

VECTORIAL CHEMICAL ALTERATION OF CRYSTALS

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ABSTRACT

Instances of the vectorial chemical alteration of crystals occurring in nature are described for pyrite, stibnite, enargite, tourmaline and other species. With barite and celestite, a partial overgrowth of white opaque substance of later generation may simulate a vectorial alteration. Chemical changes in crystals may be influenced by twin structures, zoning in composition, and by the physical nature of the bounding surface. Nucleation on crystal edges or surface imperfections is described for the topochemical alteration of azurite to malachite.

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INTRODUCTION

The variation with crystallographic direction in the rate of chemical attack was noted, for calcite and other species, by Daniell (1816) and Brewster (1837).

The polyhedral solution, or reaction, bodies yielded by metathetical chemical attack on spheres of calcite have been investigated by Goldschmidt and Wright (1), and similar studies have been made by others for a number of species. The bounding surfaces developed on such bodies, during the final stages of chemical attack, are perpendicular to the direction of greatest reaction velocity, and their orientation varies with the nature of the reagent, its concentration, and with the temperature.

Similarly, the simple decomposition of a crystalline compound may proceed with unequal velocities in different crystallographic directions, as in the thermal decomposition of certain copper compounds (2), potassium chlorate (3), and potassium hydrogen oxalate hemihydrate (4). With the latter substance, the velocity of reaction increases unequally for different directions with increase of temperature.

The dehydration figures—ellipsoids—formed on the surface of hydrous species, early studied by a number of investigators, particularly Pape (1864–68), Sohnke (1880–99) and Blasius (1885),

and more recently by Gaudefroy (5) and others (2, 6), are also instances of vectorial decomposition. The vectorial "burn-figures" produced on the surface of calcined calcite crystals (7) and diamonds are related in origin. In such instances, the reaction proceeds only at the interface between the two phases; this relation also appears to be characteristic of polymorphic inversion (8). Ice (8*a*), thymol (8*b*), sulphur (8*c*) and other crystals vaporize vectorially.

A few instances of the natural vectorial alteration of minerals, mostly of the selective tarnishing of crystal faces, have been described by Leo (9) and Mügge (10). Leo's observations were made in connection with a study of the variation with crystallographic

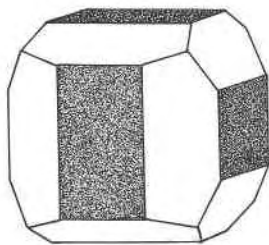


FIG. 1.

direction in intensity of etch stains on polished surfaces of ore minerals. Additional instances of the vectorial alteration of minerals, in all cases probably by metathetical reaction, are described below.

DESCRIPTION OF SPECIMENS

Pyrite

A vectorial alteration of pyrite to hematite is shown clearly by specimens from Rancagua, Chile, obtained recently (1932) by the American Museum of Natural History. The pyrite crystals average about 7 mm. in size and form closely packed drusy aggregates over slabs of wall rock. The habit is cubical, with large modifying faces of the pyritohedron (210). The cube faces are covered by a thick dark-brown to black film of iron oxide, while the faces of (210) are smooth and unaltered and possess the normal color and luster of the mineral (Fig. 1). When the film is flaked off, the pyrite surface is seen to be rather light in color and to be minutely pitted or frosted. The filming substance is hematite, but this mineral may have been derived from an original alteration layer of limonite.

The alteration was observed on several hundred crystals. Entirely unaltered crystals were present on the specimens, but there were no individuals on which both forms were altered. On one specimen, the crystals were unaltered, but were deeply etched on (100) and not on (210). On another specimen, smooth and brilliantly polished unmodified cubes were evenly tarnished in delicate shades of green and green-blue.

Watanabe (11) has observed that the intensity of the stain (hydrous ferric iron oxide) produced by an alkaline bromine solution on pyrite varies with the crystallographic direction. The stain is more intense on (100) than on (111). This observation had been made earlier by Leo (9), who also noted that the positive forms of pyrite were more readily attacked than the negative forms.

Enargite

Well formed crystals of enargite have been described by Weed (12) as occurring in vugs in veins at Butte, Montana, and “. . . it is notable that the terminal face has a clean, mirror-like surface and the prismatic faces a mossy coating of copper glance [chalcocite] . . . Specimens . . . show prisms of enargite surrounded by radial quartz, the basal pinacoids of the prisms being clean and mirror-like, and the remainder of the crystal coated with mossy glance.”

