PART I

GENERAL INFORMATION ON CALCITE AND EXPERIMENTAL TECHNIQUES.

CHAPTER 1

GENERAL INFORMATION ON CALCITE CLEAVAGES.

1.1 Introduction:

In the entire mineral kingdom, next to quartz no species are more abundant, wide spread or beautiful than calcite. The mineral by virtue of the size, abundance and perfection of its crystalline structure and its remarkable complexity of habit has attracted the attention of crystallographers and has played a prominent role in the history of mineralogy. There is such a vast literature on calcite that it is very diffult 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 (1952), Dana and Ford (1951) and Rogers (1937) have given a nice account of calcium carbonate (calcite).

1.2 Occurrence:

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) in veins, cavities and amygdules, due to penetration of calcareous solutions, (2) as a cellular tissue of many phanerogamia, e.g. cycadeae and cactaceae, (3) as a rock forming minerals in the sedimentary cycles and in great thickness in relatively pure form as chalks and limestones, (4) as a biogenic mineral forming limestones, organisms such as mollyscas, branchiopads, corals and crinoids contributing their shells or other hard parts, (5) as a diverse form, calcareous sinter or tufa or travertine; the tophus of pling and the lapis fiburtinus of pling and vitruvius and formation of stalactites and stalagmites in caves, (6) as a paramorph after aragonite, calcite is the stable form of calcium carbonate under ordinary conditions.

1.3 Crystal Composition:

Calcite, a carbonate of divalent metal of calcium has a formula $CaCo_3$, (CaO lime 56.0%, carbon dioxide 44.0%). Natural calcite is very nearly pure calcium carbonate. Small quantities of Mg, Fe, Mn, Zn and Pb may be present replacing the calcium.

Calcite is the stable form of calcium carbonate at ordinary pressure and over a large temperature range. The metastable polymorphous are known such as aragonite and vaterite. These polymorphous change irreversibly to calcite on being heated. The occurrence of a form known as α-calcite, (elatolite) stable at high temperature has been disproved.

Calcite by virtue of its relatively high chemical reactivity and ready solubility in carbonated water is very commonly found and 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. The limits of variation in the indices of refraction, specific gravity, unit cell dimensions and crystal angles accompaning variation in composition are not fully established, especially in the polycomponent systems.

1.4 Calcite Group And Its Structure:

The anhydrous carbonates include two distinct isomorphous groups, the calcite group and the Aragonite group. The metallic elements present in the former are magnesium, iron, manganese, zinc and cobalt; in the later, are barium, strontium and lead. Calcium is common for both the group. The calcite group is

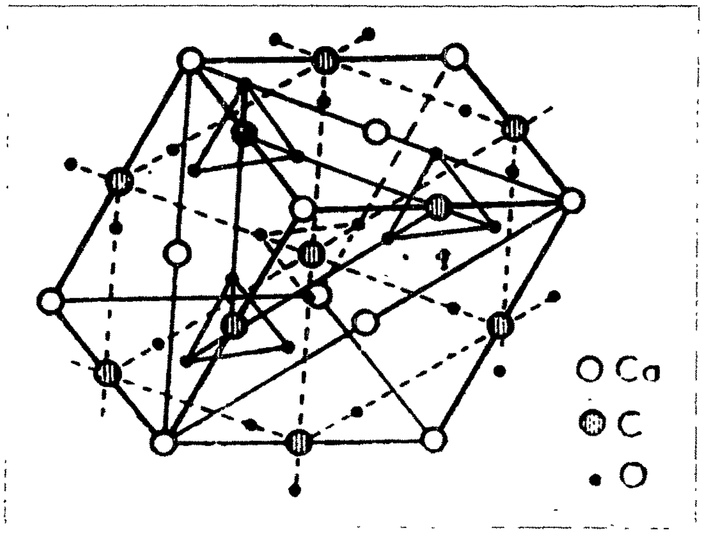


Fig.1.1

characterized by rhombohedral crystallization, perfect rhombohedral cleavage and the angle varying from 75° to 73°.

