whereas Honess (1918) made use of HNO_3, HCl and acetic acids. Ichikowa reported the study of calcite and other crystals etched in nature.

Optically active and inactive etchants produce on the cleavage faces of calcite etch pits having different symmetry (Royer 1929, 1930, Novak 1935, Honess and Jones 1937, Kleber 1940). Lowering of the symmetry of etch figures was observed by the use of optically active etchants. This was found even when a small amount of optically active etchant (Novak 1935) was present. Geometrical symmetry of crystals is always revealed by etch figures produced by optically inactive etchants. This is in accordance with Friedel's conclusion that the form of etch figures is determined by the symmetry of the solution as well as that of the crystal.

Electron microscopic investigation of calcite etched by a number of etchants (HNO_3, HCl, Acetic acid) is made by Pfeffer Korn (1950 a,b, 1951) and PfefferKorn and Westermann (1952). The study (1950a) disclosed the preferential etching of the lattice where it was disturbed, giving an indication of the chemical and physical inhomageneuties of the crystals.

The physical appearance and the behaviour towards etching with a 0.01 per cent A_cOH of surface scratches on calcite faces made with diamond points under different loads (Puchegger 1952) show that with loads of less than 30 mg., grooves without microscopic fractures can be made; the displaced matter behaves as an amorphous substance, its rate of solution in acid is accelerated. For higher loads typical fractures appear and are related to the orientation of the face and the scratch. On etching, grooves with rib structure similar to but more pronounced than that reported above and parallel to and along the diagonals of cleavage faces were observed by Watts (1959) and the present author. On rhombohedral cleavage surfaces of calcite, Watts(1959) reported the etch pits produced by one per cent nitric acid, which were of three types, three sided, four-sided and five sided etch pits. In the present investigation nitric acid was also used as one of the etchants. The shape of the etch pits changes from the 3-sided etch pit to five-sided pit by using nitric acid (A.R.quality) appropriately diluted with water. But with one dilution, most of the etch pits are of the same shape. Stanley (1959) observed similar shapes of etch pits produced by 10 per cent HCl on surfaces parallel to cleavage planes and to optic axis of the crystal and examined them under a surface finish interference microscope. Pits obtained by HCl on a surface parallel to the optic axis were boat shaped. In the present investigation such boat-shaped pits were produced by the action of strong solutions of sodium hydroxide, potassium hydroxide (or their mixture) and also by saturated solution of ammonium fluoride at room temperature on the cleavage surfaces of calcite crystals. This shows that with the same etchant, if the surfaces are crystallographically different, etch figures vary in shape and also with the same crystal face, different etchants produce etch pits of different shapes.

The present author was interested in calcite chiefly because of its plastic properties, the mechanical twinning well-known since 1815 and had made a much more comprehensive and systematic study of the etching of rhombohedral cleavages of calcite with a variety of etchants using the recently developed optical techniques described in part II. A preliminary report on the etching of calcite is already made (Pandya and Pandya 1959b)and some of the results were also presented at the Indian Science Congress Session 1960. These studies have yielded very valuable information asto the etching mechanism.

During the past few years it is increasingly recognized that etch pits can nucleate on dislocations and other surface defects. Etch pits formation,especially in the early stages of etching can be a powerful tool for revealing subtle surface microtopography on crystals. In the early stages of etching, pits form patterns intimately related to the growth phenomena provided the etch is not carried too for such that the general surface distortion sets in.

Experimental Procedure:

The etch patterns on calcite cleavages in the earlier stages of etching requires high microscope powers, such as for instance oil immersion and an ocular with good magnification. Further it is realized that a good deal of structure encountered is evidently too close, to be revealed by the optical microscope, on etched crystal surfaces as such. At high resolution and magnification, contrast in the etched pattern has, therefore, to be increased, which is achieved by depositing totally reflecting silver film on the etched surface by the silvering technique described in part II. High resolution microscopic techniques with a variety of illumination conditions, multiple beam interferometry and light profile microscopy were used to study the etch patterns on the cleavage faces of natural crystals divided in groups A and B respectively, as mentioned in the section on the "cleavage of calcite". Freshly cleaved surfaces of calcite were used every time. Etching is effected by the use of several etchants, including inorganic acids, such as nitric, sulphuric, hydrochloric, phosphor~~ed~~ic chromic and hydrofluoric acids, organic acids such as acetic, tartaric, citric, d-tartaric, benzoic acid etc., alkalies (potassium hydroxide and sodium hydroxide) ammonium salts (NH_4F, NH_4Cl, NH_4Br, NH_4I, NH_4NO_3 Ammonium succinate) and alkali salts ($NaCl$, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$ and KNO_3). With the acids (concentrated and dilute) as etchants the etching times were from 1 sec.

onwards to about 3 minutes, whereas with alkalies and ammonium salts the time required to obtain matured etch figures is different for crystals belonging to groups A and B, but generally is from 1 min. onwards to 30 minutes. The variation in etching time suggests variation in composition of the crystals. The etching is carried out at room temperatures. For other salts, the etching period is from about 45 minutes to several hours. Several samples taken from crystals of each group were studied and similar features were observed in almost all cases on all crystals of that particular group. Observations somewhat differ on crystals of group A from those of the group B and these differences in turn reveal the history of the growth of the crystal of that group.