The terminal forms of enargite (*luzonite*) crystals from Man-cayan, Philippines, have been noted by Moses (13) to be decidedly lighter in color and less brilliant than the side planes. It is stated, however, that the cause of the effect is obscure, and that chemical alteration does not appear to have been operative.

Chalcopyrite, Galena

Jimbō (14) has noted the forms (111), ($1\bar{1}1$) and (221) on twinned chalcopyrite crystals from the Abeshiro mine, Mutsu Province, Japan. The faces of ($1\bar{1}1$) are black by oxidation, while the faces of (111) are brilliant and fresh. Ordinarily, the faces of (111) on chalcopyrite are oxidized (tarnished) and those of ($1\bar{1}1$) unoxidized.

Greg and Lettsom (15) have remarked that the octahedral faces of galena are particularly liable to tarnish, and Leo (9) has cited several instances of such alteration.

A selective filming of galena cubo-octahedrons by chalcopyrite has been described (16), but this is owing to selective adsorption and super-crystallization and not to alteration. However, a described instance, of this origin, in which (100) of a galena cubo-

octahedron is selectively filmed by granular pyrite may be the result of alteration, particularly since the pyrite is not oriented to the galena.

Senaite

A peculiar instance, apparently of vectorial alteration, on crystals of senaite, $(\text{Fe}, \text{Mn}, \text{Pb})\text{O} \cdot \text{TiO}_2$, from Diamantina, Minas Geraes, Brazil, in which the composition of the alteration product differs on different forms of the crystal, has been described by Hussak and Prior (17). These authors state that: "Some of the crystals are partially decomposed. In these cases the prism faces are covered with a brown coating of limonite, while the rhombohedral faces have a yellow earthy crust consisting of titanitic acid, with only a trace of iron."

The crystals are tri-rhombohedral, like ilmenite. On unaltered crystals the rhombohedral planes are very bright, while the basal plane is uneven by twinning and, like the prism faces, is dull in luster.

Stibnite

A group of large stibnite crystals in the American Museum, from Baia Sprie (Felsöbanya), Roumania, was found to present a peculiar alteration in which the faces of the brachypinacoid (010), are coated by a yellow-brown mineral, probably wurtzite, to the exclusion of the other forms. The faces of (110) and of the terminating forms (113) and, occasionally (111) and (121), are not coated but are dull. The investing mineral not only incrusts the surface but extends into the substance of the crystal itself. As the alteration proceeds, all of the forms are coated.

The altered portion is identical in appearance and physical properties with the wurtzite crusts on stibnite crystals from this locality described by Prior (18) and Laspeyres (19), but no chemical tests were made to verify this identification. The greater attack on (010) was also noted by Laspeyres.

Prior observed that stibnite crystals from Siegen, Prussia, had their terminations wholly replaced by this substance. A similar instance, but in which the alteration product is probably cervantite, was found on crystals from Siena, Tuscany.

Tourmaline

Bischoff (20) has remarked that the alteration of tourmaline may commence on particular faces of the crystal; and that its alteration to mica sometimes takes place on one end of the prismatic

crystals only, while the other end retains its original appearance. Blum (21) has described a similar instance in which one end of a tourmaline crystal is altered to talc, and Gumbel (22) and Mallet (22*a*) instances of polar alteration to white mica.

These descriptions do not state the end of the polar axis on which the alteration has taken place. However, it is probable that it is the antilogous pole, since the rate of attack by reagents is greatest at this pole (23)—i.e., along the *c*-axis towards the analogous pole. The correlation of rate of chemical attack with the rate of growth of particular forms, made by Leo (9) and others, would also be borne out in this case; since the polar secondary enlargements of tourmaline crystals described by Stow (24) and Alty (25) show that the rate of growth is greatest on the antilogous pole.

The influence on chemical attack of zones of varying composition in crystals is well illustrated by tourmaline. The interior zone of prismatic crystals may be altered to damourite, cookeite, etc., along the vertical axis (26), while the sides remain unaltered, and the disintegration may be carried to such an extent that the crystals are completely hollowed out. The interior of such tubular crystals may be lined with crystals of lepidolite, cookeite or other secondary mineral. A fibration parallel to the *c*-axis is sometimes developed in the initial stage of alteration.

Hitchen (27) has described tourmaline crystals from Fitchburg, Massachusetts, which are replaced by quartz along a central core, parallel to *c*. The well-known tourmaline shells—perimorphs—from Roe's Spar Bed, Crown Point, New York, enclosing a core of feldspar, and from Newcomb, New York, enclosing a core of calcite, are probably skeletal growths and are not the result of interior replacement, or eutectic crystallization.

