

# SELECTIVE INCRUSTATION OF MINERALS

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## INTRODUCTION

In the sequential deposition of minerals in an open space, a tendency may be observed for a species of later formation to crystallize by preference upon the drusy crystals of one of the earlier formed species only, instead of indiscriminately incrusting all of the species present.

Such a tendency has been recognized by Miers,<sup>1</sup> who called attention to:

... the tendency exhibited by a given mineral to crystallize only upon certain minerals, and not upon others ... The reluctance of quartz to crystallize upon the metallic minerals is strikingly conspicuous. A survey of any mineral collection brings this fact to light at once.

The same tendency was noted by Smyth,<sup>2</sup> in describing an occurrence of pyrrhotite with dolomite, calcite and quartz in limestone from Lairdsville, N. Y. Smyth stated that:

The placing of the pyrrhotite with reference to the other minerals affords a very pretty example of selective precipitation ... When a cavity contains calcite with quartz and dolomite, the pyrrhotite is deposited upon this mineral almost exclusively ... When calcite is lacking in a cavity dolomite supports the pyrrhotite and it is only when the crystals of this mineral become large and very abundant that they rest upon quartz.

Cross and Hillebrand<sup>3</sup> noted that aragonite occurs as an incrusting mineral associated with zeolites in cavities in the basalt of North Table

<sup>1</sup> Miers, H. A., *Mineral., Mag.*, vol. 11, p. 275, 1897.

<sup>2</sup> Smyth, C. H., *Am. Jour. Sci.*, ser. 4, vol. 32, pp. 156-160, 1911.

<sup>3</sup> Cross, C. W., and Hillebrand, W. F., *U. S. Geol. Survey, Bull.* 20, p. 39, 1885.

Mountain, Colorado, and comment that it apparently has a special tendency for deposition upon chabazite. Elsewhere these authors stated that the thomsonite at this locality seems specially suited to attract the deposition of mesolite.<sup>4</sup> Mügge<sup>5</sup> has cited several instances in which chalcopyrite has incrustated tetrahedrite in preference to quartz and other minerals. Photographs have been published by Boutwell<sup>6</sup> of specimens apparently exhibiting incrustations of tetrahedrite upon chalcopyrite in preference to pyrite, and of sphalerite incrusting tetrahedrite in preference to quartz, but the specimens are not specifically described in the text of the papers.

On the following pages, a number of additional instances of selective incrustation are described, and the origin of the selectivity is discussed. Most of the specimens described are contained in the collections of the American Museum of Natural History, Columbia University and Harvard University. In addition, a few instances are described from the collection of the Philadelphia Academy of Natural Sciences, and from other sources. Approximately 40,000 specimens were examined for selectivity in the course of the survey.

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#### ADSORPTION CONTROL OF MINERAL INCRUSTATION

As is well known, the surface of a crystal possesses a degree of residual affinity, and can attract and hold—adsorb—atoms, ions and molecules. The crystallization of a substance from solution upon the surface of a crystal immersed in the solution is, in general, influenced by the adsorption at that surface.

*Kinds of Mineral Incrustations.* Several different kinds of mineral incrustations, illustrative of adsorption control of super-crystallization, can be recognized. With single crystals presenting several forms, the crystallization of an incrusting mineral may be favored upon the faces

<sup>4</sup> Cross, C. W., and Hillebrand, W. F., *Am. Jour. Sci.*, ser. 3, vol. 23, p. 246, 1882; ser. 3, vol. 24, p. 133, 1882.

<sup>5</sup> Mügge, O., *Neues Jahrb., Beil. Bd.* 16, p. 361, 1903.

