PART IV

DEHYDRATION FIGURES ON CLEAVAGE FACES OF SELENITE.

CHAPTER 9

DEHYDRATION FIGURES ON CLEAVAGE FACES OF SELENITE.

9.1 General Introduction on Selenite:

Gypsum is a very common sulfate mineral which in the crystalline form is often called selenite meaning 'the moon' so named probably in illusion to the soft moon-like reflection of light from some of its faces. Varieties of mineral gypsum include selenite (clear transparent crystals) satin spar (long parallel needles) and alabaster (fine grained variety white or delicately shaded). Gypsum frequently occurs together with rock salt deposited in shallow basins of salt water. Much of the calcium in sea water exists as sulfate. In volcanic districts, gypsum is produced by the action of sulphureous vapour on lime bearing minerals. Burnt gypsum is called plaster of paris. Excellent account on gypsum is available in many standard

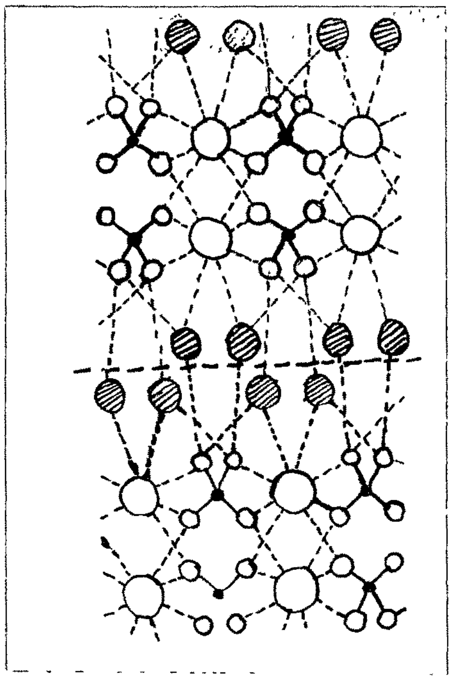

Fig. 9.1A

books (see e.g. Rogers, 1937; Dana and Ford, 1957).

9.11 Form and Habit:

Crystals are usually simple in habit, having common forms (i) flattened parallel to 'b' (010), (ii) prismatic to acicular parallel to 'c' axis, (iii) prismatic by extension of (111), (iv) lenticular by rounding of (111) and e (103). Selenite belongs to the monoclinic system, while anhydrous calcium sulphate belongs to the ortho-rhombic system.

9.12 Crystal Structure:

Selenite has rather a complex layer structure in which layers are bound together by bonds from water molecules as shown schematically in fig. 9.1A. The big and small circles represent Ca and O_2 atoms whereas the big shaded and small dark circles represent water molecules and sulpher atoms respectively. The heavy broken line in the centre of the figure indicates the cleavage which breaks only O-H-O bonds. X-ray study of the crystal structure shows eight molecules in the unit cell. This structure explains the very perfect easy cleavage of gypsum parallel to (010) face. It is a layer lattice, the layer being parallel to (010) faces. Two sheets of SO_4^{--} groups are intimately bound together by Ca^{++} ions so as to form a strong double sheet. Successive double sheets are seperated by sheets of water molecules. Each calcium atom is surrounded by six complex atomic groups consisting of four SO_4 tetrahedrons and two molecules of water. Each water molecule links a calcium atom both to an oxygen in the double sheet and to one in the neighbouring sheet. The latter bonds are comparatively week and explain the easy cleavage. The absorption spectrum studies of selenite indicate that water is not chemically combined.

9.13 Cleavage and Twinning:

Selenite is characterized by a very easy highly polished cleavage in a single direction yielding (010) cleavage plane. Two other cleavages (1) a (100) with conchoidal fracture and (2) n (111) with a fibrous fracture are also reported. The cleavage fragments have a rhombic form with plane angles of 66° and 114° . The lattice spacing of selenite cleavage given by X-ray measurement is also 15Å (Tolansky and Khamsavi, 1946b). Twinning in selenite is common, forming in some cases of s~~h~~allow - tail twins. Twin plane a (100) is very common.
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9.14 Physical properties:

The hardness of selenite on Moh's scale is 1.5 – 2.0. It is easily flexible but not elastic . Specific gravity varies from 2.314 – 2.328 in pure crystals. Luster of b (010) is pearly and shining, other faces being sub-vitreous. Massive varieties are often glistening, though sometime dull earthy. Its colour is usually white. Gypsum with quality varying from transparent to opaque character is available.

