

SPATIAL DISTRIBUTION OF MINOR ELEMENTS IN SINGLE-CRYSTALS

C. FRONDEL, W. H. NEWHOUSE AND R. F. JARRELL,
*Harvard University and Massachusetts Institute of Technology,
Cambridge, Massachusetts.*

CONTENTS

Abstract.....	726
Introduction.....	727
Spatial Distribution with Respect to Face-Loci.....	729
Spatial Distribution with Respect to Growth Zones.....	732
Simulated Compositional Heterogeneity.....	733
Spatial Distribution of Minor Elements in Galena.....	735
Differential Staining in Polished Section.....	736
Method of Spectrographic Analysis.....	738
Results of Spectrographic Analyses.....	739
Spatial Distribution of Minor Elements in Calcite.....	743

ABSTRACT

The mechanism and geometrical consequences of crystal growth are outlined. The literature illustrating the various types of compositional heterogeneity within single-crystals is reviewed in some detail. It is shown spectrographically that the minor foreign elements present in single-crystals of galena and calcite are not uniformly dispersed throughout the host crystal, but generally are distributed in adjoining or alternating regions of greater and lesser concentration. These concentration-regions are related to the growth surfaces of the host crystal, and fall into two types: (A) Pyramidal regions, or face-loci, subjacent to particular faces on crystals bounded externally by several crystallographically different forms. The concentration differences arise in the unequal adsorptive capacity of the different forms on the growing crystal for the foreign element in question. (B) Alternating zones parallel to the external growth surfaces without any or marked selectivity as to different crystal faces. Growth zoning may have two origins: a roughly periodic variation in the rate at which foreign material is taken up by the host crystal in a closed system under the control of certain properties peculiar to growth surfaces, and a zoning occasioned by progressive variation in the composition of the crystallizing solution or in other outside factors.

The spectrographic work on galena revealed that both Ag and Si are relatively concentrated in the octahedral face-loci. Other minor elements, including Cu, Fe, Al, Cr, Ba, Sr, Ca and Mg, show significant quantitative variations within galena single-crystals but apparently without any special relation to the morphology. Staining of sectioned and polished single-crystals of galena reveals a complex internal structure outlined by relatively reactive, dark-stained, growth zones and face-loci. Correlated spectrographic examination indicates that the dark stained regions are relatively rich in Ag. Spectrographic examination of calcite single-crystals further illustrates the features of distribution found with galena. Significant compositional variations are found between successive growth zones in habit-invariant single crystals and between overgrown crystals of different habit. No special connection, however, could be traced between the morphology or the color of the crystals and any of the minor elements tested (Fe, Cu, Mn, Al, Sr, Mg).

INTRODUCTION

The growth of a crystal proceeds outwardly from an original nucleus by the removal from solution and ordered attachment of substance to its external surface. It is evident that every point now in the interior of the crystal once occupied the surface, and the crystal may be regarded as a three-dimensional locus of a solution/solid interface or growth surface. More precisely, a crystal is an assemblage of growth loci, composed of individual loci each subjacent to a face of the polyhedral growth surface. It is convenient to distinguish between *face-loci* beneath the individual faces of a single crystallographic form, and groups of identical face-loci, or *form-loci*, representing different crystallographic forms present on the crystal. The essentially two-dimensional internal

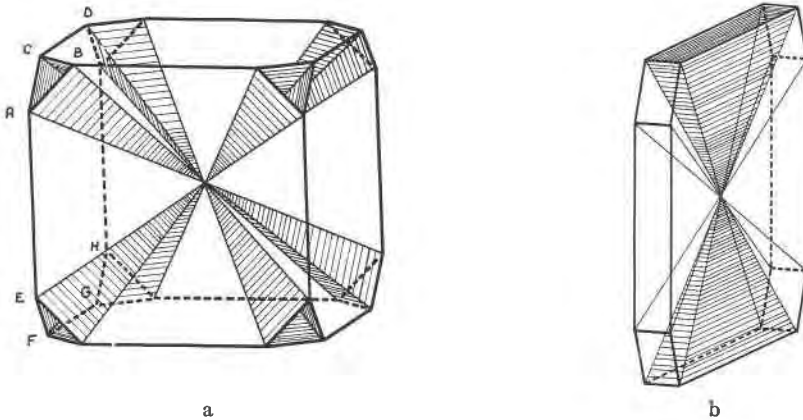


FIG. 1. Diagrammatic representation of form-, face-, edge-, and corner-loci. The isometric cubo-octahedron shown at the left is composed of: (A) two different form-loci, comprising the octahedral face-locus $ABCO$ with its 8 analogues, and the cubical face-locus $ACDEFGHO$ with its 6 analogues. (B) Two different edge-loci, comprising the octahedral edge-locus ABO with its 24 analogues, and the cubical edge-locus CDO with its 12 analogues. (C) One set of corner-loci, comprising AO and its 24 analogues. Compare Fig. 4b.

