SELECTIVE INCRUSTATION OF CRYSTAL FORMS

Clifford Frondel, *Bayside, Long Island, New York.*

SUMMARY

A number of instances of crystals which have had a particular form, or group of forms, covered by a super-deposited mineral while other forms on the crystal were not incrusted, have been described in the literature. A search of the mineral collection of the American Museum of Natural History has revealed further instances of selectivity in incrustation of this kind. The placing of the super-deposited mineral can be referred to the adsorption processes operating at a crystal-solution interface, the selectivity being due to the varying adsorptive power of the different forms as their structural makeup varies with their crystallographic orientation. Two general types may be recognized on the basis of the mode of deposition of the incrusting mineral: (a) a type represented by crystals which have selectively adsorbed during, or after completion of their growth, colloidal particles of another substance, and (b) a type resulting from the selective adsorption of a substance from true solution on the forms of a crystal which has completed its growth, followed by its crystallization on the form or forms in question.

DESCRIPTION OF SPECIMENS

One of the clearest examples of selectivity in deposition on crystal forms has been described by Haworth,[1] who found calcite crystals from Potosi, Missouri, showing the scalenohedron $(13\bar{4}1)$ modified by faces of $(21\bar{3}1)$ and $(02\bar{2}1)$ (?), with a surface film of amber colored ferric oxide (probably limonite) on the modifying form $(21\bar{3}1)$ and not on the others. As the film became thicker with increasing deposition, as shown on other specimens, it is noted that the rhombohedron $(02\bar{2}1)$ was covered next, leaving only $(13\bar{4}1)$ clean, and that the limonite covered the whole crystal only "after it became so abundant that the molecular force of the calcite could no longer control it." Haworth also speaks of the "molecular control exerted by the calcite" and of "the controlling force a crystal has over the molecules of a . . . [substance depositing] . . . on it." A similar instance of selectivity has been described on a calcite crystal from a hematite deposit in the Glenariff Valley, Co. Antrim, Ireland.[2] The crystal is composed largely of the scalenohedron $(13\cdot 11\cdot \overline{24}\cdot 2)$ with small modifying faces of the rhombohedrons $(10\bar{1}1)$, $(02\bar{2}1)$ and $(40\bar{4}1)$. Part of the scalenohedral faces are overgrown by a thin layer of calcite showing oscillatory faces of $(13\bar{4}1)$ and $(16\bar{7}1)$. The form $(02\bar{2}1)$ is selectively covered by a

---

[1] Haworth, E., *Proc. Iowa Acad. Sci.*, vol. **1**, Pt. 2, p. 35, 1892.

[2] O'Rielly, J. P., *Proc. Royal Dublin Soc.*, vol. **4**, p. 43, 1885. Plate II.

strongly marked film of iron oxide and its faces appear as red bands or stripes on the crystal. What is apparently another instance of this kind has been described by Farrington[3] on a calcite crystal from the Crystal Palace Mine, Central City, Missouri. The crystal is formed largely of $(05\bar{5}3)$ and $(01\bar{1}2)$ with the modifying forms $(40\bar{4}1)$ and $(21\bar{3}1)$. All of these, with the exception of $(01\bar{1}2)$, are stated to be coated with a thin firmly adhering layer of chocolate brown iron oxide. No specific remark is made of the selectivity.

Cook and Kraus[4] have described a datolite crystal from Great Notch, N. J., with the forms (102), (110), (012) (011), (100), (111), and $(\bar{1}12)$ in which the first four forms cited are incrusted by a thin layer of stilbite (?) and the other forms left unincrusted.

An instance has been mentioned by Miers[5] where galena crystals incrust in parallel position the prism faces of a bournonite crystal but do not incrust the base. The habit of the galena is not stated. A specimen showing the reverse of this—bournonite selectively incrusting the forms of galena—has been described by Hintze.[6] Here a galena cubo-octahedron from Przibram, Bohemia, has its cube faces heavily coated by small crystals of bournonite, oriented to the galena, while on the octahedral faces the incrustation is almost lacking.