The melting point of calcium sulphate is between 1350°C to 1375°C but the salt decomposes so readily at 1000°C that an accurate determination cannot be made. Gypsum is optically positive. The mean values of the indices for refraction are $\alpha : \beta : \gamma ::$ 1.5205:1.5227:1.5294.

9.15 Chemical properties:

Chemical composition of selenite is $CaSO_4, 2H_2O$ (Lime CaO 32.5%; SO_3 46.5%; H_2O 20.9%). Its molecular-weight is 178.18. The melting of gypsum takes place in two stages, first it loses one and half water of crystallization at 128°C and then the remaining 1/2 part of water at 163°C. Hence at a temperature 163°C it loses completely two molecules of water of crystallization and becomes anhydrite which is white in colour.

It is attacked by nitric acid, EdTA, dilute solution of sodium and potassium hydroxide in water. The heat of reaction of anhydrous calcium sulphate is 317.4 calories whereas heat of hydration of $CaSO_4$, $2H_2O$ is equal to -3.61 calories.

Gypsum is soluble in water and its solubility is 0.264 gms., in 100 gms; water at 26°C. The solubility of the crystal in a solvent depends upon its size. Solubility is decreased when water consists of other soluble salts. Gypsum is slightly soluble in acids such as HCl, HNO_3, HCOOH etc.

Gypsum is used in the preparation of plaster of paris, in various cements such as Keen's cement, Martin's cement, in fireproof building blocks due to low heat conductivity. It is also used in making some polished powders, jwelleries, as a fertilizer for restoring sulphates to certain types of soils. Delicate cleavage plates of gypsum are used in microscopic petrology for the determination of certain optical constants in the rock forming minerals.

9.2 Dehydration of Crystals:

Initial dehydration of a crystal containing water of crystallization is a less understood phenomenon, though a vast amount of literature on complete dehydration of materials is available. Brief review will be reported here on the initial stages of dehydration of crystals with special emphasis on gypsum.

Shenstone and Candell,(1888) observed that gypsum could be dehydrated by heating it to 70°C in dry air and further reported loss of 3 per cent of water by heating it at 40°C for 14 hours. Davis, (1907) also supported above observations and suggested formation of a distinct initial period of inertness during the dehydration of gypsum. He has reported that when a monoclinic gypsum is heated, it is very probably converted into a second rhombic form of gypsum. The process of conversion of monoclinic gypsum into rhombic form of gypsum, and rhombic gypsum to rhombic hemihydrate is reversible. Bhowmic, (1960) observed structural change in thermal dehydration of $Cu(NH_4)_2SO_4$, $6H_2O$. She found a change of monoclinic structure to an orthorhombic one by loss of water molecules in the dehydration process of these crystals. Chetelier, (1887) determined the time rate of rise of temperature of powdered gypsum. The temperature rose steadily upto 128°C, when there was long interval during which temperature remained stationary. There was a continuous loss of weight on heating gypsum up to 155°C until 15.6% had been lost, when the residue retained a constant weight consistent with a formula $CaSO_4$, $1/2 H_2O$. From a study of thermal analysis of gypsum Sekiya, (1960) suggested the formation of $CaSO_4$, $2/3 H_2O$. Johes et al, (1963) studied differential thermal analysis of selenite and other gypsum crystals and observed three endothermic peaks below 200°C. They concluded that the first two peaks represented dehydration of $CaSO_4$, $1/2 H_2O$ and then to soluble anhydrite. Third peak might be due to loss of last traces of water. Richard, (1962) studied the dehydration of gypsum at 99°- 142°C by means of visual observations, infrared spectroscopy, X-ray diffraction and thermogravimetric techniques. He has concluded that dehydration involves two consecutive reactions and is not a simple transformation of gypsum into anhydrite. He found that less reactive energy was needed for the dehydration of gypsum than that associated with dehydration of hemihydrite. Yamaguchi and Tokuda, (1964) studied the dehydration of brucite crystals by electron-microscopy.