The holohedral orthorhombic crystal shown at the right contains 4 different kinds of form-loci, 5 different kinds of edge-loci, and 2 different kinds of corner-loci. The brookite crystal with a selective pigmentation of the face-loci of $\{001\}$ shown in Fig. 2a has an identical habit.

bounding surfaces between adjacent face-loci also are loci, traced out by the edges of the crystal during its growth, and may be designated *edge-loci*. Similarly, the one-dimensional, line-like, juncture of three or more adjacent face-loci representing the successive positions during growth of the corners of the crystal are corner-loci. It is apparent that there may be different kinds of both edge- and corner-loci, cor-

responding to the crystallographically different kinds of edges and corners on the growth surface. The several types of loci here described are illustrated in Fig. 1.

It may now be considered that the surface of a crystal is both (1) heterogeneous, in that the surface itself is composed in general of a variety of unlike faces, edges and corners, each with different geometrical, chemical and physical properties, and (2) discontinuous, in the sense that the surface marks an abrupt boundary between two unlike phases or environments. Both the heterogeneity and the discontinuity of the crystal surface may act individually to impose non-uniform, spatial, characters on the distribution within the crystal of a foreign substance taken up by the crystal during its growth. In the first regard, the surface of a crystal may be likened to a permeable membrane, through which material is transferred from the solution to the crystal during the growth process, whose permeability, in a sense, is different in different parts as a consequence of its crystallographic surface heterogeneity. Thus, a foreign substance present in the crystallizing solution is offered a choice of different points of entry to the crystal itself. In general, the foreign substance tends to effect such a choice, for reasons which need not be discussed here, resulting in an internal compositional heterogeneity with respect to different form-, edge- or corner-loci.¹

In the second regard, the surface of a crystal, considered simply as a phase boundary, is a region in which special processes act, peculiar to interfaces, which influence the general character of the growth process. Of these processes, the most important in the present connection are the relative rates of diffusion of the foreign material and the pure material from the solution to the crystal surface, the rate of crystal growth, and the dissipation of the heat of crystallization. The interaction of these processes causes a more or less crude periodicity in the rate at which the foreign material is taken up by the growing crystal, giving rise to an internal compositional heterogeneity with respect to concentric, shell-like, zones which parallel all of the growth surfaces. The growth of a crystal from pure solution probably also is periodic, but direct experimental evidence on this point is lacking.² It must also be remarked, that compositional zoning may be occasioned by bulk changes in the composition of the solution during the course of crystallization, or by changing equilibria in a solution of fixed bulk composition accompanying varia-

¹ An introduction to this problem can be gained from investigations by Bunn, C. W., *Proc. Royal Soc. London*, **141A**, 567 (1933); Buckley, H. E., *Zeits. Krist.*, **81**, 157 (1932); **80**, 238 (1931); **88**, 392 (1934); and Frondel, C., *Am. Mineral.*, **25**, 91, 338 (1940), on the adsorption of substance by certain faces only of growing crystals.

² See, however, the observations of Miers, H. A., *Phil. Trans.*, **202**, 459 (1904), on alum.

tion in external conditions. This aspect of the problem has been well discussed by Plemister (1) in the case of the zoning of the plagioclase feldspars. Zoning due to these causes may be superposed on a zoning due to properties of growth surfaces *per se*.

The present study is concerned with the spatial distribution within the host crystal of the so-called minor elements present in spectrographic amounts. Particular reference is made to galena and to calcite. Before the description of this work is entered, however, it may be of interest to review briefly some of the recognized examples of the growth-loci and zonal types of compositional heterogeneity, and to indicate the various phenomena by which a spatial distribution of foreign material may be evidenced. A limited review of observations in this general field has been given by Nothaft and Steinmetz (2).

SPATIAL DISTRIBUTION WITH RESPECT TO FACE-, EDGE- AND CORNER-LOCI

Perhaps the most familiar examples of this type of compositional heterogeneity are the so-called hour-glass segmental or sectoral types of color distribution within single-crystals. In these instances, a pigmentsing material has been preferentially taken up, in solid solution or otherwise, by the faces of a particular crystal form during the growth of the crystal. The described instances among both natural and artificial crystals are very numerous. Particular reference may be made, however, to studies by Haberlandt and Schiener and others on the differential coloration of face-loci and growth zones in fluorite (3). A large literature on these phenomena also exists for barite (4) and brookite. Brookite crystals from Ellenville, New York, with a marked hour-glass pigmentation in certain form-loci are shown in Fig. 2; spectrographic analysis has shown that the dark regions contain relatively large amounts of Cb in substitutional solid solution for Ti. The spatial distribution of dyes within particular form-loci of crystals grown from solutions containing added dyes has been the subject of much investigation (5).