A tendency for albite to form parallel growths on only certain forms of orthoclase crystals, particularly the prism (110), has been noted by many observers.[7] Goodchild briefly ascribed the selectivity in this case to a difference in "surface tension" of the orthoclase faces.[8]

The oriented growths of quartz on calcite crystals also show a preference for deposition on certain of the several crystal forms that may be available.[9] These forms are usually $(01\bar{1}2)$ or $(10\bar{1}1)$;

---

[3] Farrington, O. C., *Field Columbian Mus., Geol. Ser.*, vol. **3**, p. 141, 1908, Pl. XLVIII, Fig. 1.

[4] Cook, C. W., and Kraus, E. H., *Amer. Jour. Sci.*, ser. 4, vol. **39**, p. 643, 1915 with fig.

[5] Miers, H. A., *Min. Mag.*, vol. **11**, p. 268, 1897.

[6] Hintze, C., *Zeit. Kryst*, vol. **11**, p. 606, 1886, with fig.

[7] See in particular Mügge (*Neues Jahrb, Beil.-Bd.*, vol. **16**, p. 432, 1903), who cites a number of instances; also G. Rose, *Pogg. Annalen*, vol. **80**, p. 123, 1850, and A. Knop, *Neues Jahrb.*, p. 53, **1858.** Goldschmidt's Atlas der Krystallformen shows many examples (Band 3: Tafel 172, fig. 73; T. 176, f. 124; T. 178, f. 153, 161; T. 183, f. 231, 242; T. 187, f. 301).

[8] Goodchild, J. G., *Proc. Royal Soc. Edinburgh*, vol. **24**, p. 324, 1902.

[9] Mügge, O., *op. cit.*, pp. 370–3.

however, Solly[10] has described a clear-cut case where the quartz (unoriented) coats $(21\bar{3}1)$ of a crystal composed of $(21\bar{3}1)$ and $(10\bar{1}1)$ and leaves the latter form clean.

Two rather doubtful instances of pyrite selectively incrusting the forms of calcite have been described. Young[11] found calcite crystals from the Rand, South Africa, apparently consisting of a scalenohedron terminated by a steep rhombohedron, no definite description being given, in which the outer zone of the calcite contains innumerable minute crystals of pyrite which give the calcite a greenish tint. The pyrite has "very evidently been precipitated by preference on edges and corners of the crystals. . . . It is quite common to find the rhombohedral terminations wholly or partially covered by an aggregation of pyrite crystals." J. D. Dana[12] described calcite crystals from Rossie, N. Y., showing $(10\bar{1}1)$ modified by (0001), in which the basal plane is stated to have been incrusted by pyrite and then overgrown, in part or completely, by later growth of the crystal.

SPECIMENS IN THE AMERICAN MUSEUM

Many additional examples of the selective incrustation of crystal forms are contained in the collection of the American Museum of Natural History.[13] Some of the most interesting of these specimens will be briefly described under the following headings.

QUARTZ

A number of instances were observed in which quartz crystals had one of their terminating rhombohedrons—in all but one instance the positive $r(10\bar{1}1)$ rhombohedron—selectively filmed by another substance. A suite of 15 specimens from West Paterson, N. J. (grouped under cat. nos. 19657, 17549, 12712) presents drusy surfaces of small (2–5 mm.) colorless or faintly amethystine quartz crystals associated with calcite and zeolites. Hundreds of quartz crystals are shown. Each of the crystals has the surface of the positive rhombohedron covered by a dense film of bright red hematite particles while the negative rhombohedron is not filmed. The film on many of the crystals can be rubbed off by using pres-

---

[10] Solly, R. H., *Min. Mag.*, vol. **6,** p. 120, 1885.

[11] Young, R. B., *Trans. Geol. Soc. South Africa,* vol. **12,** p. 93, 1910.

[12] Dana, J. D., *Amer. Jour. Sci.*, ser. 1, vol. **46,** p. 33, 1844, fig. 2.

