

Structural analysis of the most commonly encountered habit faces of calcite crystals from skarn deposits

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SUMMARY. This paper is a report on the various features of the crystallogenesi of calcite as shown in specimens collected from iron-ore skarn deposits. Although there are several forms, each showing a variety of habit, a detailed study shows that there is a unified sequence of successive habit substitution. A structural analysis of calcite based on P.B.C. (Periodic Bond Chain) vectors is then considered.

As a result of the search for a method of growing Iceland spar and of the possibility of using a calcite structure containing paramagnetic ions for creating lasers, great interest has been aroused in the peculiarities of calcite crystallogenesi. In this connection a study of the problems of the crystallogenesi of calcite under natural conditions is of vital importance.

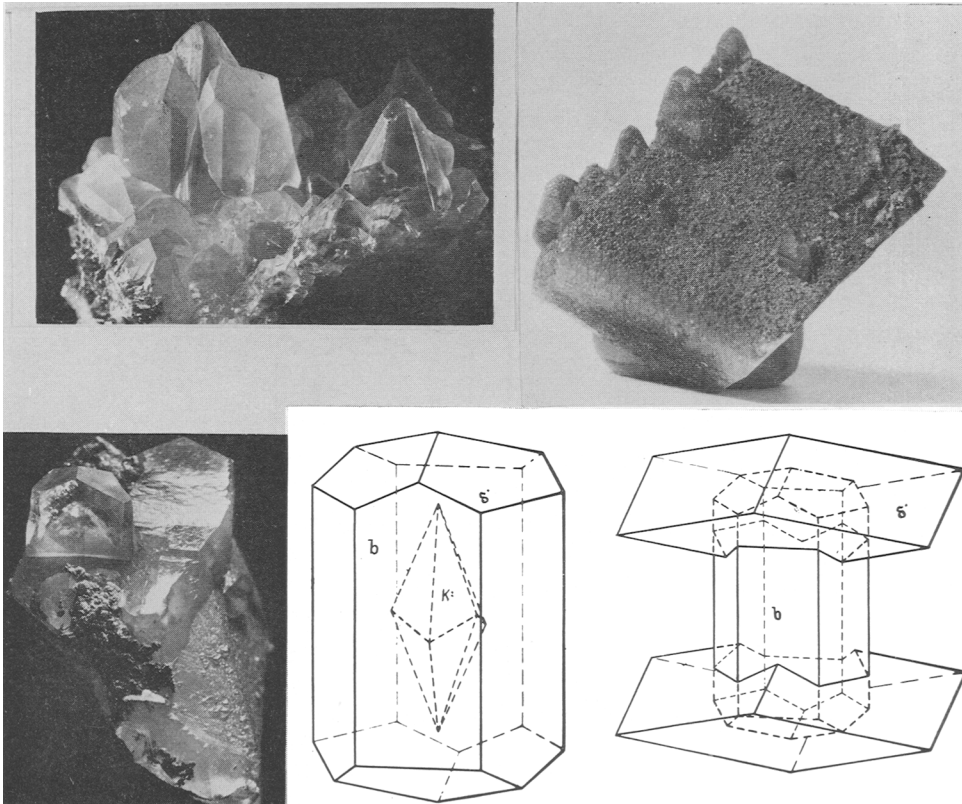
The authors (Aliev, 1969; Kashkai, 1965) carried out a prolonged investigation of a large number of calcite specimens collected from iron-ore skarn deposits at Dashkesan (Azerbaidzhan, U.S.S.R.) and also from the Kedabek group of deposits in Azerbaidzhan, the Sokolovsko-Sarbaiskaya group of iron ore deposits in Kazakhstan and Tetyukhinsky skarn polymetallic deposits of the Far East, etc.

These investigations have shown many features of calcite crystallogenesi common to all the deposits studied. Invariably the crystallization of calcite began during the later stages of skarn formation and continued throughout the stages of ore and ore-free mineralization. The various crystal habits developed show great diversification. For example, there are rhombohedral forms varying in habit from short to elongate, barrel-shaped to pole-shaped scalenohedra, and so forth.

A thorough investigation of specimens from the Dashkesan deposits shows certain regularities in the order of formation of habit forms (figs. 1-4), whilst a study of specimens from other deposits made it possible to set up a unified series of successive substitutions of habit forms during the process of crystal growth common to all the skarn deposits studied.

This series, in full accord with the data found in the literature, lists the following order of habit substitution: $\{0001\} + \{10\bar{1}1\}$, $\{10\bar{1}1\}$, $\{21\bar{3}1\}$, $\{10\bar{1}0\} + \{0001\}$, $\{10\bar{1}0\} + \{01\bar{1}2\}$, $\{01\bar{1}2\}$, $\{02\bar{2}1\}$.