Spatial distribution with respect to form-loci also may be revealed in uniformly colored or in opaque and visually homogeneous crystals by appropriate means. Colorless crystals of K_2SO_4 , $(NH_4)_2SO_4$ and some other substances when grown from solutions containing added radioactive ThB, ThX, or Po and then placed upon a wrapped photographic film give a radiograph which reveals a selective distribution of the substituted radioactive atoms within particular form-loci (6). Similarly, the uranium present in solid solution in natural crystals of various columbate-tantalates appears quite frequently to be selectively concentrated within particular form-loci in the crystal. Some examples are

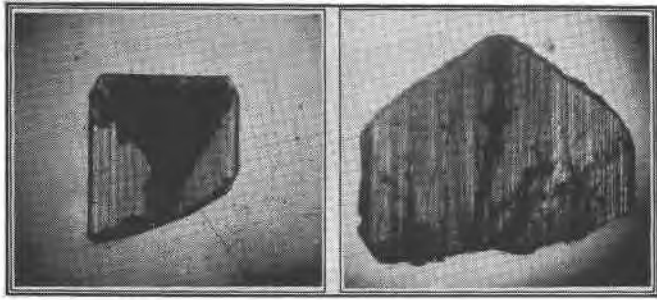


FIG. 2. At left is a photograph of a brookite crystal from Ellenville, New York, with a black selective pigmentation of the face-loci of $\{001\}$. The bottom half of the crystal is broken off. Growth zones parallel to (001) are present in the pigmented region. The vertical lines are striations. Spectrographic analysis shows that the dark material is high in Cb. The Cb is in isomorphous substitution for Ti. Arnold, W., *Zeits. Krist.*, **71**, 344 (1929), who cites many instances of selective pigmentation in brookite, also found by x -ray emission analysis that the dark material in crystals from Switzerland is high in Cb. At right is a brookite crystal from Tavetsch, Switzerland, with a narrow, selectively pigmented, face-locus of $\{001\}$. Magnification = $19\times$.

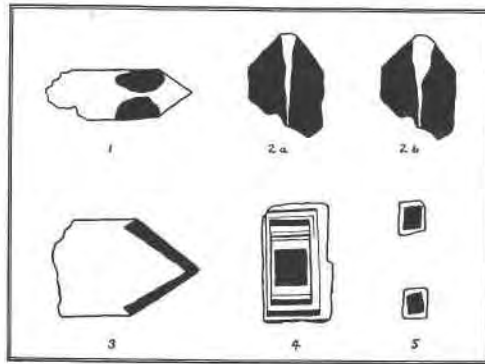


FIG. 3. Tracings of radiographs of oriented sections through single-crystals of various radioactive columbate-tantalates. No. 1 is a basal section through a blomstrandine crystal from Hitterö, Norway. No. 2a and 2b are successive sections parallel $\{010\}$ through a polycrase crystal from Marietta, South Carolina; the sections show a well-defined weakly-radioactive face-locus of $\{001\}$. No. 3 shows a zone of strongly radioactive material selectively disposed beneath the faces of $\{001\}$ on a crystal of blomstrandine from Morefjaer, Norway. No. 4 illustrates a zonal structure in a basal section of samarskite from Uba, Minas Geraes, Brazil. No. 5 shows a zonal structure in basal sections of fergusonite from Satersdalen, Norway.

shown in Fig. 3 and are described in the caption. Numerous instances have been described of the selective luminescence of form-loci in single-crystals under excitation by ultraviolet light or otherwise. Gypsum

crystals from more than six localities have been found to show strong selective fluorescence in the face-loci of $\{111\}$ (7). Certain calcite crystals from Terlingua, Texas, bounded by a scalenohedron and a rhombohedron, fluoresce selectively in ultraviolet light in the face-loci of the rhombohedron. Selective fluorescence of face-loci also has been observed in fluorite, apatite and apophyllite. The unlike sensitivity of the different forms on single-crystals of pyrite and some other metallic sulfides when used as radio-detectors apparently is connected with minor variations in the composition of the several form-loci (8). The chemical reactivity of crystals is, in general, sensitive to minor variations in composition, and chemical differences between form-loci may then be revealed in cut sections by etching or staining techniques. The compositional heterogeneity of galena single-crystals as revealed by differential staining is described on the following pages, and many further examples among opaque minerals are found in the literature (9, 10). The optical constants of crystals similarly may vary with variation in composition, and the optical heterogeneity with respect to form-loci of mixed crystals often is marked (11). A remarkable series of photographs have been published (12) of complex optical heterogeneities with respect to face-loci and growth zones in mixed crystals of the voltaite series. These effects are concomitants of chemical variations, and often are accompanied by a differential coloration of the several parts. A concomitant hour-glass type of variation in both coloration and birefringence is found in certain ferroan epidote crystals (13), among other species, and is well known in the case of the titanian augites found in igneous rocks (14). It may also be expected that exsolution products should be more abundant in or localized in particular form-loci if these varied in their original content of dissolved foreign material. Examples of this type of distribution are known among artificially grown unstable mixed crystals (15), but unqualified instances apparently have not been recognized among natural crystals.