[13] More detailed papers describing this material are in preparation.

sure but on a few it is covered over by a later deposition of quartz. The quartz surface revealed by removal of the film is brilliantly reflecting and perfectly smooth. The prism faces of the crystals are only thinly filmed by the hematite and the deposition is plainly greatest along the prism edges (Fig. 1). On a number of the crystals the prism faces are not filmed at all. Twins in which the crystals have parallel axes and faces (twin plane $(10\bar{1}0)$) were observed in which small irregularly bounded areas of *r*$(10\bar{1}1)$ were inserted in *z*$(01\bar{1}1)$, in twin position, and were filmed over by the hematite while the remainder of the *z*$(01\bar{1}1)$ face remained clean. Areas of *z* twinned into *r* were also observed and these were free from deposition.

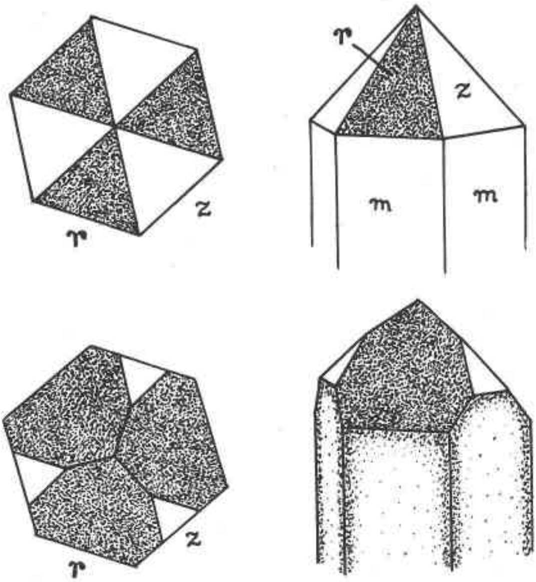

FIG. 1. Hematite (stippled) selectively filming *r*$(10\bar{1}1)$ of quartz. West Paterson, N. J. Amer. Mus. Nat. Hist., cat. no.'s 19657, 12712, 17549.

A second type of deposition on quartz, also with selectivity between the terminating rhombohedrons, is shown by two specimens from the pegmatite occurrences of North Carolina. One of these, from Burke Co., N. C. (cat. no. 3985), shows a 13 cm. quartz crystal which has included on the faces of the positive rhombohedron, during the last stages of its growth, an amount of colloidal clay material. The clay charged zone is cream-white in color and opaque, with an enameled appearance, and is about 1 mm. thick. The faces of the negative rhombohedron are the ordinary transparent quartz of the crystal. The clay substance is uniformly present over the entire surface of the faces of the positive rhombohedron, with the exception of irregular areas of the negative rhombohedron inserted in twin position which are free from deposition (Fig. 2). The crystal is right-handed and shows small faces of $s(11\bar{2}1)$ and $x(51\bar{6}1)$ and an unidentified negative rhombohedron, below z, all of which are filmed over. A second specimen, from Alexander Co., N. C. (cat. no. 3951), presents an appearance similar to the preceding specimen but differs in that it is the negative rhombohedron, judging from the relative size of the faces, that is filmed over. No readily determinable modifying forms or surface markings were observed to distinguish the forms and a further examination of this specimen is deferred to a later paper.

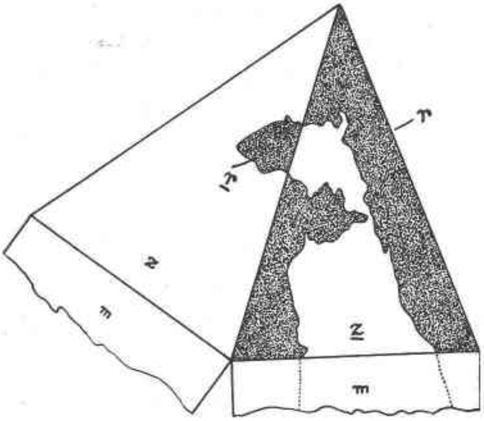

FIG. 2. Tracing of a single twinned insert (tw. pl. $(10\bar{1}0)$) of $\underline{z}$ in r and $\underline{r}$ in z showing deposition of the clay substance (stippled). Burke Co., N. C. Amer. Mus. Nat. Hist., cat. no. 3985. 2/3 natural size.