Observations:

Concentration of Etch Pits:

In this section the same region of crystal was observed each time after etching. Figure 48 a,b,c,(x 170) represent the same area of the crystal etched by dilute hydrochloric acid for 4, 6 and 8 secs. respectively. The etch pit is a four-sided figure. The number and location of the etch pits have not changed on etching. The development of groove with progressive etching should also be noted. Besides time and temperature, the shape of an etch pit depends upon the concentration of the etchant. This is shown by the photomicrographs of figures 49 (a,b,c, d). With concentrated hydrochloric acid (A.R.quality), the etch pattern observed on the crystal surface by etching it for 1 sec. is shown in figure (49a) x 90. Block patterns resembling those observed on diamond(Pandya and Tolansky 1954) and on fluorite (Pandya and Pandya 1958b) are seen. A high magnification view of a region of the picture is the phase contrast micrograph shown in figure (49b) x 360). This picture should be compared with those on diamond and fluorite. Progressive dilution of hydrochloric acid gives rise to figures 49c and 49d (both at x 170), which show respectively three-sided and five-sided etch figures. Such patterns are observable with most of the strong inorganic acids progressively diluted more and more by the addition of water to them. Figure 50 x 170 shows an etch pattern obtained by the crystals treating with dilute hydrochloric acid. The pattern is similar to that shown in figure 48a. But one more feature is of interest in this picture, regarding the shape of a pit on the right hand side and near the ribbon shaped line. The pit which is marked as A is bounded by five-sides whereas the rest of the pits are four-sided. Such features have been frequently observed on the etched crystals. It is difficult to think of a mechanism whereby a five-sided pit can arise on a rhombohedral crystal. It might be due to the presence of impurity or foreign particle at the point giving rise to the etch attack in five directions and hence resulting in a five-sided figure. Figure 51 (a,b) x 170 represent the photomicrographs showing the effect of diluting the nitric acid gradually by adding more and more water to it. The first photomicrograph figure 51a shows triangular etch pits having 'tails' at one of the vertices Scanning of the whole crystal surface has shown that at some places triangles without 'tails' have been found, which are then similar to those observed by etching the crystal with dil. HCl (figure 49c). Figure 51b was observed when more diluted nitric acid was used as an etchant. It represents four-sided pits with closed terraces. The depths of the pits were measured by light profile. A number of discrete steps were observed each of them appeared to have no correlation with each other and with the total depth. If the solution is still diluted, five-sided etch pits were observed. Attack of solution diluted beyond this results in general deterioration of the surface with the quality of the pits profoundly damaged.

It is reported (Mellore 1952) that action of H_2SO_4, HNO_3 or acetic acid on calcite suspended in absolute alcohol is extremely slow - between three to four months being required for complete neutralization. By introducing water the speed of neutralization is increased proportionally with the amount of water added. This shows that the alcohol retards the reaction to a marked degree. Not only, it retards the reaction, but the shape (or orientation) of the etch pit also changes. Thus with dehydrated acetic acid, the etch pit is a four-sided figure whereas with the addition of water in small amounts, the pit becomes triangular. Similarly, the shape of the pits may change on using different diluents. This aspect is not studied in detail in the present work.

Figure 52 (a,b,c,d,e) x 340 represent the successive stages of etching of the cleaved surfaces of calcite by a concentrated solution of tartaric acid for 4, 5, 6, ~~and~~ 7 and 8 secs. respectively. The density i.e. the number of etch pits on a given area is constant over a fairly long etching time.

Figures 53 (a, b, c) x 170 represent on the cleaved crystal surface etch patterns cleaved produced by saturated solutions of ammonium chloride (at room -

temperature) for 1, 3 and 4.5 minutes respectively. As is found with other etchants here also the number of pits does not increase but remains constant and the pits simply enlarge and deepen on successive etching. In accordance with the earlier observations on the etched cleavage surfaces of mica crystals, regarding the shift of cleavage lines on etching, this three photomicrographs show the displacement very clearly. The pits marked as A and B are not on the cleavage line in figure 53a, but as etching progresses, cleavage line displaces and finally both the pits are found on the cleavage line in figure 53C.

All the above observations show that the density of etch pits on a given region of the cleaved crystal surface is constant upto a particular etching time. This is found to be true for all the etchants mentioned in the present work. This observation, therefore, suggests that etch pits might have been nucleated at some specific defects.

Etch Pits and their Orientation:

Since percussion mark is a fundamental characteristic of the crystal face on which it is produced, the orientation of the etch figures are determined with respect to it. Fig. 54 (x 170) represents a percussion figure on a calcite cleavage surface. In order to bring out the mark very clearly, ~~by a sa~~ the surface is etched lightly by a saturated solution of sodium sulphate at a temperature of 80°C. Below it are shown the etch pits in position obtained by some of the etchants. Figures 55(a,b,c, d, e, f, g, h) x 360 represent the etch pits produced by different etchants, namely dil. HCl, chromic, tartaric, d-tartaric, citric, acetic, alkalies and ammonium chloride solution respectively. All ammonium salts, used in the present work, gave rise to four-sided pits with long diagonal of the etch figure parallel to the glide lines of the percussion figure. NH_4F gives rise to boat-shaped figures exactly similar to figure 55g. It is not quite understandable how ammonium fluoride acts differently from other ammonium halides and produces boat-shaped figures in contrast to other halides which produces four-sided figures. All other salts except sodium sulphate produce four-sided etch figures, whereas sodium sulphate gave rise to triangular pits with one vertex rounded as compared to the other two sharp vertices.

The present author had used occasionally multiple-beam-interferometry and light profile microscopy for the measurement of depth(and height) features on crystal surfaces. Fig. (56) x 44 is a transmission multiple beam interferogram taken over a cleaved surface etched by strong solutions of sodium hydroxide for 20 minutes, whereas figures (57a, b, c,)x170 are high dispersion multiple-beam-interferograms over crystal surfaces etched by dil. HNO_3 (fig.57a), dil HCl acid (figures 57b) and chromic acid. The asymmetrical nature of the etch pit clearly shows the imperfection associated with an etch pit is inclined to the surface and not perpendicular to it. Typical depths of the pits are.