The factors which affect the dehydration were studied by many workers. McCormark, (1926) observed that temperature was more important for dehydration of gypsum while no significant effect of pressure on dehydration was noted. Mitsuki, (1952) observed that once gypsum began to dehydrate at a temperature 100°C, it continued to do so even at a lower temperature ranging from 100°C to 87°C. Macdonald, (1953) reported that high salt content lowered the dehydration temperature of gypsum. Zolotov and Khurochlan, (1959) observed that dehydration of gypsum started at very low temperature (surface temperature 80°C) in ultrasonic field. Microscopic study and the differential thermal analysis of gypsum were made by Sekiya and Sugiyama, (1962). In the dehydration of $CaSO_4, 2H_2O$ to $CaSO_4, 0.5H_2O$ through $CaSO_4, \frac{2}{3}H_2O$, the higher the apparent crystallinity of dihydrate, the higher is the dehydration temperature and the slower is the rate of dehydration. Zolotov and Lankov, (1960) reported easy dehydration at sharp disruptions and deformation of a crystal lattice (cracks, cleavages etc). Defects in crystallinity made the process of detaching water molecules from the dihydrate lattice of gypsum ($CaSO_4, 2H_2O$) easy. They remarked that it was not possible to determine the exact initial temperature at which dehydration occurred.

Atoji, (1959) observed that dehydration process was largely anisotropic because water molecules were driven off in the direction parallel to plane under observations. Boldyrev and Zakharov, (1960) established anisotropy in the rate of dehydration of alums. This was attributed to the difference in the density of filling by the water molecules of the different crystallographic planes which are being dehydrated. Boldyrev and Schmidt, (1960) observed different shapes of dehydration nuclei. The condition of dehydration of $ZnSO_4$, $7H_2O$ determines shape of dehydration nuclei. Boldyrev et al, in the same year found different shapes of dehydration nuclei on the tetrahedron and prism faces of $MgSO_4$, $7H_2O$. The anisotropy in dehydration rate was attributed to the characteristic lattice of $MgSO_4$, $7H_2O$ and the arrangement of water molecules in it.

There is very little work reported in literature for the cause of dehydration nuclei at some preferential points. Bright and Ridge, (1961) observed that dehydration nuclei in general did not occur at dislocations in gypsum, while Patel and Raju, (1969) and Patel and Desai, (1969) conjectured that the dehydration nuclei preferably nucleated at the site of dislocations in gypsum and GASH crystals respectively.

Dehydration process is found to be a reversible process and dehydrated crystals can be rehydrated to its original form if proper conditions are maintained. It is difficult to obtain the same condition in gypsum because water affects it.

The aim of the present work is to study dehydration figures on selenite crystals which are easily available in nature. There are a number of controversial observations on the origin of dehydration figures. It is also aimed at comparing these dehydration figures with the chemical and thermal etch figures on c~~yr~~rystal faces.

9.3 Experimental procedure for studying dehydration figures on cleavage surface of selenite:

It was reported in literature that gypsum dehydrates at 120°C to form hemihydrate. For the dehydration the cleaved surfaces were kept in a petri dish which was placed in an incubator. The incubator is used for keeping temperature constant (room temperature to 100°C). It consists of double walls with 2" thick insulation of pure glass wool or abbastos sheets. Its temperature (± 1°C) are controlled by bimetal thermostate with calibrated dial. Air regulator is at the top of the case. Incubator is electrically heated (300 watts) by heating coils placed at the bottom with red light indicator. The specimens can be put on the shelves near the thermometer. After dehydrating crystals they were slowly cooled down in incubator to room temperature. They are then silvered by the thermal evaporation method for obtaining better contrast between various dehydration features on the crystal surface. For the study of ~~the~~ a cleavage

Fig. 9.1a (x70)