<sup>6</sup> Boutwell, J. M., *U. S. Geol. Survey, Prof. Paper* 38, Pl. 38, fig. B, 1905; *U. S. Geol. Survey, Prof. Paper* 77, Pl. 27, fig. B, 1912.

of one of the crystal forms to the exclusion of the others, as a consequence of the stronger adsorptive power of that form.<sup>7</sup>

Similarly, the edges and corners of crystals, which are regions of greater adsorptive power than the adjacent plane faces, may be selectively incrustated.<sup>8</sup> Oriented incrustations are also effected by adsorption, the atoms of the adsorbed substance being regularly arranged upon the adsorbing surface and affording an ordered foundation layer for the overgrowing crystal.<sup>9</sup> Polar incrustations, in which hemimorphic crystals are attached to the matrix by a particular end of the polar axis,<sup>10</sup> as of hemimorphite, are also a consequence of adsorption control. Here the polar orientation of the crystal is imposed by the oriented, polar, adsorption of its asymmetric molecules at the surface before the start of crystallization.

Crystallization upon an adsorbing surface may also be marked by the appearance of abnormalities in habit development, distortion, twinning and other peculiarities absent in crystals of the same substance when grown suspended in the same solution.

*Incrustations Selective Between Minerals.* In the case of incrustations that are selective between minerals, the problem presented is that of a solution which is crystallizing in the presence of crystals of several different species, and upon the surface of one of which crystallization is favored to the exclusion of the others. Crystallization from solution tends to initiate upon a pre-formed surface present in the solution, rather than in the interior of the solution itself, partly because the concentration of the crystallizing substance may be greater there, because of adsorption, and partly because less free energy is required to form an attached crystal nucleus than a freely suspended nucleus of equal size.<sup>7,9</sup> If several different species of crystal surfaces are present in the solution, crystallization will be favored at the most strongly adsorbing surface. With the appearance of the initial nuclei, the super-saturation of the solution will be discharged, and deposition will tend to be confined to that particular species of surface, giving a selective incrustation.

Selective incrustations of this origin can be obtained by experiment. Sodium nitrate, for instance, is strongly adsorbed by calcite, and when

<sup>7</sup> Frondel, C., Selective incrustation of crystal forms: *Am. Mineral.*, vol. 19, pp. 316-329, 1934. Some mineral incrustations selective upon crystal forms: *Am. Mus. Nat. Hist., Novit.*, no. 918, pp. 1-4, 1937; no. 695, pp. 1-6, 1934.

<sup>8</sup> Frondel, C., Mineral incrustations upon the edges and corners of crystals: *Am. Mus. Nat. Hist., Novit.*, no. 759, pp. 1-11, 1934.

<sup>9</sup> Frondel, C., Oriented overgrowth and intergrowth in relation to . . . adsorption: *Am. Jour. Sci.*, ser. 5, vol. 30, pp. 51-56, 1935.

<sup>10</sup> Holzner, J., *Zeits. Krist.*, vol. 65, pp. 175-179, 1927; also ref. 7, p. 328.

crystallized from solution in the presence of fragments of calcite, quartz, aragonite, pyrite, etc., it deposits selectively upon the calcite. Similarly, the super-saturation necessary for the crystallization of sodium nitrate upon siderite, rhodochrosite and calcite varies, at a given temperature, with the crystal species.<sup>11</sup> Gypsum crystallizes more readily upon hydrophobic than upon hydrophilic surfaces.<sup>12</sup> The observation of Chevalier,<sup>13</sup> that particles of alum are most effective in inducing the crystallization of alum solutions, while particles of galena, spinel and fluorite are less effective, and particles of pyrite, cuprite and sphalerite are least effective, also constitutes a selective super-crystallization. Many similar observations could be cited.

Most of the observed instances of selectivity can be identified either with experimentally determined cases of strong adsorption, or satisfy the theoretical conditions for a strong adsorptive relation. In addition, a type of selectivity can be recognized in which the incrusting mineral appears to have been localized by chemical reaction (chemisorption) between the incrusting mineral and a solution or a colloidal dispersion. Incrustations formed by the superficial alteration of a mineral, such as crusts of anglesite upon galena, are excluded from the kind of incrustation considered here, in which super-deposition is the characterizing process. Nevertheless, no sharp distinction can be made between adsorption and chemical action, the crystal forces involved in both being identical.