CALCITE

A group of calcite specimens from Guanajuato, Mexico (cat. nos. 6735, 6672, 6650), show large crystals of complex habit which are covered over by a thin continuous crust of dolomite not tightly adherent to the calcite surface. Removal of this crust reveals the original surface of the calcite to have been selectively covered by a very thin micro-crystalline layer of substance, dead-white in color.

Specimen 6735 shows a 5 cm. crystal with the forms $v(21\bar{3}1)$, $l(04\bar{4}5)$, $h(03\bar{3}2)$, $f(02\bar{2}1)$, $s(05\bar{5}1)$, $\beta(24\bar{6}1)$ and r⁝ $(35\bar{8}1)$, identified by contact measurements, of which the first three forms cited are incrusted and the last four not incrusted (Fig. 3). The incrustation is absent from an area about .2 mm. wide along the edges of the incrusted forms. The nature of the incrustation made its identification difficult but it is definitely either dolomite or calcite. Aragonite was identified as a uniform crust on other calcite specimens from this locality, without the association with dolomite, and it is possible that the incrustation may represent aragonite altered by paramorphism to calcite through the influence of the dolomite deposition.

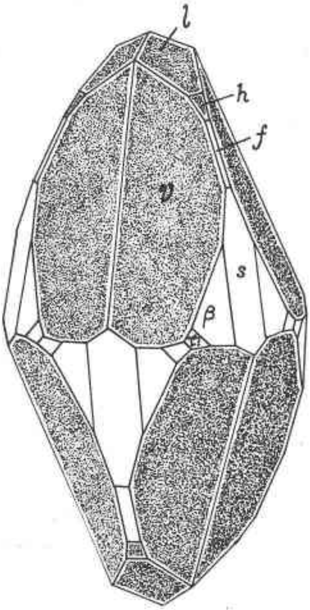

FIG. 3. Dolomite (?) (stippled) selectively incrusting the forms of a calcite crystal from Guanajuato, Mexico. Amer. Mus. Nat. Hist., cat. no. 6735.

A second type of selectivity on calcite is shown by a group of crystals from Rossie, N. Y. (cat. no. 7017) which consist of $v(21\bar{3}1)$ with $r(10\bar{1}1)$. The latter form is covered by a film of goethite (?), golden brown in color, and broken into minute flakes, which gives it a spangled appearance. This may have resulted from the desiccation of an iron oxide gel layer originally covering the surface. The goethite was deposited while the crystal was still growing as a rim of calcite, raised very slightly above the level of the goethite film, extends around the edges of the terminating rhombohedron (Fig. 4). This calcite does not extend over the goethite and the latter has evidently prevented the deposition of calcite over the area covered by it.

GALENA

Three instances were noted where galena cubo-octahedrons were selectively incrusted by other minerals. One specimen, from Gonderbach, Nassau, Germany, (cat. no. 870), shows about 40 small (up to 1 mm.) galena cubo-octahedrons scattered over a matrix of drusy quartz. On all but three or four of these crystals the cube faces are evenly and entirely covered by a thin granular layer of pyrite, while the octahedral faces have not received a trace of deposition. The remaining crystals are lightly incrusted by pyrite in a narrow area paralleling the cube edges while the interior of the cube face is clean. The crystals are notable for the brilliant and untarnished appearance of the faces and the sharpness of the edges and differ in these respects from most galena crystals.

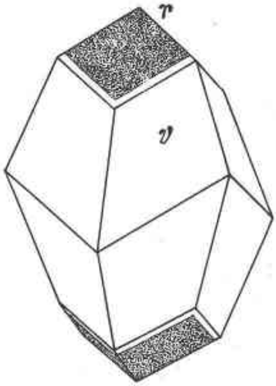

FIG. 4. Goethite (?) (stippled) selectively filming the forms of a calcite crystal. Rossie, N. Y. Amer. Mus. Nat. Hist., cat. no. 7017.

A second specimen, from Laasphe, Westphalia (cat. no. 891), shows a number of galena cubo-octahedrons, ranging in size from 1 to 3 cm., with the octahedral faces incrusted by a thin crust of chalcopyrite while the cube faces are clean. On the smaller galena crystals the incrustation is more intense and more uniform, forming a continuous dull rough surface; on the (111) faces of the larger crystals the incrustation is in scattered areas and forms in part irregular thread-like aggregates. Of the forty-odd crystals on the specimen about a dozen are free from incrustation or show only an incipient incrustation in the form of a narrow ridge of chalcopyrite on the octahedral edges. With increasing deposition the incrustation gradually extends into the octahedral faces. The cube faces are rather small and elongated and show the ordinary dull tarnish of the species.