Wolframite

Frenzel (28) has briefly mentioned a wolframite crystal from Zinnwald, Bohemia, on which the prismatic faces are altered to scheelite, while the domical faces are unaltered.

The replacement of wolframite by scheelite along the (010) cleavages has been noted by Finlayson (29), and perpendicular to the (010) cleavages by Van Horn (30).

Barite

Barite crystals that apparently have undergone vectorial alteration have been described by Williams (31) and Chester (32) from

De Kalb, Jefferson Co., New York. The forms (001), (110), (104), (203), (102) and (011) were observed, of which the last three were superficially altered to a white chalky material. The crystals are peculiar in that they are outwardly hemimorphic, on the *b*-axis.

Seemingly altered barite crystals from this locality in the collection of the American Museum show the forms (011), (203), (104), (102) and (001). A white opaque chalky layer covers all but (001), and decreases in thickness on the forms in the order given. The surface of (001) is usually entirely free from the soft white material, but on several of the crystals the surface of this form, like that of (102), was covered by a thin milky-white translucent film. The layer on (011) may extend to a depth of 1 mm. or more. Although it is outwardly soft and chalky, it grades with depth into a relatively hard and compact mass. The interior of the crystals and, ordinarily, the faces of (001) are colorless and transparent.

Both Williams and Chester speak of the chalky surface layer as an alteration product, although Williams states that a qualitative chemical analysis showed it to be barium sulphate. Chemical examination of the Museum material, by R. B. Ellestad, University of Minnesota, also showed the chalky material to be barium sulphate of practically the same composition as the clear inner portion. No carbonate was found, and only traces of Sr and Ca; the water content was negligible.

Barite crystals are often found to have certain faces overgrown or zoned by a later generation of white, opaque barite; the initial crystal being partially enclosed as a phantom. The overgrowth in such instances is usually upon the prism (110), or a macro- or brachypinacoid or dome, with the base (001) remaining unchanged. The white borders on barite crystals of this nature from Morgan Co., Mississippi, were doubtfully ascribed by Broadhead (33) to chemical alteration; however, the appearance of the crystals is probably due to overgrowth, particularly since Broadhead described similar crystals, probably from the same locality, which are of this origin. Leudeking and Wheeler (34) found the color of the white bands in partially zoned barite crystals from Pettis Co., Missouri, to be caused by myriads of minute cavities.

The De Kalb barite crystals are probably also only instances of partial overgrowth, and not of alteration. The soft chalky nature of the surface may have been caused by the collapse, during superficial weathering, of highly porous material.

Pelikan (35) has described barite crystals particular forms of which have included a foreign pigmenting substance throughout their growth. Such occurrences are to be distinguished from partial overgrowths, already described, in which only particular forms of a pre-formed crystal have received deposition during a later period of growth.

Celestite

Celestite crystals from Put-in-Bay, Lake Erie, and Mokattam, Egypt, were said by Williams (31) to be altered similarly to the De Kalb barite crystals, but the occurrences are not well authenticated. The crystals from Mokattam sometimes have what appears to be a heavy brown alteration crust on certain forms. This effect is due either to the selective solution of these forms which allowed included foreign matter to project from their surfaces, or to a later partial overgrowth of brown, inclusion-rich, celestite on these forms (36). The latter feature is well shown by celestite crystals from Wadi-el-Tih, Egypt, in the Museum collection. The writer has seen celestite crystals from Put-in-Bay with white borders on certain faces, similar to specimens described by Troost (36*a*) but the formation of these crystals is clearly to be ascribed to partial overgrowth and not to alteration.

Aside from the vectorial aspect, chemical changes in crystals may be influenced by zoning in composition, by twinning structures, and, also, in the initial stages of attack, by the physical nature of the bounding surface.

NUCLEATION ON THE EDGES AND SURFACE IMPERFECTIONS OF CRYSTALS

Malachite Altering from Azurite

Nucleation in the decomposition of a solid salt generally starts on a crystal edge or preferably at a corner (4), nuclei in the center of a face being rare. The rate of reaction is constant for any given edge, but is different for different edges. Damaged regions—scratches, surface irregularities, etc.—behave like edges, as in the dehydration of copper sulphate pentahydrate and other hydrous species (2, 5, 6) and in the absorption of water by hydrocyanite (37). The boundaries of grains in crystalline aggregates are also loci of nucleation. The initiation of metathetical reactions on the edges and corners of crystals, and the greater adsorptive power of these por-

tions of the crystal surface, are well illustrated by mineral incrustations confined to the edges and corners of the incrustated crystal (38).