Profile micrographs in the etch pits are shown in figures (58 a,b) x 720, the first one being on a pit produced by concentrated solution of ~~sodium~~ potassium hydroxide and figure 58b produced by concentrated solution of ~~potassium~~ sodium hydroxide. The etch pit depths vary along the pit. They are. $5{\cdot}9\mu$, $4{\cdot}9\mu$ and $1{\cdot}0\mu$, $0{\cdot}8\mu$ respectively.

Matching of the etched cleavage counterparts:

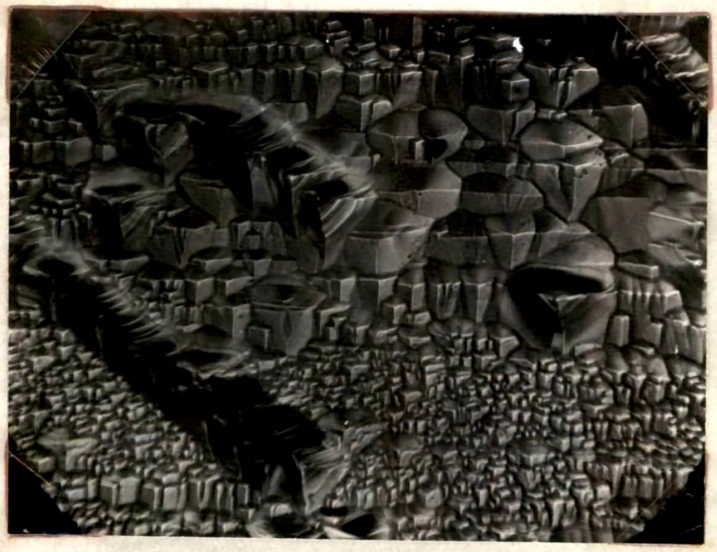
The calcite crystals were cleaved by any of the methods mentioned earlier and the resulting cleavage counterparts were simultaneous subjected to etching. Fig. 59 (a,b) x 170 show the matched regions of counterparts etched by strong nitric acid for 2 sec. The composite picture secured by superimposing the two is shown in fig. 59c. The etch patterns are not thoroughly reflected on

(a)

(b)

Fig(48) x170

Fig(48C) x 90



Fig(49a) x 90

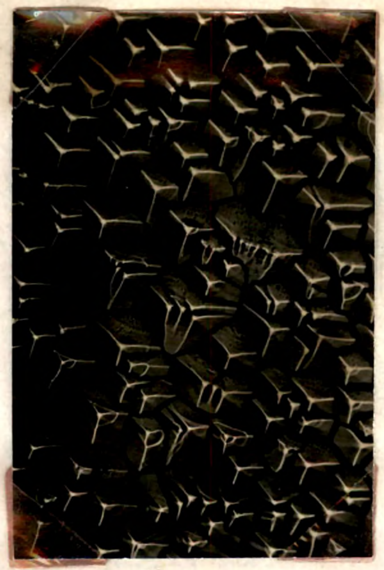


Fig (49b) x 360

Fig (49c) x 170

Fig (49d) x 170

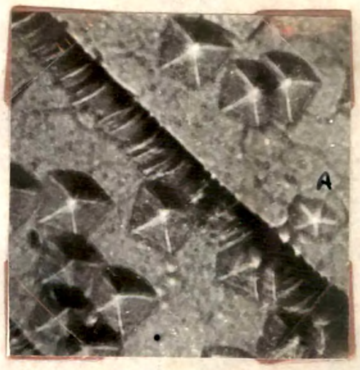
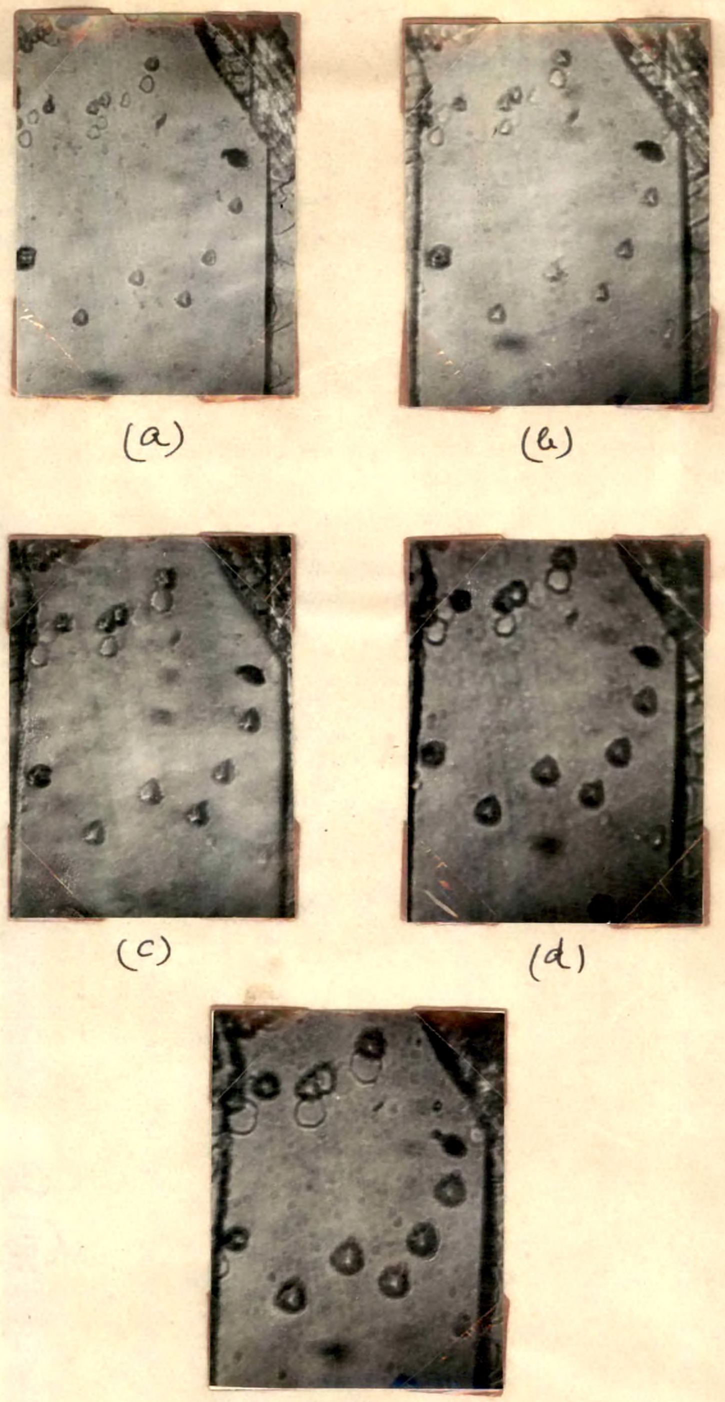