Compositional variation with respect to edge-loci and corner-loci is difficult to recognize because of the extremely small volume occupied by these regions within the crystal. Well-defined selectively colored edge-loci beneath the terminating rhombohedron are sometimes found in zoned tourmaline crystals from Madagascar (16). Differentially colored edge-loci also appear in some published photographs of sectioned fluorite crystals (17). Some of these instances may be only of extremely narrow form-loci. Substituted atoms of radioactive ThB in single crystals of lead chromate are relatively concentrated in the edge-loci (18). The edges and corners of crystals, including here surface imperfections arising in lineage or mosaic structures and striations, are, as is well known,

regions of great adsorptive capacity as compared to plane surfaces, and edge- and corner-loci can be expected to be regions of marked compositional heterogeneity. While such heterogeneity would be of little consequence on the bulk composition, it might be of marked effect on the magnetic and especially the electrical properties of the crystal.

SPATIAL DISTRIBUTION WITH RESPECT TO GROWTH ZONES

This type of compositional heterogeneity has been variously designated as zonal growth, compositional zoning, growth banding or phantom banding. The zones may be continuous around the crystal or, if there is a selective distribution of the foreign material with respect to form-loci, be confined to such loci. An instance of the latter kind in brookite is shown in Fig. 2. The zones often are continuous around the crystal but are of different thickness if different form-loci. Zoning frequently reveals a progressive or abrupt change of habit during the growth of the crystal. Changes in shape (distortion) due to growth in a solution current also may be revealed (19, 43). The thickness of growth zones at opposite ends of a polar crystal axis may be expected to be unlike, due to the intrinsically unequal rates of growth in opposite senses of the axis, and have been so found in tourmaline. Growth zoning is characteristic of mixed crystals in an isomorphous series, such as the smaltite-chloanthite series, ferroan sphalerite, the ferberite-hübnerite series (20), the plagioclase feldspars (1), pyromorphite (32) and many others. Contrary to what is probably generally believed, there is not always a progressive change in composition outwardly in zoned mixed crystals, such as would result from a regular variation in the composition of the crystallizing solution. Usually the zones are simply repeated periodically in a more or less definite ratio, and the average composition of any region of appreciable thickness in the crystal is a constant; this is the type of zoning impressed by properties inherent in the growth mechanism of crystal surfaces. Zoning of the latter type is typical of crystals containing adsorbed colloidal particles of a foreign pigmenting substance, such as amethyst (21) and crystals containing dyes.

In transparent crystals zonal growth also may be revealed by variation in optical properties and, in both opaque and transparent crystals, by etching or staining techniques. The unequal fluorescence in ultraviolet light of growth zones in diamond crystals has been recently described (22). The selective luminescence in this and in similar instances in fluorite and calcite definitely appears to be due to minor variations in composition of the several zones. Certain calcite crystals investigated

by Headden (23) exhibited internal color zones; these zones exhibited differential phosphorescence when exposed to direct sunlight or to x -rays, thermoluminesced differentially when heated, and exhibited differential triboluminescence. In one instance, the zones were shown to differ in the kind and content of rare-earths present in very small amounts in solid solution in the calcite. Fluorite very frequently shows selective fluorescence in ultraviolet light with respect to growth zones. Some fluorite crystals exhibit zonal phosphorescence (24) after exposure to sunlight, and an instance has been described of zonal thermoluminescence (25) when heated after exposure to radium rays. The thermoelectric potential of pyrite is influenced by zoning in the crystals, and in one instance the variation was found to be due to differences in composition of the zones (26). The zonal distribution of radioactive material in single-crystals of various columbate-tantalates already has been illustrated (Fig. 3). A similar distribution occurs in artificial crystals containing radioactive impurities (6). Very frequently, compositional zoning is revealed or accentuated by differential chemical alteration of the zones; the alteration of the calcic zones of plagioclase crystals to zoisite, etc., and the differential solution and alteration of longitudinally zoned tourmaline crystals are familiar examples. The oxidation of magnetite to hematite or maghemite usually takes place preferentially along particular growth zones within the magnetite crystal (27), and this presumably reflects a compositional heterogeneity. The replacement of crystals often is influenced by zoning; for instance, zoned pyrite replaced by chalcocite (32; Fig. 26). Exsolution products are sometimes restricted to particular growth zones. Thus, NaCl forms a limited range of unstable mixed crystals with AgCl, and the mixed crystals contain zones alternately rich and poor in Ag; the Ag-rich zones show anomalous birefringence and on standing become turbid due to the deposition of minute parallelly oriented crystals of AgCl (15).

Simulated Compositional Heterogeneity. Inclusions in Crystals. Internal structures which simulate both the zonal and the growth-loci types of compositional heterogeneity may be observed in crystals. The closely spaced, white and opaque growth zones in otherwise colorless barite crystals have been found in one instance (28) to be due to the presence of myriads of minute empty cavities. Zonally arranged minute fluid cavities have been observed in barite crystals from many other localities (44). A micro-composite structure may be present in certain form-loci only of Rochelle-salt crystals (29) giving rise to a turbidity which simulates the hour-glass type of compositional heterogeneity; the presence of these composite form-loci greatly enhances the piezo-electric efficiency

of the crystals. A similar turbidity of certain growth-loci only, due to the scattering of light by crystal flaws and inclusions, has been observed in artificial halite (30) and $\text{Na}_2\text{S}_2\text{O}_3$ (31) crystals.

