SOME INSTANCES OF INCRUSTATIONS SELECTIVE UPON CRYSTAL FORMS

By Clifford Frondel

STILBITE INCRUSTING APOPHYLLITE

An incrustation localized to a particular form of the incrusted crystal is shown by a specimen of apophyllite from Bergen Hill, New Jersey, contained in the collection of The American Museum of Natural History (Cat. No. 12690). The specimen consists of a slab of altered diabase about 14×17 cm. in size with its surface incrusted by datolite, calcite, apophyllite and stilbite, the sequence of deposition being in the order given. The apophyllite crystals are formed of (100), (111) and (001), the larger crystals being tabular parallel (001), and comprise about 20 individuals, the largest measuring 4 cm. across the prism. The (001) form of the crystals is incrusted by stilbite which is lacking or forms only a few isolated crystals on the faces of (100) and (111). Apophyllite crystals attached to the matrix by their sides show the incrustation at both ends. The stilbite, which incrusts both the datolite and the apophyllite, being selective with regard to forms only on the latter, is also peculiar in that when incrusting datolite the crystals are large (4–12 mm.) and scattered and are attached randomly. On the base of the apophyllite, however, the stilbite forms a dense crust of small (1–2 mm.) crystals which are oriented with their vertical axes perpendicular, or approximately so, to the apophyllite surface. The few stilbite crystals noted upon (100) and (111) are also relatively large and of random orientation to the incrusted surface.

Other apophyllite specimens from Bergen Hill and other localities were observed in the collection in which the crystals were incrusted by stilbite, but these did not show selectivity upon the forms. Laumontite, analcite, natrolite, stilpnomelane, calcite and pyrite were also observed indiscriminately incrusting the forms of apophyllite. A specimen showing stilpnomelane selectively incrusting the forms of datolite crystals, from Snake Hill, N. J., is contained in the collection and is to be described.

1An incrustation of stilbite selective upon the forms of a datolite crystal from Great Notch, N. J., has been described by C. W. Cook and E. H. Kraus (1915, Amer. Jour. Sci., Ser. 4, XXXIX, p. 643).
Structurally apophyllite can be compared to the zeolites, with which it is sometimes classed, and in which, as typified by analcite, the relatively open but strongly bonded anionic framework permits the passage of cations in base exchange and of water in dehydration or hydration through the meshes of the structure without destruction of the crystal. The structure of natrolite is such as to allow the movement of water in dehydration or sodium ions in base exchange through channels along (001), and, similarly, the speed of diffusion of water into dehydrated heulandite has been experimentally determined to be greater for (001) than for other forms. The natural alteration of apophyllite to albin in which Ca is substituted into the structure is observed to start on the basal plane and to proceed thence into the interior, with the prism and other forms not being altered directly. The alteration appears as a white opaque layer extending into the crystal from the surface of (001). Basal plane alterations in various stages of development were seen on apophyllite specimens from Bergen Hill, West Paterson and Great Notch, N. J., Nova Scotia, and other localities. The nature of the chemical change in these instances is unknown. An incipient, paper-thin, alteration of this kind is developed on the specimen described underneath the stilbite incrustation.

The vertical direction in apophyllite is also the one of most rapid attack by solution. The difference in rate of solution relative to other directions is quite pronounced. Cornu notes that (111) is between (100) and (001) in resistance to solvents. A selective etching of (001) is not infrequently seen on natural crystals.

The basal plane of apophyllite when examined under the microscope shows a markedly composite structure. This is true to a much lesser extent of (111) while (100) is generally smooth and lustrous, although strongly striated.

The tendency for localization of the stilbite deposition to the basal plane of the apophyllite is believed to reflect the strong adsorption of substance upon that plane from a solution capable of depositing stilbite and in which solution the datolite, calcite and the (100) and (111) forms of apophyllite were weakly or non-adsorbing. The effect of the adsorption is to facilitate the formation of crystal nuclei upon the adsorbing surface and, with the crystallization of the stilbite solution, the (001)

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6 Cornu, F., op. cit., p. 211.
7 Freundlich, H. 1926. 'Alexander's Colloid Chemistry,' New York, 1, p. 588.
surfaces will tend to become incrusted in preference to the adjacent (100) and (111) surfaces. The thin white altered layer of apophyllite noted as forming the surface of (001) is probably in genetic relation to the stilbite deposition and may then represent a diffusion of the adsorbate into the crystal. The densely packed nature of the incrustation upon (001) and the small size of the crystals point to closely spaced centers of crystallization, and the tendency of the stilbite crystals to orient themselves perpendicular to (001) suggests an orientation of the adsorbate at the interface.

Efforts by the writer to form selective crystallizations of various salts upon (001) by using large well-formed apophyllite crystals as nuclei in the crystallizing solution have not yet proven successful. What amounts to a selective crystallization of sodium nitrate upon the forms of calcite has been obtained experimentally by Settele.\(^1\) Sodium nitrate is strongly adsorbed by calcite and readily forms parallel growths upon it, the two substances being isomorphous. By using a polished sphere of calcite cut from a single crystal, Settele obtained six isolated groups of oriented sodium nitrate rhombohedrons upon its surface, each group of crystals being centered above the poles of (10\(\overline{1}\)), that is, at (1011), (1101), (0111) 0111), (1011) and (1101), the surface of the sphere representing the spherical projection. This method shows directly that under the conditions of the experiment calcite crystals composed of (1011) and any other form or forms will be selectively incrusted by sodium nitrate upon (1011). Conversely, calcite crystals grown from solutions containing sodium nitrate will tend to assume the (10\(\overline{1}\)) habit. This sphere method should be applicable in determining the influence of adsorption on the crystal habit of mineral species whose chemical nature is such as to prevent an experimental investigation by direct crystallization from a solution containing additives.