Fig (50) x 170

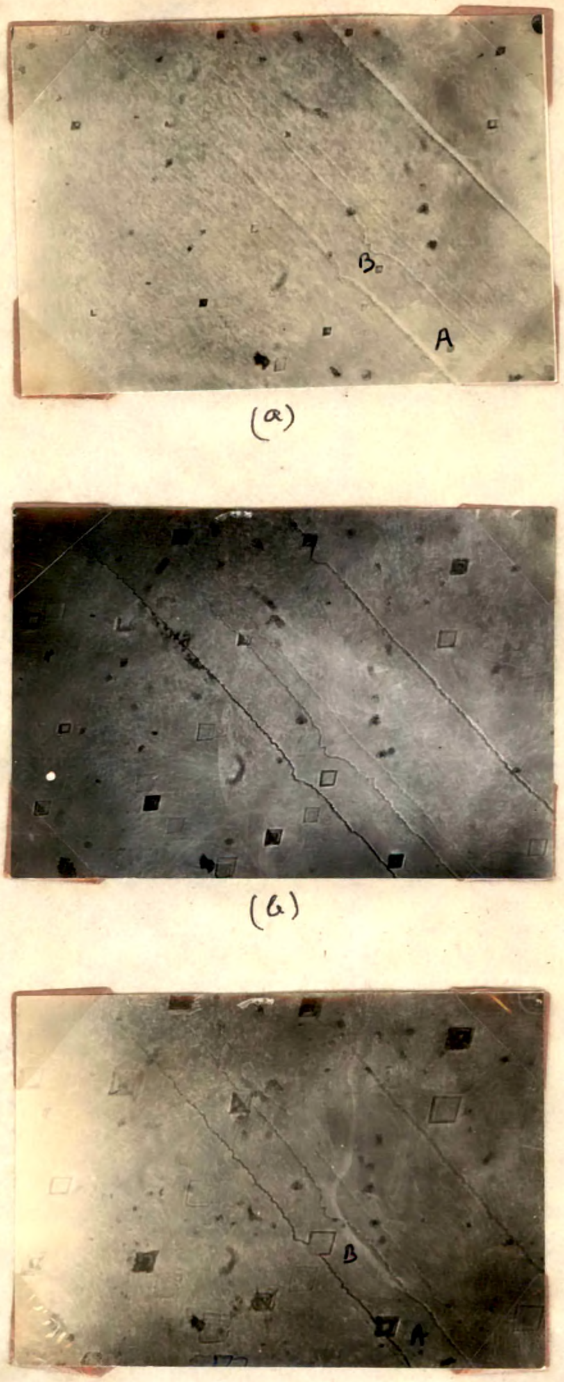
Fig (51a) x 170

Fig (51b) x 170



(a) (b) (c) (d) (e)

Fig (52) x 340



(a)

(b)

(c)

Fig (53) x170

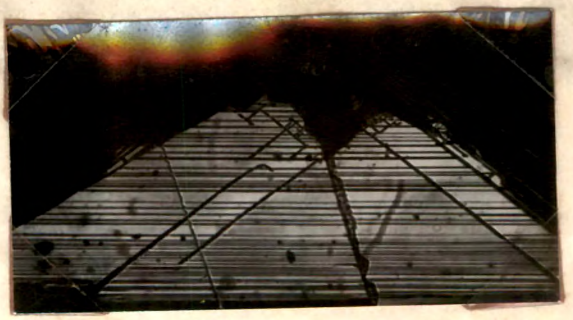


Fig (54) x 170

(a)

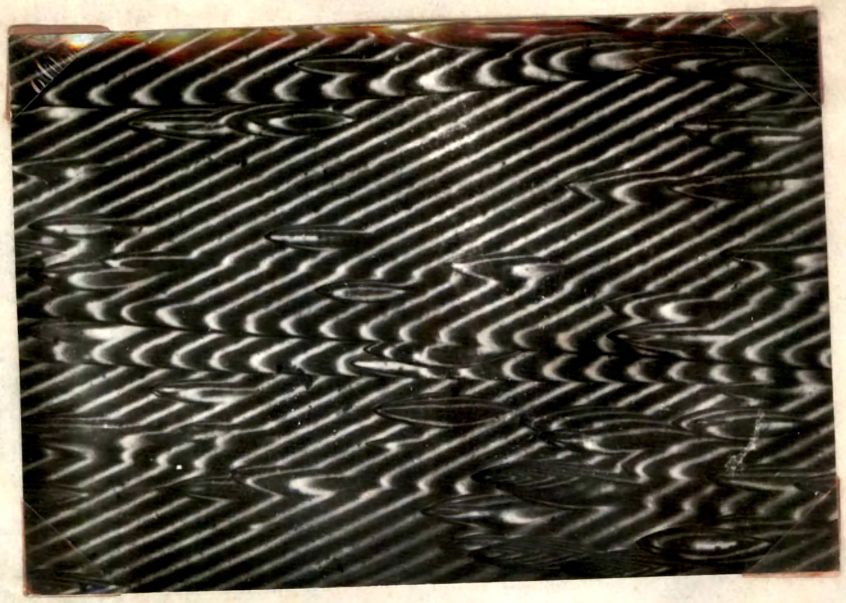
(b)