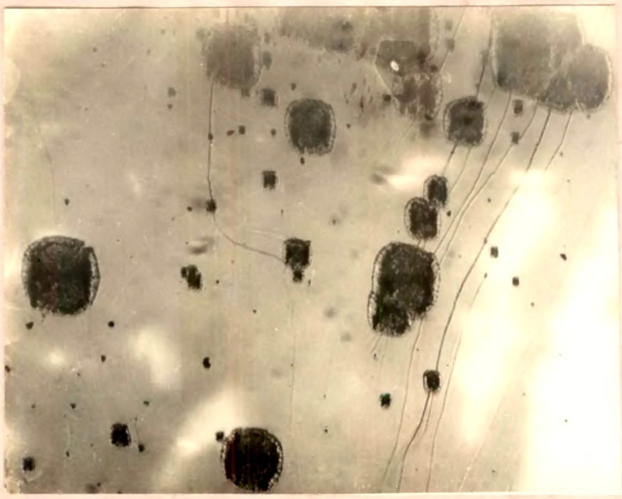

Fig. 9.1b (x70)

Fig. 9.2a (x70)

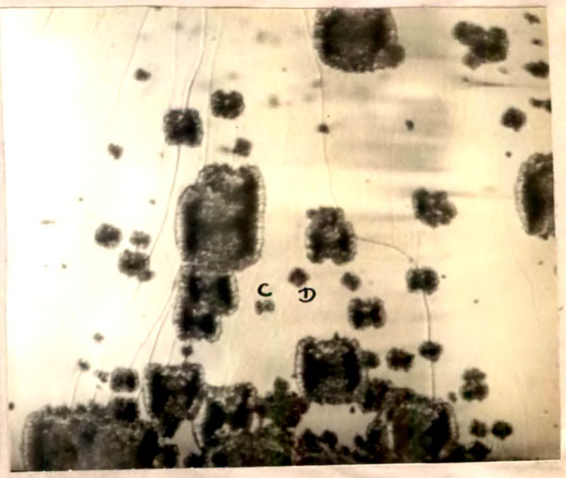

Fig. 9.2b (x70)

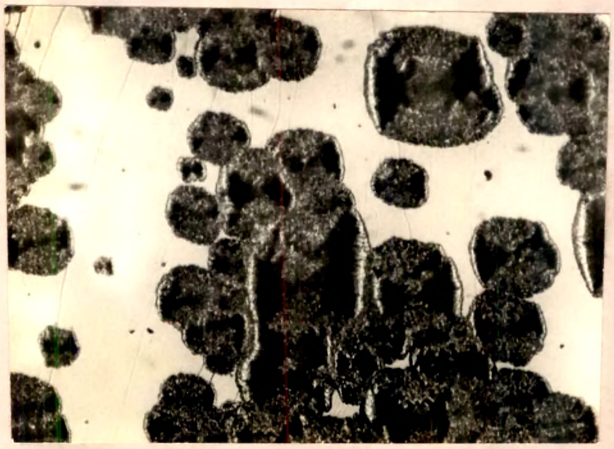

Fig.9.3b (x70)

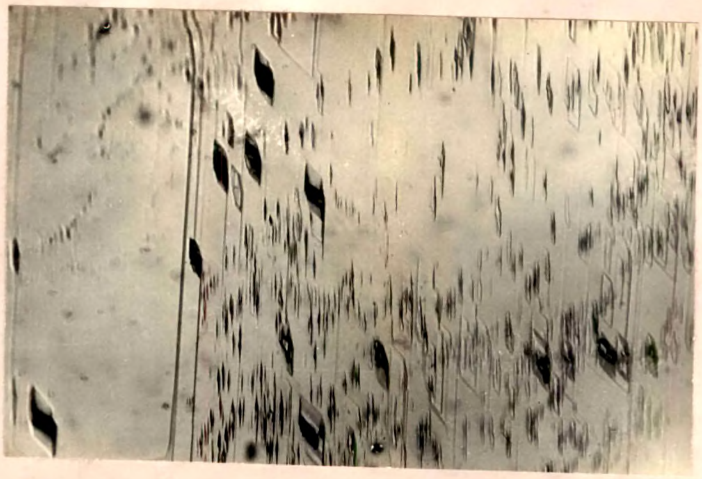

Fig. 9.4a (x100)

Fig . 9.4b (x100)