*Colloids and Mineral Incrustations.* Adsorption by large crystals differs from adsorption by colloidal particles, largely in the nature of the effects produced. With crystals in the colloidal range of size, say from 1 to 500  $\mu$ , the effect of the adsorption may be to colloiddally disperse them, or to produce other colloidal phenomena. With large crystals, on the other hand, the mass of the adsorbent is too great to permit dispersion, and the crystal, with its attached double layer, can be visualized as a massive, immobile micelle. Adsorption by crystals in this range of size may be manifested by the control exerted over super-crystallization; or, if the crystal is growing, by a modification of crystal habit, the development of a segmental coloration, or otherwise. The adsorptive relations of a substance as exhibited in the colloidal state, however, are those of large crystals of that substance, although the effects may be different, and the data of one field is relevant to the other.

Processes usually associated with the colloidal state may be extended to the interaction of true colloids and large crystals. Thus a sol may be

<sup>11</sup> Stranski, I. N., and Kuleliw, K., *Zeits. phys. Chem.*, vol. **142A**, p. 467, 1929.

<sup>12</sup> Serbina, N. N., and Dubinsky, V. G., through *Chem. Abstr.*, vol. **29**, p. 7738, 1935.

<sup>13</sup> Chevalier, J., *Mineral. Mag.*, vol. **14**, p. 142, 1906.

coagulated by contact with the oppositely charged surface of an immobile micelle, just as two oppositely charged sols may be coagulated by mixing. Growing crystals may act similarly, and include colloidal or suspended, charged material; the inclusion of colloidal hydrous iron oxide (ordinarily a positive colloid) by amethyst quartz (a negative, immobile colloid by adsorption of OH) is an instance.

#### LIST OF SELECTIVE MINERAL INCRUSTATIONS

The observed instances of selectivity are tabulated below. The criteria for their recognition are discussed in a later section. A special notation is used to facilitate description of the specimens as follows:

Third formed, selectively incrusting, mineral  
First formed mineral—Second formed, selectively incrusting, mineral

Other sequences are indicated by numbers in parenthesis; numbers cited with the localities denote the number of specimens found.

- Calcite
- (1) Quartz—Dolomite. Cornwall, England; Guanajuato, Mexico (3); Lockport, N. Y.
- Dolomite
- (2) Pyrite—Rhodochrosite. Alicante, Colorado (2).
- Dolomite
- (3) Quartz—Calcite. Guanajuato, Mexico (5); Příbram, Bohemia.
- Dolomite (3)
- (4) Pyrite (1)—Calcite (2)—Goethite (4). Příbram, Bohemia.
- Dolomite (4)
- (5) Galena (1)—Calcite (2)—Sphalerite (3). Ems, Germany.
- Siderite
- (6) Quartz—Calcite. Cornwall, England (2); Guanajuato, Mexico (2); Antwerp, N. Y.
- Siderite
- (7) Pyrite—Calcite. Gilpin Co., Colorado.
- Siderite
- (8) Galena—Calcite. Neudorf, Germany.
- Albite (3)
- (9) Microcline—Quartz (2). Pikes Peak region, Colorado (3).  
Similarly with quartz earlier than microcline; and with orthoclase in place of microcline, from several localities (4).
- Chalcopyrite
- (10) Quartz—Sphalerite. Schemnitz, Czechoslovakia.
- Chalcopyrite
- (11) Galena—Sphalerite. Joplin, Missouri (2).
- Chalcopyrite
- (12) Dolomite—Sphalerite. Joplin, Missouri.
- Chalcopyrite
- (13) Siderite—Tetrahedrite. Clausthal, Germany (2).
- Chalcopyrite (3)
- (14) Tetrahedrite—Dolomite (2). Gersdorf, Germany.