(c)

Fig (55) x 360

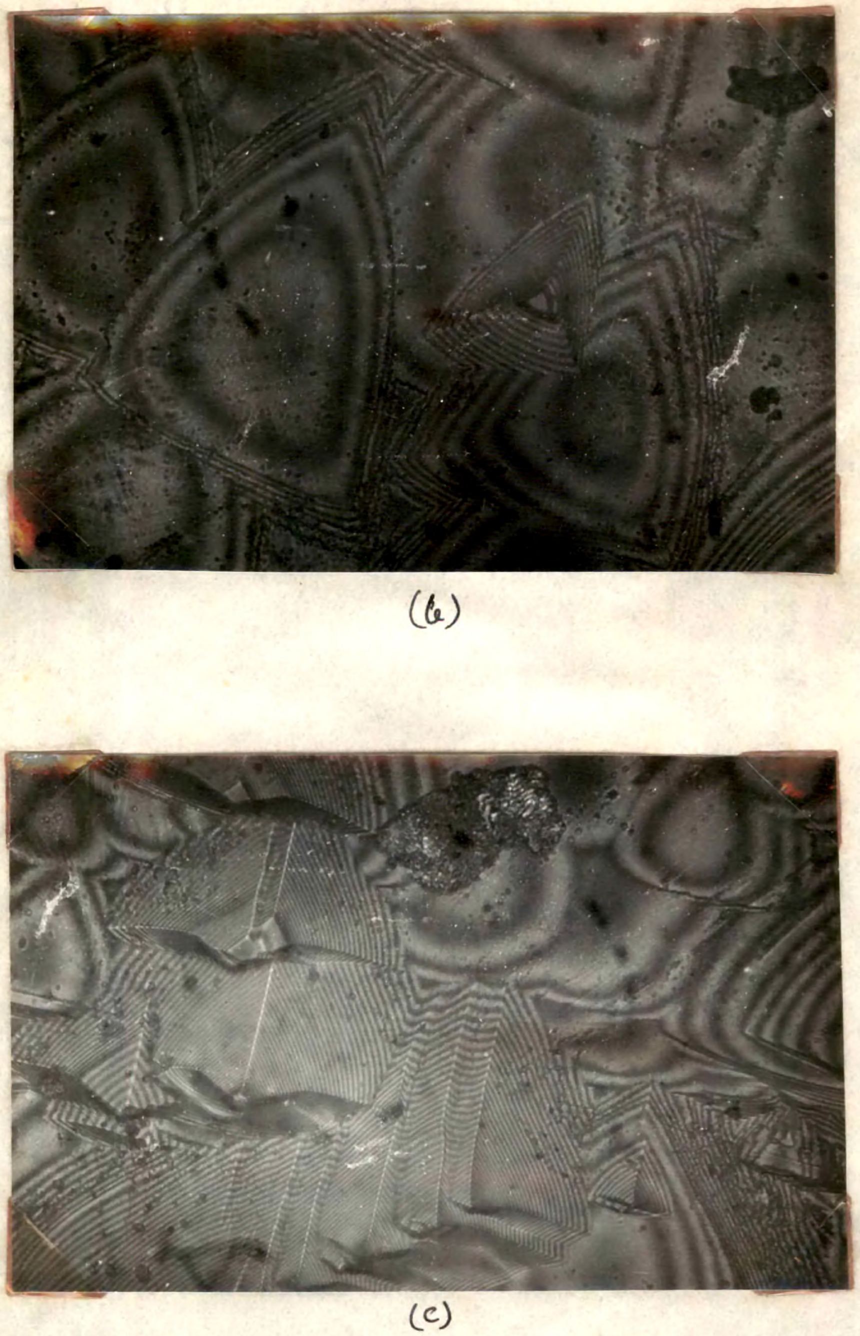
h

Fig (55) x 360



Fig(56) x 44

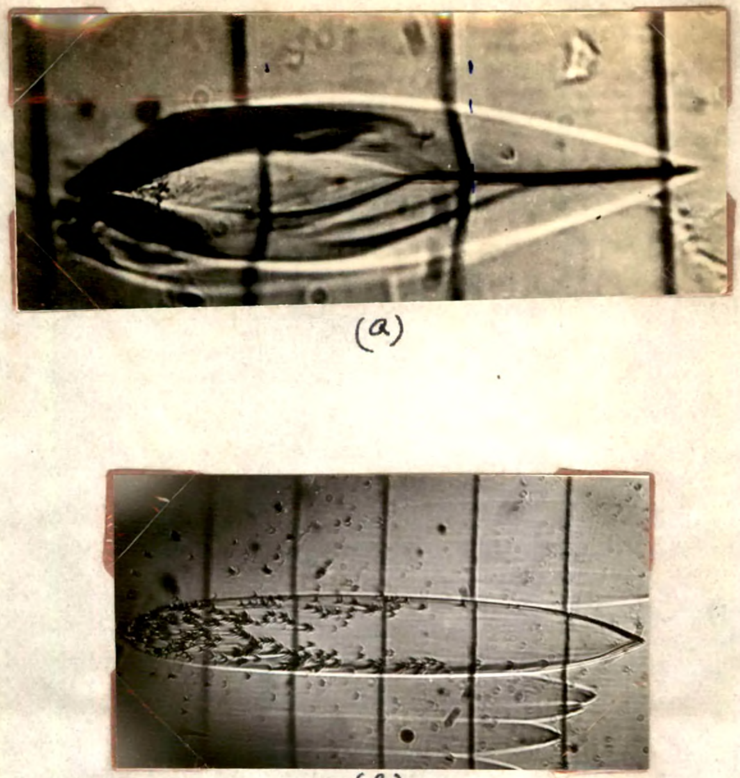
Fig(57a) x 170



(b)