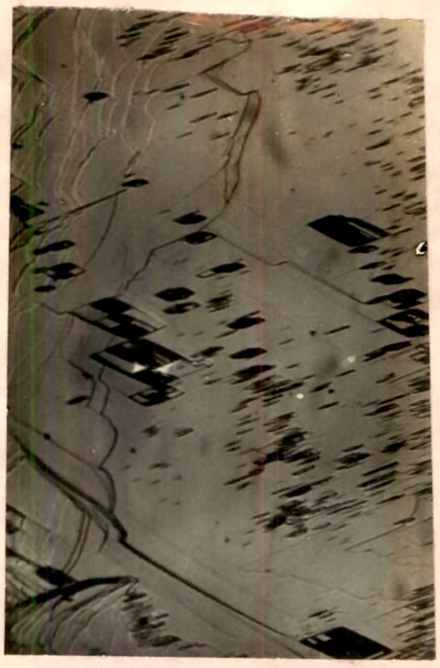

Fig.95a (x 70)

Fig. 9.5b (x70)

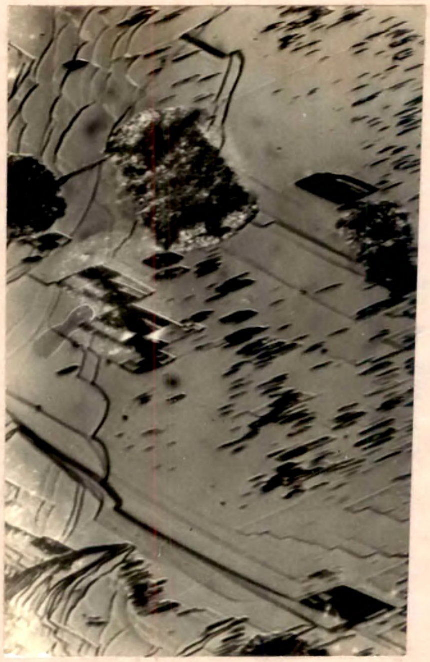

Fig. 9.6 (x70)

Fig. 9.7a (x 70)

Fig. 9.7b (x 70)

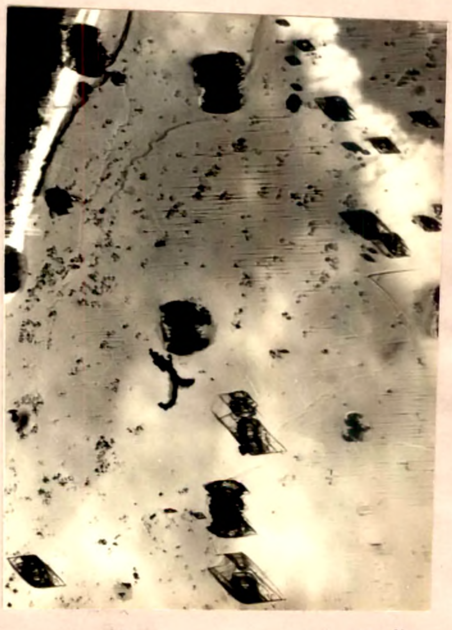

Fig.9.8 (x70)

surface of selenite subjected to multiple dehydration or etching, the crystals could not be silvered.

9.4 Observations, Results and Discussion:

Selenite crystals dehydrate at about 120°C so experiments were carried out on selenite cleavage surfaces at 100°C. When a cleavage surface was kept in an incubator at 100°C for less than ten minutes it was covered with a white layer and did not show any meaningful microtopographical features. The experiments were therefore carried out at lower temperatures, i.e. 96°C, 88°C and 84°C. It was found that when the temperature was kept lower than 84°C for 24 hours, practically no effect of dehydration could be found on the cleaved surfaces of selenite observed at very high magnification and resolution. The microscopically observable pits are formed at the temperature range from 96°C to 84°C for etching time varied between 1/2 hour to 8 hours. There is practically no change of etch pit shape for all these dehydration temperatures. Systematic study of matched cleaved faces of selenite which were dehydrated under identical conditions are reported here.