The crystal structure of calcite, one of the earliest studied by X-rays, was described by Bragg in 1914. He later on derived (1924) the optical properties of both calcite and its polymorph aragonite in terms of the atomic structure. In the figure 1.1; calcium atoms are represented by blank circles, carbon atoms by lined circles and oxygen atoms by black circles. The calcite lattice may be regarded as a deformed rock salt lattice. The later 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 central carbon atoms surrounded by an equilateral triangle of oxygen atoms in a plane at right angles to diagonal, (i.e. the plane of the paper). On account of the space occupied by these ions, the cube expands in a horizontal direction and forms the cleavage rhombohedral of calcite. Calcium and carbon atoms are spaced at equal intervals along the crystal axes. In contrast to other XO_3^{--} ions (e.g. NO_3^- ClO_3^- etc.) the carbonate ion CO_3^{--} is having a planer structure. The distance between central carbon atom to oxygen atom is $1.23\ A^{\circ}$ while each side of equilateral triangle (made by oxygen atoms) has a length of 2.13 A^o.

1.5.1 Form And Habit:

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

Crystals show four distinct habits (1) rhombohedral, (2) prismatic, (3) scalenohedral and (4) tabular. Calcite is the typical example of the hexagonal scalenohedral class, embracing some of the finest, the 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 rhomohedral being very frequently the dominant form in the combinations. Calcite, quartz, apatite, etc. are most remarkable for their outstanding size in the mineral kingdon. Special names have been given to the more peculiar habit of calcite for instance, there are the so-called dog-tooth spar, nail-head spar and satin spar. It is a fibrous variety with a silky lustre resembling the satin spar variety of gypsum, the later is harder than the former. There are several varieties of minor importance which have been named after some admixture or the color, use of locality and do not generally indicate important structural or chemical differences, for example dolomite, calcite contains manganese carbonate and is known as mangano-calcite, ferro-calcite containing ferrous carbonate and calcite etc.

1.5.2 Cleavage, Gliding And Twinning:

It has a perfect rhombohedral cleavage, a cleavage in three directions at oblique angles (74^{o} 55') to each other, and is susceptible to abrasion or scratching. Some crystals exhibit areas upto 0.2 mm x 0.2 mm free from cleavage lines. Over such an area the crystals appear to have cleaved true to a single molecular plane (Tolansky and Khamsavi, 1946). The cleavage spacing between rhombohedral faces is 6.1 A^{o}. 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 excercised in handling them. There is often parting parallel to $\{01\bar{1}2\}$ and this is sometimes better developed than the cleavage itself. Some specimens of calcite show parting parallel to $\{0001\}$. Fracture is conchoidal but difficult to produce, since it is brittle.

Four twinning laws are known for calcite (1) Twin plane $\{0001\}$ as the composition surface. Re-entrant angles are about the equator of the crystal except when bound laterally by $\{10\bar{1}0\}$, the twinning then revealed by cleavage or by the apparent horizontal plane of symmetry. (2) Twin plane $\{01\bar{1}2\}$ is very common with $\{01\bar{1}2\}$ as the composition face. This is often known as polysynthetic twinning with striations parallel to the long diagonal. (3) Twin plane $\{10\bar{1}1\}$ is not common with composition surface $\{10\bar{1}1\}$. The twinned individuals have their axes nearly at right angles and also have a cleavage plane in common. (4) Twin plane $\{0\bar{2}21\}$ is rare with composition plane $\{0\bar{2}21\}$.

1.53 Percussion Mark:

The results of the study of the impact of solid polished steel spheres on the optically polished surfaces (or cleavages) of calcite show that the general nature of the effects observed is a characteristic property of the crystal itself and is related both to the structure of the crystal and to the orientation of the face on which the impact occurs.

It is observed from the study that on either side of the area of contact between the impinging sphere and the crystals, two cleavages making an obtuse angle (102°) with each other developed and extended outwards from the edges of that area (Fig. 1.2). These cleavages are clearly visible on the face of the crystal and they sharply limit the area within which fracture develops. Another interesting feature is the appearence 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 may be explained due to glides occurring within the crystal along the direction of a rhombohedral edge (Raman 1959).