(c)

Fig(57) x170



(a)

(b)

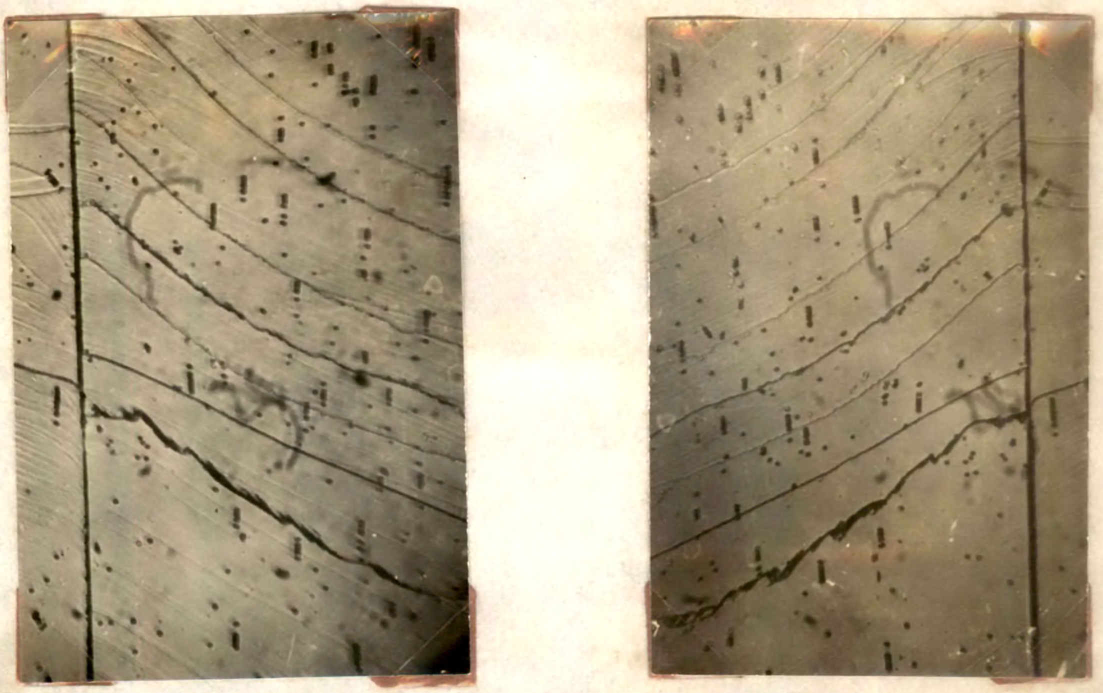
Fig(58) × 720

(a)

(b)

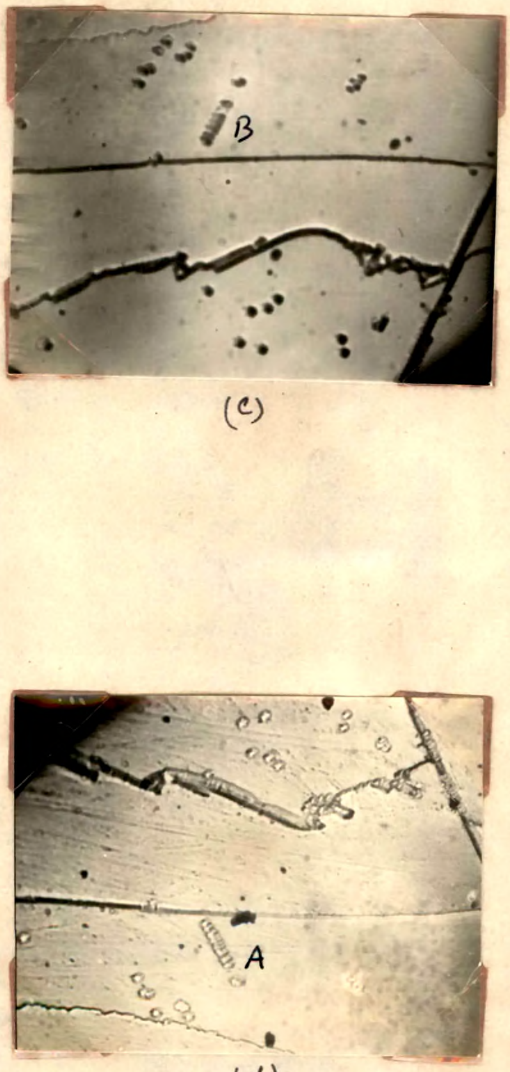
Fig(59)×70

Fig(59C) ×170



(a) (b)