Figs. 9.1a and 9.1b (x 70) presents the matched cleavage faces of selenite simultaneously dehydrated at a temperature of 94°C for 2 hours. It is seen from these figures that surfaces were found to be covered with curved rectangular etch pits of assorted sizes usually referred to as dehydration figures. Many figures are formed on the cleavage lines, and at places free from them. The cleavage lines are almost completely reflected on the matched faces; however, dehydration figures do not show much correspondence. The density of these figures is practically same in both regions; $2 \times 10^3/\text{cm}^2$ in fig.9.1a and $4 \times 10^3/\text{cm}^2$ in fig. 9.1b. The same surfaces were further dehydrated at 94°C for one hour in usual manner. Figs. 9.2a (x 70) and 9.2b (x 70) show photomicrographs of the advance stage of dehydration of same region shown in figs. 9.1a and 9.1b respectively. Comparing figs. 9.1a and 9.2a and 9.1b and 9.2b following points are of interest:

(1) Formation of new etch pits such as a, b, c, d, due to further period of etching.

(2) Unequal increase in size of dehydration figures.

(3) No changes in the position of cleavage lines.

(4) Overlapping of some pits with consequent formation of bigger pits.

Similarly comparison of the figures 9.2a and 9.2b shows that there is no correspondence of dehydration marks on the matched dehydrated surfaces.

Fig. 9.3b (x70) represents the photomicrograph of the same region of the surface showing fig. 9.2b dehydrated for a further period of one hour at 94°C. some figures increase in size so they coalesce with each other and form bigger pits of irregular size. Some parts of cleavage lines are also not visible due to the overlapping of these figures. Cleavage lines do not shift on dehydration of the crystals and background etching or micropitting is absent.

In the dehydration process, water of crystallization goes to the atmosphere from the crystal. It is known that selenite is slightly soluble in water and when matched surfaces of the selenite were kept in distilled water for some time, beautiful rhombic pyramidal and needle shaped etch pits were seen. Figs. 9.4a and 9.4b (x 100) show photomicrographs of the matched cleavage surfaces kept in distilled water for five minutes at room temperature. Good correspondence of the black rhombic etch pits are seen. It is also found that the cleavage lines are displaced due to chemical etching. Surfaces are covered with small needle shaped pits on matched surfaces. These pits may be originated at some impurities or point defects while black rhombic pits may be formed at line defects. These observations clearly point that the dehydration figures and the pits produced by distilled water are having different origin.

Elaborate study of chemical pits and dehydration figures on a surface which is treated successively for chemical etching and dehydration and vice-versa is made to determine the origin of these figures. Fig. 9.5a (x 70) is photomicrograph of a crystal surface etched by distilled water for 4 minutes at room temperature. It is easy to distinguish three types of pits on the cleavage surfaces. (1) Small linear pits scattered all over the surface, (2) Medium sized pyramidal pits with rhombic outline on the surface. (3) Very large rhombic pyramidal pits. It is observed that some cleavage lines became wavy instead of straight and curved lines. It suggests that they donot move uniformly due to chemical etching. Fig. 9.5b (x 70) is a photomicrograph of the counterpart of the surface shown in Fig. 9.5a dehydrated at 95°C for 2 hours. A comparison of these two figures show that cleavage lines are much affected by chemical etching while dehydration has negligible effect on them. This is also clear from figures 9.1a and 9.2a; and 9.1b, 9.2b and 9.3b. Dehydration figures have a little correspondence with the extremely big pits while there is absolutely no correspondence with medium black rhombic etch pits. Surface shown in fig. 9.5a is dehydrated for a period of 3 hrs. at 95°C and is shown by a photomicrograph (fig. 9.6; x 70) showing the formation of dehydration figures which donot exactly correspond either with extremely big pits or medium size black pits or needle-shaped pits. The cleavage lines are not shifted during dehydration. There is thus no matching of pits produced by etching or by dehydration on the same surface. When this experiment was conducted in a reverse order i.e., first dehydrating a crystal surface followed by chemical etching, it was found that all the characteristics mentioned above are not repeated. Fig. 9.7a (x 70) shows a cleavage surface dehydrated at 95°C for 2 hours whereas fig. 9.7b (x 70) is the corresponding region on the counterpart etched by distilled water for 4 minutes. These surfaces exhibit patterns with characteristics similar to those mentioned above. It is interesting to note that when surface shown in fig. 9.7a was chemically etched by water for 3 minutes (fig. 9.8; x 70), out of the three types of chemical etch pits mentioned above, a few small needle shaped pits are only found. The dehydration figures are chemically preferentially attacked with a clear attempt to change these figures into rhombic pyramidal etch pits. The rhombic pyramidal pits (large and medium sized) characteristic of chemical etching are not found elsewhere on the surface. Hence the points where dehydrated nuclei are formed are easily attacked by the chemical etchant. The dehydrated surfaces donot behave in the same way as the virgin surfaces. While chemically etched surfaces or untreated surfaces behave in a similar fashion when exposed to thermal dehydration at constant temperature and for a given period of dehydration. This is exactly opposite to the thermal etching of calcite surfaces. In this case the chemically etched and virgin surfaces behave differently when exposed to thermal etching. However, the thermally etched and virgin surfaces behave in identical manner when subjected to chemical etching. The cleavage lines have not moved from the original positions during thermal etching of calcite cleavages and dehydration of selenite while movement of cleavage lines are observed in chemical etching of calcite and selenite crystals. The comparison of dehydration etching with chemical etching is given in table 9.1. This suggests that the origin of dehydration nuclei is not similar to that of chemical etch pits. They may be formed at the point defects or impurities. There is practically no change in density of chemical etch pits while there is a little change in etch pit density in dehydration. Exact matching on counterparts is not observed in dehydration of selenite crystals.