It also has been observed that inclusions ranging in size from dust-like particles to macroscopic crystals have been included in great numbers during particular stages of growth of the host crystal. Turbid or pigmented zones of this nature may closely simulate a true compositional heterogeneity. In some instances, such as the microscopic ilmenite (?) inclusions in the accessory apatite of igneous rocks, the included material appears to have been available in continuous supply throughout the growth of the host crystal but nevertheless was taken up in a discontinuous, roughly periodic, fashion. The mechanism proposed (33) to account for the periodicity is similar in its essentials to that which acts in true compositional zoning. The so-called capped quartz crystals, consisting of repeated separable shells parallel to the terminating rhombohedral faces, apparently owe their origin (34) to the periodic deposition and inclusion of clayey or micaceous material which locally reduces the cohesion of the crystal. Zonally separable barite crystals of similar origin have been described, and the cleavage or parting induced in certain artificial crystals by the adsorption of dyes also appears to be of this nature. In other instances, as in drusy crystallization in cavities from traversing solutions containing suspended particles, the included material seems to have been available only intermittently during the course of crystal growth. Deposition of scattered crystals of another mineral species upon the surface of a host crystal with concomitant growth of the host crystal gives rise to what may be termed buried overgrowths. Crystal inclusions of this origin may be crystallographically oriented to the host crystal, or be selectively disposed with respect to crystal forms or to edges and corners (35). An arrangement of minute inclusions along edge-loci has been described in zircon, garnet, gypsum and other species (36), and tiny pyrite crystals have been found arranged along certain corner-loci in calcite crystals.

In the so-called anomalous mixed crystals, two structurally related but distinct crystal phases are inter-crystallized in an intimate, oriented fashion. Such bodies characteristically exhibit zoning on a closely repeated, microscopic, scale. Successive zones are alternately rich and poor in one of the phases. The zoning, and the circumstance of formation of the intergrowth itself, is a consequence of the periodic interaction of diffusion processes acting at the growth surfaces, and stands in closest relation to the zoning observed in true mixed crystals. The different expression of the interface processes in the two cases is a result of phase equilibria in the solution: in the one case the foreign atoms can be housed by isomorphous substitution in a single-phase host crystal, and the

periodic variation in concentration of the foreign atoms at the interface gives rise to compositional (isomorphous) zoning; in the other case, the variation in concentration at the interface periodically oversteps a phase boundary and a layering of phases rather than of isomorphous zones results. The zones in anomalous mixed-crystals may be continuous around the crystal, but sometimes the intergrown phase which causes the zoning is restricted to particular form-loci.

It is hoped that the foregoing discussion has emphasized the point of view that crystals are heterogeneous and discontinuous structures not only with respect to their surface geometry, as is ordinarily considered, but also with respect to their internal characters. Crystals have an internal morphology, defined by chemical and physical properties rather than by geometrical characters. This internal heterogeneity can be revealed by appropriate means, and can be applied variously to problems of crystal- and mineral-genesis.

SPATIAL DISTRIBUTION OF MINOR ELEMENTS IN GALENA SINGLE-CRYSTALS

The spatial distribution within single crystals of galena of Ag, Cu, Mg, Al, Fe, Si and other minor elements was investigated by correlated spectrographic and polished section methods. The galena crystals employed were single euhedral individuals bounded externally by two or more crystallographically different forms. A description of the specimens is given in Table 1.

TABLE 1. LOCALITY AND HABIT OF GALENA CRYSTALS

Number	Locality	Habit
1	Telhadela, Portugal	{001} and {111} same size
2	Mina da Mathada, Portugal	{001} and {111} same size
3	Mina da Braçal, Portugal	{001} and very small {111}
4	Alston Moor, England	{001} and small {111}
5	Breckenridge, Colorado	{001} and small {111}
6	Joplin, Missouri	{111} and small {001}
7	Bingham, Utah	{001} and small {111}
8	Summit Co., Colorado	{001} and small {111}
9	Silesia	{001} and small {111}
10	Joplin, Missouri	{001} and very small {111}
11	Joplin, Missouri	{001} and {111} same size
12	Webb City, Missouri	{001} and {111} same size
13	Joplin, Missouri	{001} and small {111}
14	Derbyshire, England	{111} and small {001}
15	Ottawa Co., Oklahoma	Octahedra overgrowing cubes (separate crystals)
16	Neudorf, Saxony	{001}, {011} and small {111}

Differential Staining in Polished Section. Interior sections oriented parallel to $\{001\}$ of the galena crystals were polished and treated with a solution containing 1 volume conc. HNO_3 to 8 volumes H_2O . Several sections usually were cut at different levels in the same crystal. A differential staining was obtained which clearly revealed that the crystals were internally partitioned into regions of greater and less chemical reactivity. The appearance of some representative stained sections is shown in Fig. 4. Unimportant detail was eliminated in drawing some of