Percussion mark can also be observed by a sharp, quick blow with a dull conical point on a calcite cleavage surface. The percussion mark is much helpful in determining the orientation of the crystal. 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 orientated oppositely with respect to the corner of the crystal, where the three obtuse angles meet. The line which is perpendicular to the series of parallel lines and passing through the

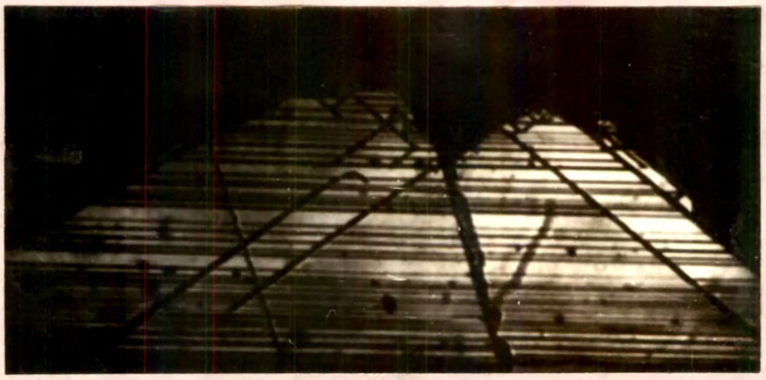
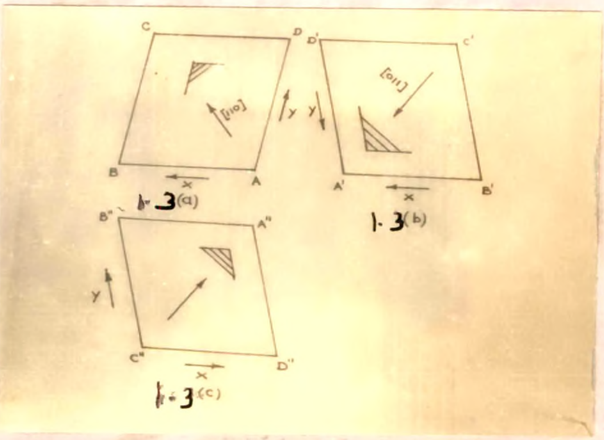


Fig. 1.2



Fig,.1.3

vertex of the triangle has direction [110] , which is also the line of symmetry for the cleavage surface and percussion mark. The figures on the matched cleavage faces are shown in the figures 1.3a, 1.3b and 1.3c. The calcite crystal is cleaved in the usual way and the matched cleavage counterparts are shown in figures 1.3a, 1.3b or figures 1.3a, 1.3c, depending upon the way in which they are placed side by side. The corners; where all three obtuse dihedral angles meet are A (fig. 1.3a), C' (fig. 1.3b) and C'' (fig. 1.3c). The percussion figures and the direction of the line of symmetry are also schematically shown in the figures. They are very important in the present studies, since with reference to them the orientation of etch pits and their boundaries are determined.

1.6 Properties Of Calcite Crystals:

For pure calcite specific gravity is 2.7102 (± 0.0002) at 20°C, but varies somewhat widely in impure forms as in those containing iron, manganese etc. It is usually colourless and transparent or white when pure. The colour varies from white to various pale shades of gray, red, green, blue, violet, yellow; also brown and black when impure. It may be translucent or opaque due to isomorphous substitution. Lustre is vitreous to subvitreous to earthy. Many specimens are fluorescent and often show phosphorescence upon heating and other luminescent properties upon being exposed to sunlight or radium emanations. Calcite is optically negative and birefringence is very high. Refractive indices for sodium D line are N_o = 1.658 N_e = 1.486 (Bragg, 1924). Birefringence is due to the different polarization of oxygen atoms in different directions. Several workers have determined birefringence of calcite at several visible wavelengths and at different temperatures (See for example Smartt and Steel, 1959).

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 $\{10\bar{1}0\}$. Calcite decomposes into calcium oxide and carbon dioxide at 850° C and it melts near 1289° C under a pressure of 110 atmospheres.

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 carbon dioxide it dissolves to some extent (1.56 gms at 0°C in a litre solution saturated by carbon dioxide at one atmosphere) 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 calcium carbonate can always be easily recognized by their easy solubility with brisk effervescence in cold diluted acids, the properties possessed by no other common minerals resembling calcite.

1.7 Uses:

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. An excellent account on calcium carbonate and its multifarious uses is given by Searle (1935) and a physico-chemical survey of high grade Indian limestones is done by Bijawat and Sastri (1957). In the manufacture of mortars, cements, as a building and ornamental material calcite is used. It is also used as a fertilizer in the form of chalk. At the time of second world war, calcite was replaced by sodium nitrate in polarizing microscope, due to shortage of calcite. Since sodium nitrate is hygroscopic, precautions were taken to keep it free from moisture. However it could not completely replace the calcite crystals..