Transition from one form to another may be sudden (where there has been a stop



FIGS. 1-4: Fig. 1 (top left). Selective incipency of later negative scalenohedral calcite crystals according to $\{4.16.\bar{2}0.3\}$ on the earlier scalenohedral crystals according to $\{21\bar{3}1\}$. The crystals of later generation are formed only on the three blunt edges of the scalenohedron. Parallel orientation. $\frac{4}{5}$ natural size. The large crystal on the photo is rotated at 60° around $[0001]$ axis. The facet $\{02\bar{2}1\}$ is seen on the earlier crystal as a narrow band. Fig. 2 (top right). The growth of scalenohedral habit according to $\{21\bar{3}1\}$ of calcite crystals of later generation on the early rhombohedral crystal according to $\{10\bar{1}1\}$. Parallel orientation. $\frac{4}{5}$ natural size. Fig. 3 (bottom left and centre). The growth of prismatic crystals with $b\{10\bar{1}0\}$ and $\delta\{01\bar{1}2\}$ on the earlier crystals with the scalenohedral $k\{21\bar{3}1\}$ habit faces. Parallel orientation. $\frac{4}{5}$ natural size. Fig. 4 (bottom right). The growth of rhombohedral calcite crystals according to $\delta\{01\bar{1}2\}$ on a prismatic crystal of earlier generation with $b\{10\bar{1}0\} + \delta\{01\bar{1}2\}$. Parallel orientation.

or other sudden change in the process of crystallization) or may be gradual. In this latter case a rich variety of other forms may appear complicating the external form of the crystal.

This paper is restricted to a study of the habit forms most frequently encountered in skarn deposits, together with the negative scalenohedron $\{4.16.\bar{2}0.3\}$. This scalenohedron, despite the high value of its indices, was of not uncommon occurrence. A characteristic of its faces was their high degree of perfection, which, on the goniometer, made possible a high degree of accuracy in the determination of the form symbol.

Since, as has been recently accepted by many authors, the form of crystal growth is conditioned by the bond energy within the rows and structural chains of the space lattices, then the working hypothesis suggested by Hartman and Perdok (1952, 1955) forms the basis of the most convenient method of face determination and is in full agreement with the fundamental principles of the molecular theory of crystal growth (Kossel, Stransky, Kaister, and their school).

The morphology of many crystals of varying structural types can be accounted for by a structural analysis based on a study of P.B.C. vectors. By this method three face-types may be distinguished according to the location of periodic chains of strong bonds relative to the faces. They are *F*-faces (*f*lat), structurally the most important, *S*-faces (*s*tepped), which are less important, and *K*-faces, (*k*inked), which are seldom, if ever, observed.

In calcite with the space group $D_{3d}^6 = R\bar{3}c$, the flat triangular carbonate radicals $(\text{CO}_3)^{-2}$ are characterized by the preferentially strong covalent bond (by means of hybridization electrons sp^2) and only to a much lesser extent by ionic bonding. These anions are then linked into the general structure by weaker ionic bonds with the calcium cations (fig. 5). As the carbonate ion is an independent building unit the P.B.C. directions of importance during the growth of the calcite space lattice are parallel to the edges of the cleavage rhombohedron and to the vertical rows parallel to the zone axis $[0001]$ (fig. 5). Because of the relatively large spacing between particles in a direction parallel to $[0001]$ and of the considerable decrease in bond energy for negligibly small increases in this spacing, it follows that the influence of P.B.C.s parallel to $[0001]$ is insignificant in comparison to those parallel to the edges of the cleavage rhombohedron. Thus the only *F*-faces for calcite are the faces of the cleavage rhombohedron with two P.B.C.s involved in their structure, whilst $\{21\bar{3}1\}$ and $\{01\bar{1}2\}$ are determined as *S*-faces, and $\{0001\}$, $\{10\bar{1}0\}$, and $\{02\bar{2}1\}$, together with $\{4.16.\bar{2}0.3\}$ are *K*-faces.

According to Hartman (1966), if the influence of external factors is not considered, the faces of crystal growth must be exclusively formed by *F*-faces. Thus the presence of external factors during crystal growth is indicated by the presence of *S*- and more especially *K*-faces.

Kern (1953, 1955) found by experiment that *K*-faces often appear in the region of certain values of supersaturation, whilst Kleber (1957 *a* and *b*), investigating the structure of such faces, established that *K*-faces are most strongly developed at high degrees of supersaturation and are characterized by the maximum number of P.B.C. vectors crossing the face per unit of area. In many such cases these faces were found to be *K*-faces possessing the highest d_{hkl} values (Hartman, 1966) and consequently the greatest atomic density.