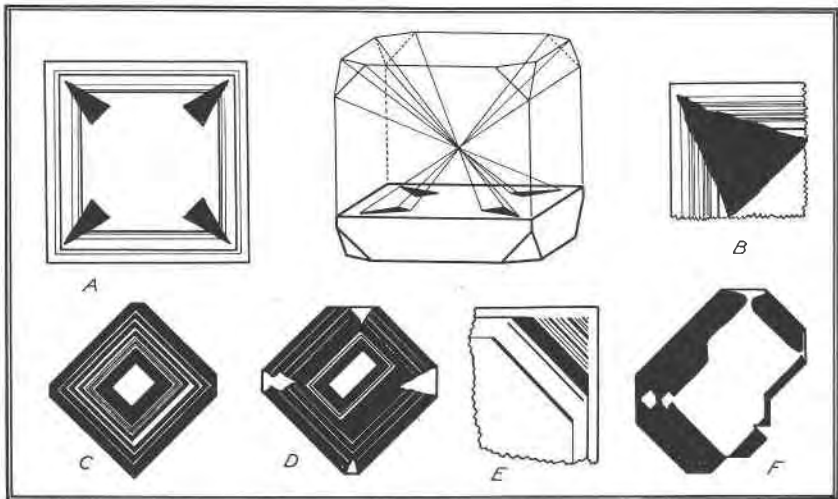


FIG. 4. Differentially stained sections of galena revealing face-loci and growth zones. The sections are parallel $\{001\}$ and the separate crystals are parallelly oriented. The dark areas and zones are relatively reactive, Ag-rich, galena. Section *A* is a shallow cut through a large cubo-octahedron of galena from Joplin. Triangular areas are exposed which are seen from the accompanying sketch to represent the face-loci of $\{111\}$. Section *B* is one corner of a large cube and exhibits both a face-locus of $\{111\}$ and growth bands parallel $\{001\}$. Growth bands parallel $\{111\}$ in an octahedral crystal are shown in section *C*. Section *D* is a crystal from Mina da Mathada, Portugal, with Ag-poor face-loci of $\{001\}$ and octahedral growth zones in a dominantly octahedral crystal. Section *E* shows an enlargement of growth zones in a $\{111\}$ face-locus of a cubo-octahedron. Section *F* shows a distorted cubo-octahedron with Ag-poor face-loci of $\{001\}$.

the figures and minor differences in intensity of the stain are not distinguished. The dark areas in the drawings represent the relatively reactive, dark-stained, portions of the crystals. These portions were found by spectrographic analyses, described beyond, to be distinguished by a relatively high content of Ag.

The spatial distribution of the Ag in the crystals illustrates both the zonal and the face-loci types of arrangement previously described. The Ag tends to enter solid solution preferentially via the growth faces of {111}. The Ag presumably substitutes for Pb atoms. In some sections no selectivity is shown between the several form-loci, but a zonal distribution appears always to be present. The zones may be confined to particular form-loci or be continuous around the crystal. The zones sometimes die out laterally, or are more strongly developed on one side of the crystal due to growth in a current (19). Relatively broad bands of Ag-rich material probably are composed of a multitude of closely spaced, extremely narrow, zones. The size and shape of the several equivalent face-loci as they appear in a given section may be quite varied, but their chemical reactivity and Ag-content always appears to be identical. It is important in interpreting the sections to visualize the several form-loci in three dimensions. Difficulties arise if the habit of the crystal has varied during growth, or if the form-loci are asymmetrically arranged due to an unequal development of the bounding faces. The relations between face-loci as revealed in irrationally oriented sections may be especially confusing. In sections parallel {001}, growth zones arranged parallel to the lateral cube faces are perpendicular to the plane of the section, but in the interior of the section, where the roots of the face-locus of the cube face parallel to which the section was cut are exposed, the zones are parallel to the plane of the section. Two sections cut at right angles through the same crystal are especially useful in interpreting the relations of the growth zones and face-loci.³

Several earlier observers also have recognized an internal partitioning of galena crystals of the nature here described. Becke (37) found an often "wonderfully delicate" zonal structure to be revealed by the action of hot HCl on cleavage sections. Specimens from Pribřam, Bohemia, contained inclusions of minute (0.01–0.001 mm.) unidentified needle-like crystals which were oriented to the galena and which were confined to particular growth zones; this may be an instance of localized exsolution. Recently, Fackert (38) has made a study of the internal *Gefügeausbau* of many galena crystals. His photographs of polished and differentially etched crystals strikingly reveal a distribution of relatively reactive galena with respect to growth zones and to face-loci. A mixture of HNO₃ and absolute alcohol was used as the etching reagent. The chemical

³ Statements made in a previously published abstract by the authors, *Am. Mineral.*, 26, 197 (1941), that Ag becomes more abundant in the crystals during the later stages of growth and that the early stages of growth usually were marked by an octahedral habit are not now considered sufficiently substantiated.

composition of the crystals was not investigated. Photographs of zoned galena crystals also are given by other authors (9, 10).