TABLE 9.1

COMPARISON OF DEHYDRATION ETCHING WITH CHEMICAL ETCHING OF SELENITE CLEAVAGES.

	Dehydration etching	Chemical etching
1.	There is no change in shape of etch figures.	Systematic changes in shape of etch pits are observed due to changes in concentration of an etchant or conditions of etching, or both.
2.	Density of dehydration figure increases.	It is nearly constant, for successive etching.
3.	Movement of cleavage lines on dehydration is not observed.	Movement of cleavage lines on etching is observed.
4.	Dehydration is accompanied by a change in structure.	No structural change is observed.

Table 9.1 continued:

5.	Size of dehydration figures increases with dehydration period.	Size of chemical etch pits increases with etching time.
6.	Matching of dehydration figures on cleavage counterpart is not observed.	Matching of chemical etch pits on cleavage counterpart is observed.
7.	Chemically etched surfaces and untreated surfaces behave in the same manner for thermal dehydration.	Thermally dehydrated surfaces and untreated surfaces donot show identical behaviour for chemical etching.

It is hard to explain the occurrence of dehydration figures on selenite cleavages on the basis of the observations on matching of cleavage counterparts and successive etching of isolated cleavages only. However, when a dehydrated surface was compared with a counterpart chemically etched by an etchant, it was crystal clear about the mismatching of dehydration figures with chemical etch figures on crystal surfaces. Further the density of dehydration figures is less than that of chemical etch pits produced by an etchant. Since chemical etch pits are produced at the sites of dislocations ending on the surface (Bright and Ridge, 1961; Patel and Raju, 1969), it is very likely that dehydration figures are formed at impurity centres on the crystal surface. This view is supported by the experimental observations that when a dehydrated crystal was chemically etched the density of etch pits is reduced by a factor of 100. This can happen only if the dislocations revealed by chemical etching diffuse during dehydration towards impurity centres where dehydration figures are produced. Further for a very long induction period it is reported that structure of the selenite crystal also changes. This shows that a mechanical stress is generated in the crystal during dehydration as a result of which the mobility of dislocation increases, and these dislocations will move at those places which are relatively highly strained. Hence, when a chemically etched surface is dehydrated, dehydration figures are formed at those points where comparatively large pyramidal etch pits with rhombic outline on the surface were found on earlier etching. For a chemical etchant revealing dislocations it has been shown that cleavage lines shift on etching. However this is not found to be the case of a dehydrated crystal. This also supports the contention that dehydration figures are in all probability formed at the impurities.

9.5 Conclusions:

(1) The lowest temperature at which dehydration of the selenite initates is 86°C.

(2) It is difficult to obtain reversibility of dehydration figures because water or water vapor also acts as an etchant on selenite cleavages.

(3) Cleavage lines do not move during thermal dehydration.

(4) Dislocations appear to diffuse towards impurity centres during dehydration of selenite.

(5) Dehydrations figures are formed at impurity sites and not at dislocations.