Fig(60)×90



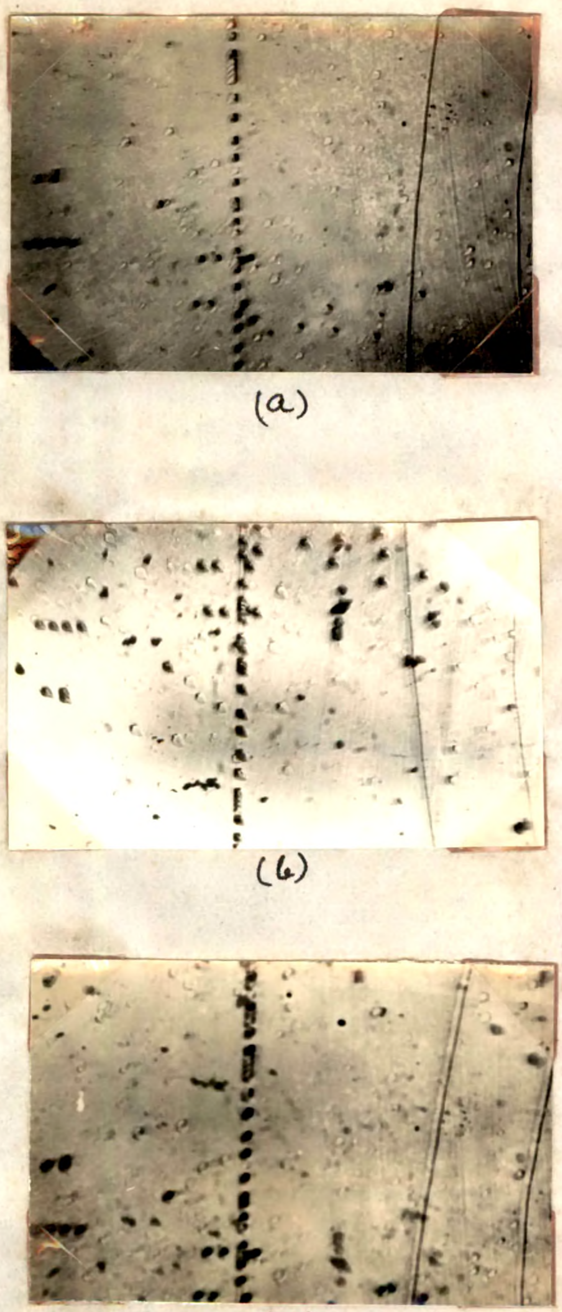
(c)

(d)

Fig(60) × 360

matched areas. Also note the cleavage shift and the occurence of T shaped boundary. Such boundaries are frequently observed and at high magnification they show in them the clearly spaced etch pits, suggesting the occurence of etch pits at some specific defects. This observation is referred to later on while deciding the origin of pits. Imperfect matching is due to inappropriate concentrations of the etchant. This is clearly indicated by photomicrographs of figures (60 a,b) x 90 which represent the matched regions etched by dil. HNO_3 (1:200) acid. The pits are found to be five-sided figures when observed under high powered objectives. It should be noted that there is perfect one to one correspondence regarding the number and positioning of etch pits. The parts of same regions at relatively high magnification are shown in figures (60c,d) x 360 . The groups of etch pits marked as A in fig.60c are nearer to the cleavage line than those corresponding pits marked as B in fig. 60d, showing that the cleavage line has moved on etching.

Fig. (61 a,b) x 170 represent the matched regions of the crystal counterparts etched by saturated solution of tartaric acid. Photomicrographs figures (62 a,b) x 170 show the same regions etched for 2 secs. more.

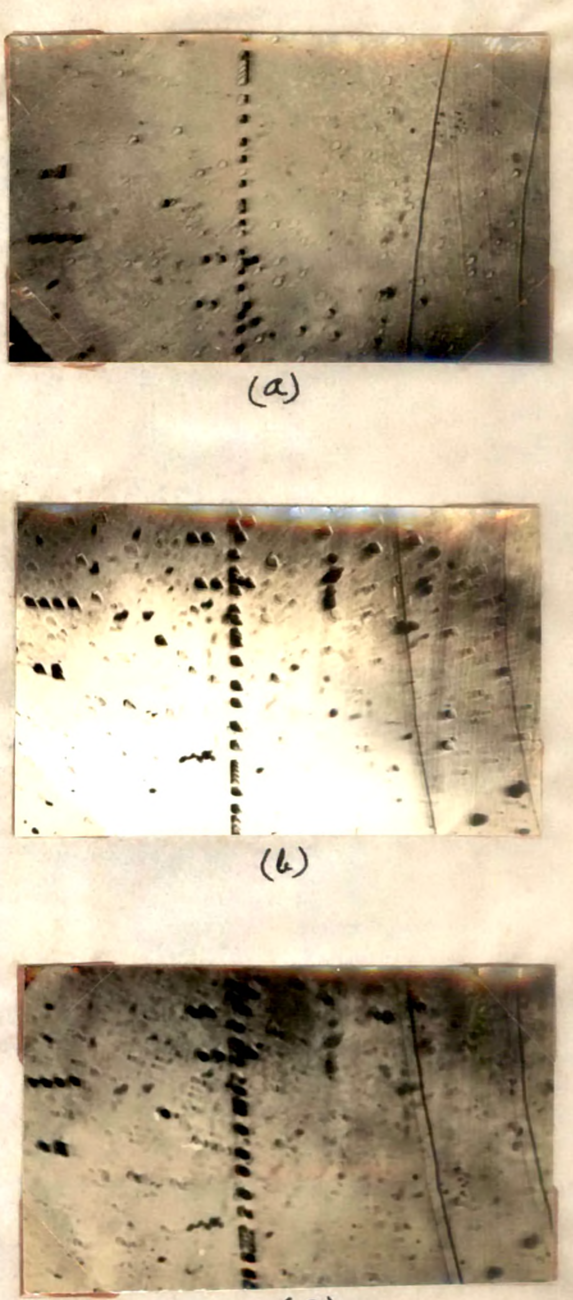


(a)

(b)

(c)

Fig(61) ×170

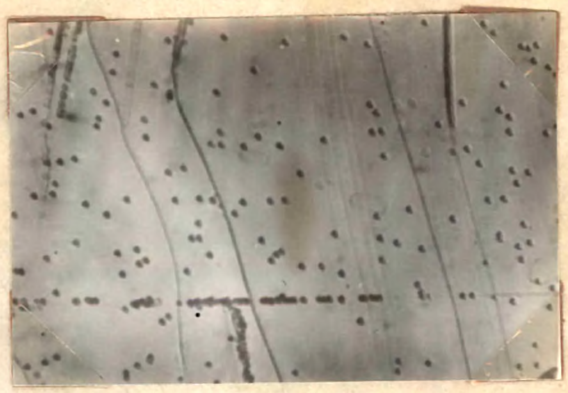


(a)

(b)

(c)

Fig(62) ×170



(a)

(b)

Fig(63) × 170

Figures 61c and 62c are the composite pictures secured by superimposing figures (61a,b) and (62a,b) respectively. The matching of etch patterns, the displacement of the cleavage lines and orientation of the pits on both the counterparts should be noted.