Method of Spectrographic Analysis. The analyses were made on the Wadsworth grating spectrograph of the Cabot Spectrographic Laboratory of the Department of Geology, Massachusetts Institute of Technology. The method used was that of the carbon arc cathode layer (39), with microphotometer readings of the line densities. All samples were mixed with three parts of carbon powder to ensure smoother burning. The load for each exposure weighed about 10 mg. The lower electrodes containing the sample were National Carbon Special Spectrographic Carbons, $\frac{3}{16}$ " diameter turned down to 3 mm. diameter for a distance of 5 mm. from the end, with a 1.5 mm. hole drilled to a depth of 6 mm. The upper electrodes were National Carbon Spectroscopic Graphites, $\frac{3}{16}$ " diameter. The current supply was 220 D.C. with ballast resistance and inductance to limit the current to about 7.5 amperes. The voltage across the terminals fluctuated between 50 and 60 volts. The cathode layer was projected on a $\frac{1}{8}$ " diaphragm which in turn was focused on the collimating mirror of the spectrograph.

It proved to be difficult to obtain a suitable internal standard which either did not already occur in the samples in appreciably irregular amounts or did not contain considerable amounts of the elements to be analyzed. Accordingly, a variation of the usual internal standard method was employed, similar to the technique long used to determine the relative intensities of lines of widely different wave-length. Several weak Pb lines were used as internal standard lines and all analysis lines, some as much as 1000 Å away, were compared with them. In order to obtain $\log \frac{\text{intensity analysis line}}{\text{intensity Pb line}}$ the densities of the Pb

lines were converted into logarithm relative intensities by a characteristic curve for that wave-length made up from a stepped sector disc exposure of an Fe arc, and were then subtracted from the logarithm relative intensities of the analysis lines determined from their own characteristic curves. Since the logarithm relative intensity of each line was read from its own curve, the effect of variation of contrast with wave-length was compensated for to a first degree, as it would be by restricting the wave-length separation of the standard and analysis line and reading both from the same curve.

The values of $\log I$ obtained by subtracting lines read on one curve from lines read on another naturally depends not alone on the individual readings but also on the separation of the characteristic curves themselves. This in turn is, of course, a factor of the relative intensity in the source of the Fe calibration lines used and, because of the reciprocity law failure of the emulsion, of the intensity level of the exposure. For this reason the arc conditions and exposure times of the Fe sector exposures were carefully reproduced. Even then, the separation of the characteristic curves was found to vary slightly from film to film. Accordingly, the results were brought to a uniform basis by adding to or subtracting from the results on each film an amount equivalent to the difference between the separation of the curves for that film and the separation of the same curves for another film taken as standard. These separations were measured at a blackening level of $d=1.0$. Since increased development has a more pronounced effect on the slope of the characteristic curve at higher wave-lengths, there is a second order error introduced by variations in development conditions, even after the curves have been brought to a consistent basis for $d=1.0$. Development conditions were therefore reproduced insofar as possible. Three or four independent analyses were run for each sample, and the results were averaged. The resultant accuracy was not as great as that normally obtained under more favorable conditions. The average for $\log I_A/I_{Pb}$ for samples on the same film may be considered reliable for purposes of comparison to ± 0.05 in the case of Ag and ± 0.10 for the other elements.

The majority of the results were somewhat better than this. Comparisons from film to film are not so reliable, with the uncertainty at times as great as ± 0.10 for Ag and ± 0.20 for the others. For this reason the exposures for the material from the {001} faces were always made on the same film as the material from the {111} faces of the same crystal.

Results of the Spectrographic Analyses. The galena crystals were sampled by drilling out material from individual octahedral and cubical face-loci. A $\frac{1}{8}$ " hardened steel metal-working drill on a motor-driven flexible hand mounting was employed. A steel hand pick was used in sampling polished sections. Material taken from the faces of the several forms of a single-crystal should be spectrographed individually and not as an aggregate sample in order to recognize chance errors such as would be introduced by cutting into a foreign inclusion or by penetrating into an adjacent face-locus or growth zone.

The analyses made on the drilled samples are reported in Table 2. The larger numbers in the table denote larger amounts; thus, in Crystal 1, the octahedral face-loci contain more Ag and more Cu than do the cube-face loci. The limits of error for purposes of comparison are ± 0.05 for Ag and ± 0.10 for the other elements reported. Results marked *a* denote an absence of the element tested.