Another instance of chalcopyrite selectively incrusting (111) of galena cubo-octahedrons was found on a specimen from Aini, Japan (cat. no. 18373). This specimen presents cubes, up to 4 cm. in size, with small octahedral modifications. The latter are plated by a smooth brightly reflecting layer of chalcopyrite similar to the chalcopyrite films sometimes seen on sphalerite and tetrahedrite crystals. It was noted on this and on the preceding specimen that the edges of some of the larger crystals had been slightly rounded or scalloped by solution before the formation of the incrustation.

ORIGIN OF THE SELECTIVITY

General Theory

The investigation of adsorption at crystal-solution interfaces has lagged somewhat behind that of the other kinds of interface and it is only in recent years, with the increase in knowledge of crystal structure, that this part of the field has seen any definite advance. While a complete knowledge of the factors that influence adsorption at this kind of interface is still far from being realized the primary cause of the phenomenon is firmly established in theory. This refers adsorption on a crystal surface to the existence of an open field of force at the surface of the crystal lattice, the field varying in intensity with the crystallographic orientation of the surface plane and its structural makeup, and the interaction of this field with the surface fields of molecules, ions, colloidal particles, etc., which may come into contact with the surface. The interior of the lattice is electrically neutral as the force field of each lattice unit is saturated by the surrounding units, however, the removal of certain lattice units from the interior of the structure may open up the force field in the interior and give it a holding power for foreign substances. The adsorption of gases, silver salts, alcohol, etc., by dehydrated zeolites has been suggested to be of this nature, the adsorbate diffusing into the interior of the crystal through relatively open channels in the structure.

The relation between the adsorption of ions or molecules on a crystalline surface and crystal growth can be brought out in a general way by drawing the distinction that the holding of lattice units similar to those forming the crystal by the surface forces constitutes growth, and of dissimilar lattice units is adsorption. Both adsorption and growth depend on the size, shape, structure and magnitude of the force fields of the accreting substance and the crystal surface and their interaction. If these factors are identical for both adsorbate and adsorbent, permitting an exact dovetailing, we get growth, the velocity varying in different crystallographic directions and varying with the external conditions; as the factors diverge we pass from pure growth through isomorphism to adsorption proper, the adsorption finally becoming restricted to some particular plane on which there is a minimum coincidence of the factors. Beyond this, as the factors diverge further, as in the case of a crystal growing from a solution containing an amount of a very dissimilar foreign substance, there will be no adsorption, although the foreign substance by changing the internal condition of the solution may affect the growth.

The selective nature of adsorption on the planes of a crystal is known experimentally largely from indirect evidence afforded by the modification of the habit of artificially grown crystals through the adsorption of foreign substances present in small amounts in the crystallizing solution. The treatment of this phenomenon as due to adsorption dates from the work of Marc[14]; recent investigations include those of Buckley,[15] Saylor,[16] Walcott,[17] Marc and co-workers,[18,19] Gaubert,[20] Wherry,[21] and France and co-workers. In the

---

[14] Marc, R., *Zeit. physik. Chem.*, vol. **81**, p. 641, 1912; *Zeit. Elektrochem.*, vol. **20**, p. 515, 1914. F. Haber in a note in the latter paper is the first to suggest that adsorption is due to open valencies on the surface of a crystal.

[15] Buckley, H. E., *Zeit. Kryst.*, vol. **73**, p. 443, 1930; vol. **75**, p. 15, 1930; vol. **76**, p. 147, 1930; vol. **78**, p. 412, 1931; vol. **80**, p. 238, 1931; vol. **81**, p. 157, 1932: vol. **82**, p. 285, 1932.

[16] Saylor, C. H., *Jour. Phys. Chem.*, vol. **32**, p. 1441, 1928; *Colloid Symp. Ann.*, vol. **5**, p. 49, 1928.