Chalcopyrite

- (15) Barite—Quartz—Tetrahedrite. Liskeard, Cornwall.  
Similarly, without barite, from Cornwall (2), and Katenik and Příbram, Bohemia.
- Tetrahedrite
- (16) Quartz—Pyrite—Chalcopyrite. Central City, Colorado.  
Similarly, without quartz, from Clear Creek Co., Colorado.
- Tetrahedrite
- (17) Pyrite—Siderite—Chalcopyrite. Clear Creek Co., Colorado (2).  
Similarly, without pyrite, from Horhausen, Germany.
- Tetrahedrite
- (18) Quartz—Sphalerite. Bohemia
- Tetrahedrite (4) Quartz (6)
- (19) Quartz—Pyrite—Sphalerite (3)—Dolomite (5). Butte, Montana
- Quartz
- (20) Sphalerite—Dolomite. Butte, Montana (2).
- Quartz
- (21) Pyrite—Quartz—Dolomite. Cornwall, England.
- Quartz
- (22) Specularite—Ankerite. Tavetsch, Switzerland.
- Quartz
- (23) Pyrite—Rhodochrosite. Alicante, Colorado (2).  
Dolomite (3)
- (24) Quartz—Galena (2). Raibl, Tyrol.  
Dolomite (3)
- (25) Quartz—Sphalerite (2). Kapnik, Roumania; Freiberg, Germany.  
Dolomite
- (26) Sphalerite—Tetrahedrite—Quartz. Ratiborgitz, Bohemia.  
Ankerite
- (27) Pyrite—Quartz. Brosso, Italy.  
Similarly, with quartz earlier than pyrite, from Traversella, Italy (2).  
Dolomite
- (28) Arsenopyrite—Quartz. Freiberg, Germany (2).  
Similarly, with quartz earlier than arsenopyrite, same locality.  
Siderite
- (29) Microcline—Quartz. Pikes Peak region, Colorado.  
Siderite (3)
- (30) Quartz—Sphalerite (2). Cumberland, England.  
Rhodochrosite (3)
- (31) Quartz—Galena (2). Freiberg, Saxony.  
Chalcopyrite
- (32) Quartz—Dolomite. Cornwall, England; Schemnitz, Czechoslovakia; Schneeberg, and Freiberg, Germany.  
Chalcopyrite
- (33) Quartz—Calcite. Příbram, Bohemia.  
Chalcopyrite
- (34) Barite—Siderite. Wildemann, Germany.  
Chalcopyrite
- (35) Arsenopyrite—Siderite. Freiberg, Germany.

- Pyrite
- (36) Barite—Calcite. Příbram, Bohemia.  
Pyrrhotite.
- (37) Quartz—Dolomite. Morro Velho, Brazil (5).  
Pyrrhotite
- (38) Albite—Dolomite. Minas Geraes, Brazil.  
Sphalerite
- (39) Fluorite—Siderite. Cumberland, England.  
Marcasite
- (40) Quartz—Fluorite. Thunder Bay, Lake Superior.  
Chalcopyrite
- (41) Quartz—Fluorite. Caradon Mines, Cornwall (2).  
Pyrite (3)
- (42) Fluorite—Quartz (2), Cumberland, England.  
Quartz
- (43) Galena—Fluorite. Cornwall, England.  
Quartz
- (44) Pyrite—Fluorite. Isle of Giglio, Italy.  
Rutile
- (45) Quartz—Specularite. Switzerland (7).  
Similarly with quartz later than specularite.  
Dolomite (4) Pyrite (3)
- (46) Quartz (1)—Pyrrhotite (2). Cornwall, England; Elba, Italy.  
Pyrite
- (47) Quartz—Barite. Gersdorf, Germany.  
Pyrite
- (48) Quartz—Galena. Gonderbach, Germany.  
Galena
- (49) Quartz—Chalcopyrite, Arakawa, Japan.

#### DISCUSSION OF TYPES OF INCRUSTATIONS

##### *Incrustations Between the Members of the Calcite Group, the Feldspar, and Sphalerite—Tetrahedrite—Chalcopyrite*

Approximately one-half of the observed instances of selectivity comprise incrustations between the members of the calcite group (Nos. 1–8), the feldspar group (No. 9), and between sphalerite-tetrahedrite-chalcopyrite (Nos. 10–19). The incrusting and incrustated crystals on all of the specimens were found to be parallelly oriented.