HEMATITE FILMING CALCITE

A suite of 19 specimens from West Paterson, New Jersey (Cat. Nos. 19657: 1–13; 19697: 1–4; 12712, 17549), presents drusy surfaces of small quartz crystals implanted on altered diabase, associated with calcite, babingtonite and zeolites. The quartz crystals are peculiar in that their forms are selectively filmed by red hematite of colloidal origin, the film generally being present on (10\(\overline{1}\)) and (10\(\overline{1}\)) and absent from (0111)\(^2\), and the calcite crystals associated with them are likewise selectively filmed by the hematite. The calcite crystals are white and trans-

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\(^2\)Frondel, C. 1934. Amer. Min., XIX, p. —.
lucent, running between 2 and 6 mm. in vertical length, and about a hundred distinct crystals are developed on the specimens.

The habit of the crystals is highly complex and is characterized by a strongly marked zone of negative rhombohedrons, usually limited by the basal pinacoid, and three well-marked zones of scalenohedrons. Their crystallography has been studied by Whitlock\(^1\) and the reader is referred to his paper for a detailed description and figures of the crystals. The habit of the crystals varies in minor respects on different specimens, and single crystals do not present all the observed forms, but the suite as a whole is closely integrated by the zonal relations of its forms and represents, in its entirety, a generation of calcite (Type V of Whitlock) distinct from other generations of calcite that can be distinguished in the zeolite occurrences of the New Jersey diabase region. The forms present on the most common habit and which may be said to represent the generalized habit of the suite (Combination 15, Fig. 20, of Whitlock) are tabulated in Table 1, together with minor variants of this habit (Combination 16, Fig. 21, and Combination 17, Fig. 22, of Whitlock) on which additional new or rare forms are developed. The forms (15.8.23.10) and (15.8.23.13) may be vicinal to (8.4.12.5) and 8.4.12.7). Crystals which approach Combination 17 in habit are relatively few.

The form (0221) is present on all of the crystals and in all of the combinations was observed to be filmed by red hematite in preference to the other forms. The film is present on all but a few of the hundred or so crystals present on the specimens. The film is rather less intense than on the associated quartz crystals, where it has a deep red or brick-red color, and in many instances the faces of (0221) appear only as faint rose-colored areas. It is closely adherent to the surface and cannot be removed without injury to the calcite; the film on the quartz can be rubbed off by using pressure. The edges of the filmed faces are generally strongly marked by a deep red line of hematite, and this edge deposition seems to represent the initial stage of formation of the film.

The origin of the film is ascribed to the selective adsorption of colloidal hydrous ferric oxide from a sol which bathed the crystals in the druse at some time after the completion of their growth. Four other instances of colloidal hydrous ferric oxide selectively filming calcite have been mentioned elsewhere.\(^2\)

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\(^2\)Frondel, C., op. cit.
MARCASITE INCURSTING CALCITE

J. E. Pogue\textsuperscript{1} has described a marcasite incrusted calcite from Joplin, Missouri, which shows a peculiar arrangement of the incrustation with respect to the calcite forms. The crystal is a large honey-yellow individual showing the scalenohedron (2131) modified by faces of (5164), (6178) and (1011). The marcasite is present only on (2131), and the incrustation on the faces of this form extends only to within 4 mm. of the edges between it and (5164). Here the boundary of the incrustation forms a sharp even line running parallel to the edge to within a few mm.

of the acute edges of (21\overline{3}1) where it bends down sharply in a direction roughly parallel to the cleavage and intersects the edges at a sharp angle.

Study of a suite of crystals from Joplin similar to the crystal described by Pogue shows that the features of his specimen are not due to a selective action exerted by the calcite forms over the marcasite deposition, as would appear, but to a complete incrustation of the surface of the crystal followed by a partial overgrowth of calcite which hid from view part of the incrustation. These specimens are large modified scalenohedrons with an inner phantom completely incrusted by marcasite visible under the surface of the terminating forms. The overgrowth took place only on the terminating forms of the early crystal so that the original surface of (21\overline{3}1) with its marcasite incrustation forms part of the present surface of the crystal. In view of this, the boundary of the marcasite incrustation on Pogue’s specimen traces the edges of incrusted forms earlier present on the crystal and later overgrown. The reentrant angles along the acute edges of (21\overline{3}1) evidently mark the edges of small faces of a negative rhombohedron or scalenohedron that was suppressed during the overgrowth. The crystal nuclei of the marcasite were carried against the calcite by a current, as is evidenced by a tendency for concentration of the marcasite on one side of the crystals; this was also noted by Pogue.

This same feature is illustrated by a calcite specimen from Bergen Hill, New Jersey (Cat. No. 6975), which shows stubby crystals composed of (10\overline{1}1) and (21\overline{3}1) with their entire surface colored brick-red by earthy hematite. The faces of (10\overline{1}1) were later overgrown by white opaque calcite which nearly completed (21\overline{3}1) and formed a white crystal with a central zone of red calcite.