Experiments were also conducted by etching one counterpart with one etchant and the other with a different etchant. The matching regions on the two counterparts were then examined. Figures(63a,b) x 170 represent the matched areas on the counterparts, one etched by tartaric acid solution and the other by ammonium chloride solution. There is a remarkable degree of correspondence of the etch patterns on both the counterparts. Several such paired samples have been studied not only with the above etchants but also with all the etchants mentioned earlier.

The matching of the counterparts therefore leads one to conclude that the imperfections associated with the pits are revealed with equal ease by all the etchants. In some cases the matching is not exact, some pits are more on one face than on the other, even with the same and different etchants. At present, the reason is not well-understood. It is possible that plastic deformation might have occurred during the act of cleavage which might then be responsible for the unidentical reflection of the etch patterns on the matched areas. Also matching was not usually found exact on regions near the tapped point from where the cleavage proceeds, but on opposite sides of the tapped point, good matching is obtainable.

Discussion and Results:-

For determining the origin of pits, the following points are worthnoting.:-

(i) successive etching causes growth of pits at the unchanged locations.

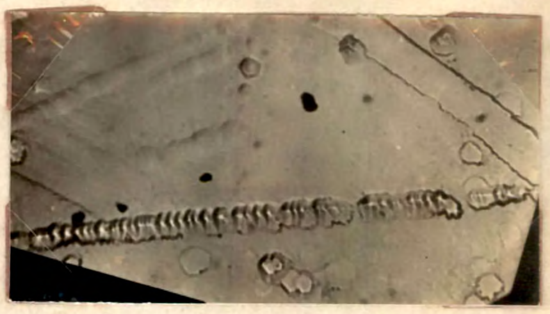
(ii) Identical etch pits were observed on matching cleavage faces.

(iii) Pair arrangements, linear arrays of etch and occurence of T and L shaped etched boundaries were observed (fig.64 x 700, 65 a,b,c,d all at x 360).

(iv) Dislocation motion is observed on the application of sufficient amount of stress to the crystal.

The above points are now considered in detail. Points (i) and (ii) are discussed fully earlier. The observations have shown that all etchants with appropriate concentrations are equally suitable. Pair arrangements and linear arrays of closely but regularly spaced etch pits are observed. Fig. 64 shows such pair of pits produced by the saturated solution of ammonium iodide. The direction of the tips of the pits is found to be [110.]

Fig (64) × 700



(a)

(b)

(c)

Fig (65) × 360

(d)

Fig (66a) x 720

Fig (66b) x 720

Fig (67) x 170

Figure 65a represents the linear array of pits obtained by dil. HNO_3 acid (1:200) whereas in figures 65 b,c,d, the pits were produced by 40 per cent HF acid. Such arrays of pits are typical of dislocation etch pits. The figures represent slightly advanced stage of etching. Most decisive experiment is application of sufficient amount of stress to move dislocations. For these two experiments were performed. In one experiment a fine scratch was made on the crystal and the crystal was etched to reveal the dislocations resulting from the scratch. A second scratch was placed just near the one so that its stress field would move the old as well as the newly introduced dislocations. The crystal was then again etched to reveal the new positions of the initial dislocations. Movement of the dislocations must correspond with that calculated from stress considerations. Although the results were somewhat encouraging. Yet there were difficulties in calculating the stress applied during the scratch. The method was therefore abondoned, and a second series of experiments were performed in which the crystal was compressed, extended and bent. Of all these, bending of the crystal was proved to be very convenient. In this case, to induce plastic deformation the crystal was bent initially and etched for a suitable time to produce large etch pits. Then it was bent again in order to move the dislocations and re-etched for a smaller period of time to form the small pits and enlarge the original pits. If the dislocation has moved from its place and its position is not occupied by any other dislocation the pit representing the dislocation would become truncated or flat bottomed during the second etching whereas the shifted position of dislocation would be represented by a new smaller point bottomed pit. This is indeed what is happening in actual practice. In the present investigation such movement of dislocations has been observed by using most of the etchants. Among them are the ammonium salts except ammonium fluoride, and most of the acids appropriately diluted. No such movement is noticeable with the alkali etchants. Ammonium salts are ideally suited for revealing dislocation sites. Figures 66 a,b represent the photomicrographs of etched crystals treated as mentioned above. The etchants used were saturated solutions of NH_4Br and NH_4I respectively. The crystals were etched for 90 secs. and 60 secs. and 2 minutes and 1.5 minutes. respectively at a temperature of 50°C. Recently Keith and Gilman (1960) and Bengusff et al (1960) have also reported the study of dislocation etch pits on calcite cleavages. Keith and Gilman used various inorganic and organic acids to etch the crystals. By using formic acid they have shown the etch pits to be at dislocation sites. Bengusff et al (1960) used a 10 per cent solution of tartaric acid to reveal dislocations in calcite crystals.

The etching of crystals belonging to group B disclosed two sets of lines, one set of lines running parallel to the edges of the crystal whereas the second set of lines run parallel to the long diagonal of the crystal fig. 67 x170. The first set of lines are identified as being revealing cleavage directions whereas the second set of lines are twin lines. All these lines are found all over the surface suggesting their formation at the start of the growth of the crystal. The observations suggest that crystals consist of small blocks, each one fitted with the other with some slight misorientation. Thus pointing to the mosaic block structure.

Twins induced by compressing the crystals have also been etched. Prolonged etching showed that these markings existed only in shallow regions near the surface and have not penetrated very much.