While it is not possible to predict in every case on which of several crystal adsorbents the adsorption of a given substance will be strongest, it was early recognized that a crystal adsorbs most strongly substances that are closely related to it in crystal structure. Marc<sup>14</sup> concluded that crystals adsorb substances that are isomorphous with it, and cited the adsorption of rhombohedral sodium nitrate by calcite, and of ortho-

<sup>14</sup> Marc, R., *Zeits. phys. Chem.*, vol. 75, p. 710, 1911; vol. 81, p. 641, 1913.

rhombic potassium nitrate by aragonite, but not conversely, as examples. The greater effectiveness of crystal fragments identical or isomorphous with the dissolved substance in inducing the crystallization of supersaturated solutions is a familiar illustration of the rule.

In the present type of incrustation, the incrusting and incrustated minerals are characterized by an identity or near identity of crystal structure, and the selectivity can be ascribed to a preferential inoculation of a crystallizing solution, by the adsorption of a dissolved, structurally-like, substance. The experimentally obtained selective incrustation of sodium nitrate upon calcite is entirely analogous. It can be expected that the minerals of any isomorphous series, such as those of the barite, aragonite and apatite groups, would form mutual incrustations in preference to other, dissimilar, species.

#### *Incrustations Between Quartz and the Calcite Group.*

A number of instances were observed in which quartz incrustated members of the calcite group in preference to other species (Nos. 19–23); also in which minerals of the calcite group selectively incrustated quartz (Nos. 24–31, 46). A mutual affinity for incrustation is also suggested by experimental adsorption data.

The members of the calcite group may selectively incrust quartz, except when another member of the group is also present, as in Nos. 1, 3 and 6, and in several doubtful instances of selectivity not cited in the list. In this case, the earlier carbonate may be incrustated in preference to the quartz. This would indicate that the incrusting affinity between the members of the calcite group is stronger than that of the carbonates for quartz. In most such instances, however, both the quartz and the earlier carbonate are incrustated indiscriminately.

Quartz was not found to incrust another mineral in preference to a carbonate, although many specimens were noted in which the circumstances of association and sequence were such as to make this possible. It was occasionally noted in cases where quartz indiscriminately incrusts calcite, fluorite or barite in company with other species, that the quartz crystals which covered the surface of the former minerals were smaller and more densely aggregated than those which incrustated the adjacent crystals of other species. Such behavior suggests that the deposition of the quartz was affected by the calcite, but that the conditions of deposition were not such as to maintain or establish selectivity.

ADSORPTION OF SILICA BY ALKALINE EARTH COMPOUNDS. The coagulation of silica sols by massive alkaline earth carbonates is well known. Bischoff found that calcite crystals placed in a sodium silicate solution containing  $\text{CO}_2$  became covered by a coagulated layer of silica gel, and similar experiments with calcite or aragonite crystals, using dialyzed



silica sols or sodium silicate, were described by Thomas Graham and many others.<sup>15</sup> Gypsum and potassium silicate behave similarly.<sup>16</sup>

A selective deposition of silica upon calcite can be obtained by placing a fragment of this mineral with quartz, sulphides, etc., in a silica sol. The coagulation has been variously regarded as effected by electrolyte, produced by partial dissolution of the calcite (Graham); by direct, hydrolytic adsorption; or by a chemical reaction forming a silicate and CO<sub>2</sub>. There is little real distinction to be made between these processes.

Since silica, as such, very probably exists largely in the colloidal state in natural solutions, the observed instances of selective deposition of quartz upon calcite, etc., are presumably exactly represented by the experimental instances.