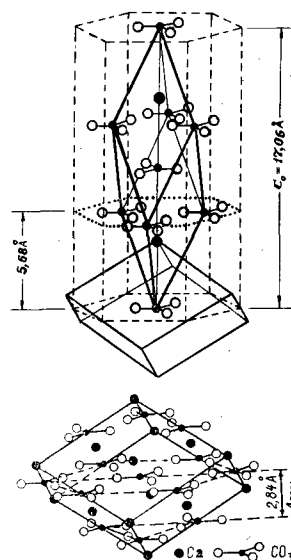
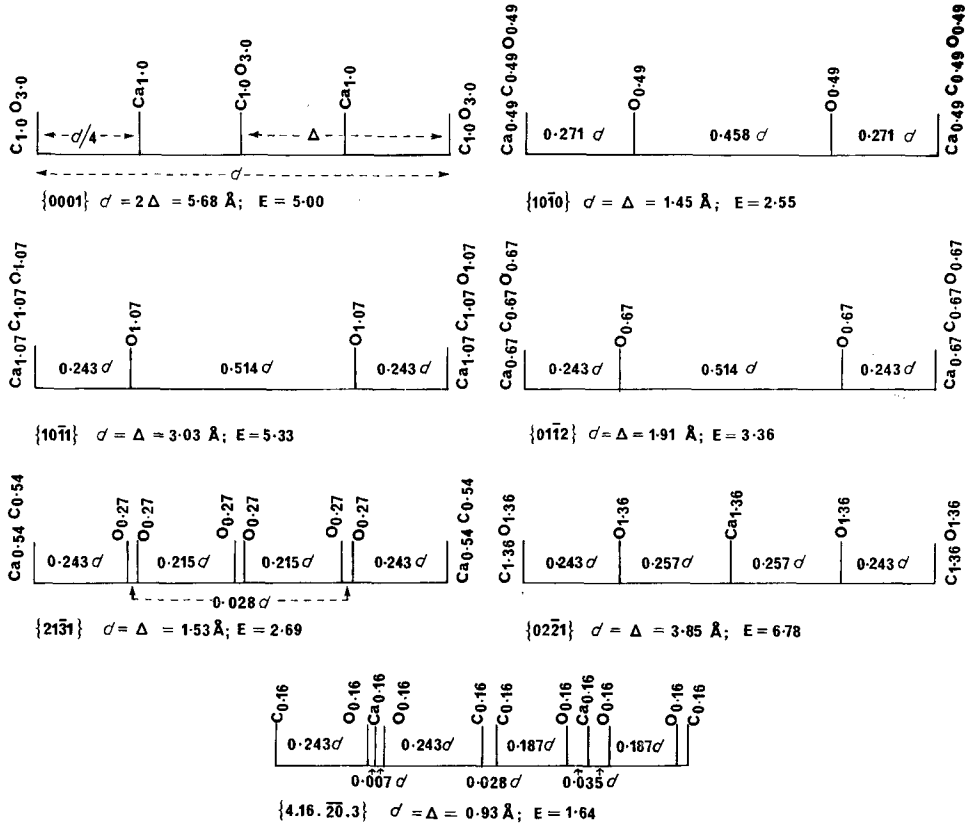


FIG. 5. Crystal structure of calcite.

Table I gives the structural schemes of the calcite faces considered and shows both their d_{hkl} values and atomic densities. In addition the table shows the density for certain planar nets of the space lattice. The indices of the chemical elements give the density of the planar net according to the type of atom given. The table is in full

TABLE 1. The structure of some faces of the habit forms of calcite crystals



agreement with the principles of structural-geometrical analysis according to N. Z. Evzikova (1964, 1965). Details of the procedure of this analysis can be found in these papers and in the paper by Aliev and Evzikova (1969).

As will be seen from table I, $d_{0001} = 5.68 \text{ \AA}$ and involves four planar nets. One of these is a planar net set with planar triangular divalent negative carbonate radicals, i.e., its composition is $\text{C}:\text{O} = 1:3$. This net has a very high electrostatic field. The next planar net, at a distance of $d_{0001}/4 = 1.42 \text{ \AA}$ from the first is qualitatively and quantitatively of a quite different composition, consisting of only one calcium ion. The third and fourth planar nets are identical with the first and second nets respectively.

In the same way that the atomic structure of calcite as a whole is characterized by

an elementary cell, so the atomic structure of its pinacoidal face will be characterized by the infinite amount of layer with $\Delta_{001} = 2.84 \text{ \AA}$ in thickness consisting of two planar nets each with the composition C:O:Ca = 1:3:1. This is an elementary layer of the face (0001), with an atomic density of 5.

The table also shows the atomic structure and relative densities of the other faces.

The evaluation of atomic densities for a large number of observed possible calcite forms shows that *K*-faces listed above as habit forms are in fact characterized by high values of density and d_{hkl} . This is consistent with the aforementioned data (Hartman, 1966). It should be noted that in spite of the high values of the indices of the form $\{4.16.\overline{20}.3\}$, it in fact has a greater density than the faces with simple indices such as $\{10\overline{1}2\}$, $\{11\overline{2}1\}$, $\{12\overline{3}0\}$, $\{12\overline{3}1\}$, etc.

It should also be noted that the application of the method of Donnay and Harker (1937, 1940) to calcite gives as morphological aspect for calcite $\{11\overline{2}0\}$, $\{10\overline{1}1\}$, $\{12\overline{3}1\}$, $\{10\overline{1}0\}$. The strong development of the prism $\{11\overline{2}0\}$ (at the head of the list) has often been observed by other authors on calcite from deposits elsewhere, but the present writers did not observe it as a habit form on calcite crystals from the skarn deposits. In this connection it is worth noting that faces of this form are of the *K*-face type but are characterized by rather high values of atomic density, $E_2 = 4.39 \text{ \AA}$ ($d_a = 2.49 \text{ \AA}$).

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