Frequently, the alteration of azurite to malachite seems to start at some point of imperfection on the surface of the crystal. This alteration involves the loss of carbon dioxide and the gain of water. Palache and Lewis (39) have described malachite pseudomorphs after azurite from Tsumeb, South Africa, and note that "The alteration has the appearance of starting at some center and progressively attacking fresh azurite, completely converting each crystal to malachite and spreading to the next at the point of contact." On one crystal "The malachite fibers radiate from one important center on the front pinacoid, and many interfering centers on the prism, giving a confused network of interwoven, splendant fibers. The front of the invading malachite is roughly concentric normal to the fibers." A number of excellent photographs of such altered crystals are given.

These writers have also described malachite pseudomorphs after azurite, from Bisbee, Arizona, and Tsumeb, which are overgrown by a later generation of azurite in parallel position to the original crystal. The malachite of the pseudomorphs apparently retains a structure adequate to control the orientation of the later azurite deposited on their surface (39). An identical occurrence, from Bisbee, has been described by Hills (40), who also noted the phenomenon of radial fibrous alteration, extending from the point of attachment.

Many malachite pseudomorphs after azurite from various localities present radial surface alteration. The alteration may start from one or more points on the surface of the crystal, but more frequently begins at the point of attachment to the matrix or along the plane of intersection with other crystals.

The free boundary of the altered area may be nearly circular, but is often ellipsoidal, and sometimes sharply so. The constituent fibers, which, on different specimens, range in size from indistinct silky threads to large needle-like prisms, generally terminate in a common boundary. However, individual fibers may sometimes project a considerable distance beyond the common front.

A feature of the alteration is an abrupt boundary between the unaltered azurite and the encroaching malachite. This was also noted by Palache and Lewis. The alteration seems to progress more rapidly over the surface of the azurite, and a thin fibrous layer may

cover an otherwise unaltered crystal. In the final stages of alteration, the crystal may be entirely replaced by a few radiating bundles of fibers.

Analogous alterations have been observed with other, artificial, copper compounds, and all may be classed in Kohlschütter's category of "topochemical" reactions.

CHEMICAL ALTERATION OF TWINNED CRYSTALS

From the work of Judd (41) and others, the composition planes of secondary twinning lamellae are well known to be directions of relatively rapid chemical attack and solution.

The lines of intersection of two twin planes in repeatedly twinned calcite crystals may be marked by tubular solution cavities—the "höhle Canalen" of Rose and von Koksharov. In one instance (42), the loci of such planes were found to be replaced by a lattice-like arrangement of rods of spadaite.

Canfield (43) ascribed the interior "walls" in hollow pseudomorphs of quartz after anhydrite from New Jersey to replacement along twin planes, as a consequence of the greater rate of solution of such planes, but this view is not verified by recent work. No mention of twinning is made in Schaller's study (44) of the quartz—anhydrite pseudomorphs of this region, and the quartz walls are ascribed to parallel growth and to penetration along cleavages.

Ichikawa (45) observed that the alteration to mica of pseudo-hexagonal trillings of cordierite from Japan was most extensive along the composition planes of the crystal. Funnel-shaped altered regions also extended in from the (001) faces of the crystal along the vertical axis—the locus of intersection of the composition planes.

CHEMICAL ALTERATION OF ZONED CRYSTALS

The velocity of reaction in the decomposition of crystalline solids is, in general, decreased by the presence of foreign substances in solid solution. Differential effects may be expected as a consequence of composition zoning, or of the zonal adsorption of impurities, during crystal growth. Inequalities in the rate of reaction caused by adsorbed impurities have been noted for KH oxalate hemihydrate (4).

A selective alteration along zones of more favorable composition has been described for tourmaline on a preceding page. Schouten (46) has described a synthetic zonal replacement of pyromorphite

by galena by reaction with an alkaline polysulphide solution, and also several naturally occurring instances of this nature among other minerals. The replacement of pyromorphite by galena in nature has been said (10) to progress more rapidly in the (0001) direction.

Zonal alteration is of frequent occurrence in plagioclase, in which case the inner calcic zones may be preferentially altered to secondary calcic minerals. Similarly, the albite lamellae in perthites may be preferentially altered or replaced, as by tourmaline (47) and bornite (48). Sometimes the albite lamellae may apparently be left as replacement residuals, as in an instance of replacement by fluorite (49).

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