**ADSORPTION OF ALKALINE EARTH COMPOUNDS BY SILICA.** The adsorption of electrolytes by quartz suspensions and silica sols has been frequently investigated.<sup>17</sup> In general, the alkaline earth cations are strongly adsorbed by silica, the alkali cations less strongly adsorbed, and the heavy metal cations weakly or negatively adsorbed. The nature of the anion present influences the adsorption to a large extent. Carbonates are adsorbed less strongly than hydroxides, but much more strongly than chlorides, sulphates or nitrates. Bicarbonates are adsorbed less strongly than carbonates. The inorganic acids are not adsorbed and their salts are adsorbed hydrolytically. The alkaline earth hydroxides are very strongly adsorbed, and the presence of (OH) increases the adsorption of the normal salts of the alkaline earth and other cations. The promoting effect is greatest for the alkaline earth cations.

The experimental results with solutions of the alkaline earth hydroxides and powdered quartz indicate a slow reaction between these, with the formation of a hydrated silicate containing adsorbed impurities.<sup>18</sup> The reaction becomes complete at elevated temperatures and as

<sup>15</sup> Bischoff, G., *Chemical Geology*, vol. 1, p. 7, 1859; vol. 3, p. 14, 1863; Graham, T., *Phil. Trans.*, vol. 151, p. 205, 1861; Gavelle, P., *Chemie et industrie*, vol. 18, pp. 564-585, 1927; Liesegang, R. E., *Koll.-Zeits.*, vol. 10, pp. 273-275, 1912; Linck, G., *Koll.-Zeits.*, vol. 33, p. 274, 1923; Linck, G., and Becker, W., *Chimie der Erde*, vol. 2, pp. 1-14, 1925; Dean, R. S., *Am. Jour. Sci.*, ser. 4, vol. 45, pp. 411-415, 1918; Church, A. H., *Jour. Chem. Soc. London*, vol. 15, p. 107, 1862; vol. 16, p. 31, 1863.

<sup>16</sup> Becquerel, H., *Compt. rend.*, vol. 36, pp. 210-211, 1853.

<sup>17</sup> Mattson, S. E., *Koll. Beihefte*, vol. 14, pp. 227-313, 1922; Pappada, N., and Sadowski, C., *Koll.-Zeits.*, vol. 6, pp. 292-297, 1910; Mehrotra, M. R., and Dhar, N. R., *Zeits. anorg. Chem.*, vol. 155, pp. 298-302, 1926; Sallinger, H., *Koll. Beihefte*, vol. 25, pp. 360-378, 401-412, 1927; Oakley, H. B., *Jour. Chem. Soc. Lond.*, pp. 3054-3065, 1927; Bartell, F. E., and Ying Fu, *Jour. Phys. Chem.*, vol. 33, p. 676, 1929; Ahobalacharya, C., and Dhar, N. R., *Jour. Ind. Chem. Soc.*, vol. 9, pp. 441-453, 1932; Moore, E. S., and Maynard, J. E., *Econ. Geol.*, vol. 24, pp. 272-303, 365-402, 506-527, 1929.

<sup>18</sup> Baylis, J. R., *Jour. Phys. Chem.*, vol. 32, pp. 1236-1262, 1928; Patrick, W. A., and Barclay, E. H., *Jour. Phys. Chem.*, vol. 29, p. 1405, 1925.

the silica approaches a molecular degree of dispersity. With relatively large quartz particles the reaction is a surface one only (chemisorption).

In view of this data, adsorption by quartz surfaces in natural alkaline solutions would be such as to favor the super-crystallization of alkaline earth carbonates. Barite and other dominantly alkaline earth compounds can also be expected to have a tendency, to some degree, for deposition upon quartz.

#### *Incrustations Between Quartz and the Metallic Sulphides*

Quartz and the metallic sulphides appear either to be without control over the super-crystallization of each other, or to be antipathic in this relation. The latter view, in line with the opinion of Miers,<sup>1</sup> is suggested by certain experimental observations. Instances of quartz selectively incrusting a sulphide or of a sulphide selectively incrusting quartz were not found, although a large number of specimens were noted on which the association and sequence was such as to allow selectivity. These facts do not necessarily indicate that an antipathy for incrustation exists, since the incrusting relation of the associated minerals to the super-depositing quartz or sulphide must be considered, but do suggest the absence of an affinity for incrustation.