[17] Walcott, A. J., *Amer. Min.*, vol. **11**, pp. 221, 239, 1926.

[18] Marc, R., and Ritzel, A., *Zeit. physik. Chem.*, vol. **76**, p. 584, 1911.

[19] Marc, R., and Wenk, W., *Zeit. physik. Chem.*, vol. **68**, p. 104, 1910.

[20] Gaubert, P., *Ann. Rept. Smithson. Inst.*, p. 271, 1909–10; *Bull soc. min. franc.*, vol. **38**, 149, 1915; *Compt. rend.*, vol. **180**, p. 378, 1925; *ibid.*, vol. **190**, p. 1230, 1930.

older literature reference should be made to Beudant,[22] von Hauer,[23] and Retgers.[24] The habit change in such cases is due to the modification of the relative growth rates of the various forms by a selective adsorption on one (or several) of them. In the well known case of sodium chloride with urea as an additive the octahedral habit is due to a selective adsorption of the urea on (111) which slows the growth velocity of this form relative to (100), ordinarily the slower growing form, and allows it to develop as the dominant habit.[25] The retardation of the growth velocity by the adsorption is due to the adsorbed substance acting as a protecting blanket and slowing or preventing the normal accretion on the surface.

More obvious evidence of selectivity is offered by crystals grown from solutions containing a dye which have adsorbed the dye on certain planes yielding a crystal with colored zones, as studied particularly by France and co-workers,[26] and, earlier, by Milligan.[27] The adsorption is usually accompanied by a change in habit, the dye adsorbing forms extending their boundaries at the expense of the faster growing forms. The hour-glass augites found in igneous rocks are also believed to owe their color distribution to the selective adsorption of a colored titania-rich molecule, or TiO_2, on certain crystal forms.[28]

In the adsorption of dyes by a growing crystal France[29] cites as controlling factors in the adsorption the force field of the crystal surface, the interionic distances, and the presence and distribution of polar groups in the dye molecule. In a typical example, the adsorption of diamine sky blue by potassium alum, the dye is selec-

---

[21] Wherry, E. T., *Amer. Min.*, vol. **6,** p. 39, 1921; vol. **9,** 45, 1924.

[22] Beudant, F. S., *Traité elem. de Min.*, 2nd ed., vol. **1,** p. 189, 1830.

[23] Von Hauer, K., *Verh. der k. k. Geol. Reichsanst. Wien*, **1877,** pp. 45, 57, 75, 90, 162, 296; **1878,** pp. 185, 315; **1880,** pp. 20, 181 (abstr. in *Min. Mag.*, vol. **1,** p. 243, 1877; vol. **2,** pp. 95, 241, 1879; vol. **4,** p. 73, 1882.

[24] Retgers, J. W., *Zeit. physik. Chem.*, vol. **9,** p. 267, 1892; *ibid.*, vol. **12,** p. 600, 1893; *Zeit. Kryst.*, vol. **25,** p. 512, 1896.

[25] Gille, F., and Spangenberg, K., *Zeit. Kryst.*, vol. **65,** p. 204, 1927.

[26] France, W. G., *Colloid Sympos. Ann.*, vol. **7,** p. 59, 1930. Foote, F. C., and France, W. G., *Jour. Phys. Chem.*, vol. **34,** p. 2236, 1930. Lash, M. T., and France, W. G., *Jour. Phys. Chem.*, vol. **34,** p. 724, 1930. Bennet, G. W., and France, W. G., *Jour. Amer. Ceramic Soc.*, vol. **11,** p. 571, 1928.

[27] Milligan, A. G., *Jour. Phys. Chem.*, vol. **33,** p. 1363, 1929.

[28] Scott, A., *Min. Mag.*, vol. **17,** p. 104, 1914.