Gore<sup>19</sup> found that a number of heavy metal compounds were negatively adsorbed by powdered silica, the solution becoming more concentrated. No adsorption—which may mean an equal adsorption of solute and solvent—or a weak adsorption was observed with other heavy metal compounds, the adsorption in every case being much less than that of alkaline earth and alkali compounds. Mathieu<sup>20</sup> observed that solutions of several metallic salts were negatively adsorbed by porous ceramic plates and capillary glass tubes, and considered that very narrow tubes would adsorb water alone, since the decrease in concentration increased with decreasing radius. It is stated that pure silica gel does not adsorb compounds of the heavy metals directly, but that if the gel has already adsorbed NaOH the Na can be replaced by heavy metal cations.<sup>18</sup>

Negative adsorption of heavy metal compounds would preclude their crystallization upon quartz, except under forced circumstances. Even with a weak adsorption, their selective crystallization upon quartz would probably be prohibited by the stronger, displacing, adsorption of alkaline earth compounds ordinarily present in natural solutions.

#### *Incrustations Between the Metallic Sulphides and the Calcite Group*

A number of occurrences were observed in which metallic sulphides had crystallized selectively upon minerals of the calcite group (Nos. 32–39).

<sup>19</sup> Gore, G., *Chem. News*, vol. 69, pp. 22–24, 33, 43–46, 1894.

<sup>20</sup> Mathieu, J., *Ann. Physik*, ser. 4, vol. 9, p. 340, 1902.

Sulphide sols, like silica, are coagulated by contact with carbonates,<sup>21</sup> and selectively so, but there does not appear to be any further experimental or other evidence bearing on the adsorptive relations between these substances.

On many of the specimens it was noted that the deposition of the sulphide was accompanied by the development of solution effects upon the carbonate. This feature suggests that the deposition was induced by the interaction of a solution or sol with the comparatively soluble carbonate. Smyth,<sup>2</sup> in describing his selective incrustation of pyrrhotite upon calcite or dolomite in preference to quartz, remarked that the pyrrhotite occupied solution cavities in the surface of the carbonate, and was inclined to the view that the deposition was caused by chemical reaction with the carbonate.

Tetrahedrite, chalcopyrite and sphalerite were found in a few instances to incrust each other in preference to carbonates. Usually both the earlier sulphide and the carbonate are incrustated without selectivity. The selectivity in these instances illustrates on a hand-specimen scale the tendency of limestone formations to localize deposition from traversing ore solutions. Selective incrustations of carbonates upon sulphides were not noted, although many specimens were observed in which this was feasible. The metallic sulphides are probably without any marked control over the crystallization of the minerals of the calcite group.

#### *Miscellaneous Incrustations*

A few instances of selectivity remain which have not been previously discussed (Nos. 40-49).

Of these, the selective incrustations of chalcopyrite, pyrite and marcasite upon fluorite (Nos. 40-42) may have originated by the interaction of a sol or solution with the fluorite, as with the sulphide incrustations upon the carbonates, in view of the relatively high solubility of this species. Sulphides can apparently incrust carbonates in preference to fluorite, from the evidence of No. 39 and of a few doubtful instances of selectivity, not cited in the list. The selective incrustations of quartz upon fluorite (Nos. 33, 34) are probably similar in origin, and can be classed with the incrustations of quartz upon the calcite group.

The selectivity in the remaining instances can not be correlated with any particular known adsorptive relation. The incrusting and incrustated minerals are seen to be mutually oriented in the selective incrustations of rutile upon specularite (No. 45) and of pyrite upon pyrrhotite (No. 46), so that adsorption has evidently operated in their formation. Sulphide sols may be selectively coagulated by contact with massive sulphides.<sup>22</sup>

<sup>22</sup> Rust, G. W., *Jour. Geol.*, vol. 43, p. 419, 1935.

<sup>21</sup> Tolman, C. F., and Clark, J. D., *Econ. Geol.*, vol. 9, p. 577, 1914.

FACTORS INFLUENCING THE RECOGNITION AND  
PRESERVATION OF SELECTIVITY

It is obviously a requisite for the existence of selectivity that the incrusting mineral be crystallizing in the presence of drusy crystals of at least two other species of earlier formation. Recognition of selectivity thus requires an exact determination of the sequence of deposition. Many incrustations which on casual examination appear to be selective are eliminated by a study of sequence. Particular difficulties are often encountered when the seemingly selectively incrustated mineral is the first formed of the sequence.

The recognition of selectivity is influenced by the ratio of size of the incrusting and incrustated crystals. Selectivity is most apparent when the crystals of the earlier formed minerals are large and the crystals of the incrusting mineral are small and abundant. The crystals of the several species available for incrustation should also be about the same size and equally distributed over the specimen. Uncertainty as to the validity of selectivity arises in specimens on which the incrusting mineral forms a few scattered crystals only, or where the incrustated mineral forms the greater part of the specimen and the non-incrustated mineral is present as a few small crystals only. Most of the doubtful instances of selectivity observed were of this nature.

Many instances were also noted in which the last formed mineral, while dominantly incrusting one of the earlier formed species, was also present as a few scattered crystals upon the associated minerals. A record kept of these occurrences, and of the doubtful occurrences, none of which are included in the list given, showed that they conformed closely to the types of incrusting behavior as recognized.

Although the tendency for selective incrustation is a general one, unequivocal examples of selectivity are not common. In part, this is due to the infrequency with which the fortuitous conditions of association and sequence requisite for the manifestation of selectivity on a hand-specimen scale are satisfied. More generally, the development and preservation of selectivity requires conditions of crystallization which are probably rarely satisfied in natural solutions.

The control of crystallization solely by adsorbing interfaces present in the solution would be favored by slow crystallization from quiet solutions which did not contain suspended nuclei. Deposition from natural solutions, however, may be characterized by more or less hurried crystallization from moving solutions that contain transported, suspended nuclei. Rapid crystallization also tends to form free nuclei within the solution as well as at interfaces. The mechanical lodging of such nuclei upon drusy crystals would obscure a tendency for selectivity

under adsorption control by setting up numerous accidentally placed centers of crystallization.

Further, the preservation of selectivity requires that the incrusting mineral be not deposited in amount greater than that just sufficient to cover the selectively incrustated crystals. An incrustation that is selective in an early stage of its development may have the selectivity obscured by the continued growth and lateral spreading of the incrusting mineral.

#### SUMMARY

The crystallization of one mineral upon another in the formation of a mineral incrustation is, in general, influenced by adsorption at the boundary between the incrustated crystal and the solution.

When a mineral crystallizes in the presence of drusy crystals of several earlier formed species, adsorption may induce the selective incrustation of one of the species. Chemical reaction between a solution or sol and the surface of the incrustated crystal (chemisorption) may also effect selectivity.

In the present study, instances of incrustations selective between minerals are described, and the incrusting relations of several groups of common minerals are discussed in light of such evidence and of experimental adsorption data. It is found that:

(1) Minerals which are identical or nearly identical in crystal structure, such as the members of the calcite group, the feldspars, and sphalerite—tetrahedrite—chalcopryrite, have a marked tendency to incrust each other in preference to other species.

(2) Quartz and the members of the calcite group have a tendency for crystallization upon each other. The tendency for crystallization of a carbonate upon quartz is less strong than that for crystallization upon a related carbonate.

(3) Quartz and the metallic sulphides either are without a tendency for crystallization upon each other or, more probably, are antipathic in this relation.

(4) The metallic sulphides have a tendency for crystallization upon the minerals of the calcite group and upon fluorite. Sulphides appear to incrust carbonates in preference to fluorite, and sphalerite—tetrahedrite—chalcopryrite may incrust each other in preference to carbonates. The sulphides are probably without control over the crystallization of the minerals of the calcite group.