[29] France, W. G., *op. cit.*

tively adsorbed on (100), leaving (111) uncolored, and the habit changes from the ordinary octahedral one to cubic. The (100) form has the more intense surface field, and is the stronger adsorbing, since the lattice units composing the surface are either all positive or all negative, in alternate layers, while the (111) form is of the checker-board kind, composed of both positive and negative units, and its surface field is lowered by partial polarization. With halite this is reversed, the (100) form being of the checker-board kind (i.e., with both Na^+ and Cl^- on the surface) while (111) is of the all-alike kind (i.e., with either all Na^+ or all Cl^- in alternate layers); the ordinary habit is determined by the low field (100) form but in the presence of many foreign substances adsorption takes places on the high field (111) form, slowing its growth velocity below that of (100) and allowing it to develop as the dominant habit. Buckley and Cocker[30] in recent work on the adsorption of dyes by growing crystals find that the adsorption may be many times greater than that of an inorganic ion. The seat of the attaching power in the dye molecule is stated to be groups of the nature of COOH, OH, NH_2, or SO_3Na. The force field surrounding the dye molecule is asymmetric and the region of these groups has the more intense field. It is not possible to predict which one of the forms present on a given crystal will be stronger adsorbing solely on the basis of the relative field intensities of the forms, although this control is apparent with halite and in most cases of dye adsorption on alum. The adsorption of inorganic substances and dyes by growing crystals, with respect to the forms of the adsorbing crystal, quite generally varies with the nature of the adsorbate, and, in a given instance, may vary with the external conditions. The galena cubo-octahedrons cited earlier which are selectively incrusted on the (111) form on two specimens and on the (100) form on two other specimens, although galena has a NaCl type structure, and an analysis of the various incrustations on calcite with respect to the crystal forms, assuming these to be due to the adsorption of substance, clearly illustrates this. This behavior shows that in adsorption on a crystal it is necessary to consider the properties of both the adsorbing and adsorbed substances, as has been already noted, and, since this knowledge cannot be realized at present, the

---

[30] Buckley, H. E., and Cocker, W., *Zeit. Kryst.*, vol. **85**, p. 58, 1933. Further literature on the adsorption of dyes by crystals, with habit change, is cited in this paper.

adsorbing power of the forms on a crystal is best described as being specific for different substances.

ORIGIN OF SELECTIVITY ON NATURAL CRYSTALS

Among the examples of incrustations selective on the forms of natural crystals it is possible to distinguish two general types on the basis of the mode of deposition of the incrusting substance. One type is represented by the hematite on quartz, clay material on quartz and the iron oxide on calcite examples in which the deposited substance originally existed as a colloid in the solution surrounding the crystal and from which its particles were adsorbed by the crystal during or after the completion of its growth. These examples are analogous in their origin to the cases cited where artificially grown crystals have selectively adsorbed colloidal particles of dyes (or molecules of colloidal dimensions, in the case of some dyes) with the formation of a zonally colored crystal. The well known crystals of amethyst from Uruguay and Brazil which show in a basal section a distribution of color into three triangular sectors while the other three sectors are colorless, the sectors representing the horizontal projections of the faces of the terminating rhombohedrons, also appear to owe their color distribution to the selective adsorption of colloidal iron oxide by one of the rhombohedrons throughout the growth of the crystal. On the specimens which the writer has seen the colored sectors correspond to the positive rhombohedron.

In contrast to the preceding type the deposited mineral in the selective incrustations of albite on orthoclase, bournonite and chalcopyrite on galena, dolomite on calcite, etc., was not adsorbed as colloidal particles of an already defined substance but evidently crystallized from solution on the surface in question and grew to crystals of considerable size. The existence of the selectivity in this type is believed due to a selective adsorption of the substance from true solution, preceding crystallization, on certain forms of the crystal. Crystallization will tend to initiate on the strongly adsorbing forms since: (1) The concentration of the crystallizing substance will be greater there, because of the adsorption, than in the solution or on the adjacent forms of lower adsorbing power. This will favor the formation of crystal nuclei on that surface. (2) The work required for the formation of crystal nuclei on the adsorbing surface is smaller than in the solution because the free energy for the formation of the surface of the nucleus adjacent to the adsorbent will as a rule be less than that required to form a surface of equal extent in the solution.[31] (3) The adsorbate may be oriented at the interface. This would facilitate the development of the ordered structure of a crystal at the interface rather than in the randomly oriented interior of the solution. Molecular orientation at an interface is believed to be responsible for the increase in crystallization velocity observed at the gas surface of some supercooled liquids[32] and of water (during freezing) in sols containing non-spherical particles.[33] In the latter case the phenomenon is attributed to the orientation of the water molecules at the surface of the particles. Similarly it is found that in the crystallization of solutions in a magnetic field crystal nuclei appear more rapidly and grow faster. This is due to the orientation of the field on the molecules making it easier for them to enter the regular arrangement of a crystal lattice.[34,35]

A regular arrangement of the adsorbate on the adsorbing surface, the pattern of the adsorbed substance following the pattern of the surface lattice units of the adsorbent, might also favor selective incrustation in that crystallization could be expected to start on planes of the adsorbing crystal whose atomic arrangement and spacing are closest to a principal plane of the crystals of the adsorbed substance. In parallel growths of two substances, by superdeposition, the surfaces of contact are like, or nearly like, planes; in for example, the oriented growths of alkali haloids on mica cleavages the planes of contact are mica (001) and haloid (111)

---

[31] Freundlich, H., in Alexander, J., *Colloid Chemistry*, vol. **1**, p. 588, 1926.

[32] Söllner, K., *Kolloid-Zeit.*, vol. **59**, p. 58, 1932.

[33] Freundlich, H., and Oppenheimer, F., *Ber. deutsch. chem. Ges.*, vol. **58**, p. 143, 1925.

[34] Schaum, K., and Scheidt, E. A. *Zeit. anorg. Chem.*, vol. **188**, p. 52, 1930. Samuracas, D., *Compt. rend.*, vol. **194**, p. 1225, 1932.

[35] The orientation of organic molecules with an asymmetric field by adsorption at an interface, such as the orientation of alcohols or fatty acids at a water-air interface in which the high field —OH end of the alcohol molecule or the —COOH end of the fatty acid molecule goes into the water phase and the hydrocarbon end extends into the air, as studied by Langmuir, Harkins and others, seems to find a parallel in the mode of attachment of hemimorphic crystals to their matrix. Crystals of the common mineral calamine (orthorhombic-hemimorphic) are almost always attached by the antilogous end of the polar axis and this is presumably determined by the orientation of its asymmetric molecules by adsorption at the matrix-solution interface before the start of crystallization.

since these are almost identical geometrically. The oriented intergrowths, by unmixing or otherwise, in some sulphide minerals also take place on those planes in which the atomic arrangement and spacing are almost alike, both minerals sharing the structural plane at the contact.[36]

Selective incrustations of the crystallization kind have been found only in nature and the origin of both these and the colloidal particle kind does not appear to have been previously recognized. The nearest approach to an experimental example is in an observation by Kreutz[37] that parallel growths of $NaNO_3$ seemed to be more perfect and easy to obtain on the (110) form of barytocalcite than on (001).

ACKNOWLEDGMENT

The writer takes this opportunity to express his gratitude to Mr. Herbert P. Whitlock for his courtesy in placing the facilities of the Department of Mineralogy in the American Museum of Natural History at his disposal and for assistance in the study of the crystallography of certain of the specimens described.

MEMORIAL OF GEORGES FRIEDEL

J. D. H. Donnay, *The Johns Hopkins University.*

Another giant among crystallographers has passed away. Georges Friedel our distinguished honorary life fellow died at Strasbourg, France, on December 11, 1933. He was born at Mulhouse, France, on July 19, 1865. He was the son of the great French chemist and mineralogist, Charles Friedel (1832–1899) and the father of Edmond Friedel (1895–), the third of a dynasty of scientists.

Georges Friedel was graduated from the Paris School of Mines, where he was the enthusiastic disciple of Ernest Mallard. He had a double career: in the French Bureau of Mines, he reached the high office of *Inspecteur général des Mines;* at the same time he was engaged in teaching and research, first at the Saint-Etienne School of Mines, later at the University of Strasbourg where he was appointed the head of the Mineralogical Institute. Since 1917, he was a correspondent of the French Academy of Sciences. His publications extend over a period of 43 years. Although they deal

---

[36] Gruner, J. W., *Amer. Min.*, vol. **14**, p. 227, 1929.

[37] Kreutz, St., *Min. Mag.*, vol. **15**, p. 233, 1909.