Comparison of the results for the octahedral and cubical faces shows that in the great majority of instances there is a difference beyond the limits of error in the content of the minor elements between the respective form-loci. In other words, the minor elements are not, in general, uniformly distributed within the host crystals. This is true for all of the elements tested. Further, there is clear evidence that some of the elements, at least, tend to be selectively concentrated in particular form-loci. Silicon is contained in greater amounts in the face-loci of {111} in 13 of the 15 crystals which contained this element; but in 4 instances the excess of Si in the {111} loci is not above the experimental error. Silver also appears to be relatively concentrated in the octahedral face-loci. Although half of the crystals examined contained an excess of Ag in the cube face-loci, only in one instance is the amount significantly greater than the experimental error, while of the other half, which contain Ag in excess in the octahedral face-loci, 7 of the 8 crystals contain a significant excess of this element.

It must be remarked, however, that the analytical results given in Table 2 were intended to represent the bulk or average composition of the face-loci, and thus do not necessarily indicate the maximum differences in composition between the dark, relatively reactive, galena and the ordinary galena as recognized in polished section. This is obviously the case for the individual face-loci may themselves be zoned, and hence, in a sense, diluted, or, as in other cases, the dark galena does not pre-

TABLE 2. RESULTS OF SPECTROGRAPHIC ANALYSES OF GALENA

Specimen	Form	Ag	Cu	Si	Mg	Al	Ca	Fe	Cr	Ba	Sr
1	111	1.10	-.18	-.47	.62		.92	.46	-.21		
	001	.80	-.62	-.76	.59		.83	.18	-.45		
2	111	1.09	.22	.49	.84	-.12	1.43	-.38	<i>a</i>	.42	-.42
	001	.98	.45	-.16	.61	-.70	1.00	-.72	<i>a</i>	.41	-.58
3	111	.85	.35	.19	.53	-.60	1.06	-.60	<i>a</i>	.36	-.80
	001	.93	-.31	-.30	.42	-.60	1.28	-.60	<i>a</i>	.59	<i>a</i>
4	111	.63	-.70	-.76	-.16		1.02	-.39		<i>a</i>	<i>a</i>
	001	.68	-.34	-.38	.24		1.26	-.06		<i>a</i>	<i>a</i>
5	111	1.36	.46	<i>a</i>	.33	-.34	1.14	-.39	<i>a</i>	.52	<i>a</i>
	001	1.34	.40	<i>a</i>	.32	-.51	1.10	.39	<i>a</i>	.54	<i>a</i>
6	111	-.31	-.23	-.01	.16			-.32	<i>a</i>	<i>a</i>	<i>a</i>
	001	-.24	-.13	-.08	.59			-.24	<i>a</i>	<i>a</i>	<i>a</i>
7	111	-.03	.92	.72	<i>a</i>		1.03	.88	<i>a</i>	-.14	<i>a</i>
	001	-.34	.68	.67	<i>a</i>		.84	1.15	<i>a</i>	-.38	<i>a</i>
8	111	1.64	.68	.40	.75		1.29	-.03	<i>a</i>	-.36	<i>a</i>
	001	1.73	.45	.08	.61		.74	.12	<i>a</i>	-.42	<i>a</i>
9	111	1.67	.11	.51	.99		1.36	.63	<i>a</i>	-.33	
	001	1.69	.37	.33	1.08		1.53	.30	<i>a</i>	-.30	<i>a</i>
10	111	-.03	-.38	-.33		.65		-.51	-.44	<i>a</i>	
	001	-.37	-.01	-.51		-.40		-.46	-.39	<i>a</i>	
11	111	-.06	-.38	.03		.66		-.38	-.42	<i>a</i>	
	001	-.22	.29	-.06		-.64		1.08	-.37	<i>a</i>	
12	111	.10	.10	.10	.16	-.33		-.26	-.51	-.39	
	001	-.03	-.03	-.35	.02	-.64		-.50	-.66	-.51	
13	111	-.20	-.20	.71	.45	-.28		.17	-.50	-.36	
	001	-.13	-.13	.40	.50	-.19		.29	-.50	-.39	
14	111	.89	.94	-.14	.03	-.80		-.29	<i>a</i>	<i>a</i>	<i>a</i>
	001	.95	1.01	-.17	.38	-.45		.09	<i>a</i>	<i>a</i>	<i>a</i>
15	111	-.96	-.51	-.82	-.07	.15	1.15	-.94	<i>a</i>	<i>a</i>	<i>a</i>
	001	-.34	-.61	.00	-.26	.13	.74	-.95	<i>a</i>	<i>a</i>	<i>a</i>
16	111	1.56	-.51	-.47	-.18	.23	.73	-.95	<i>a</i>	<i>a</i>	<i>a</i>
	001	1.56	-.61	-.48	-.29	.15	.52	-.99	<i>a</i>	<i>a</i>	<i>a</i>
	011	1.54	-.50	-.51	1.18	.19	.75	-.74			

ponderate in face-loci of a particular kind. The data of Table 2 thus probably possess minimum contrast. The maximum differences in composition between the dark and the ordinary galena are more accurately represented by the additional analyses reported in Table 3, following. These

TABLE 3. SPECTROGRAPHIC ANALYSES OF "DARK"
AND "ORDINARY" GALENA

Number	Kind	Ag	Cu	Al	Mg	Si
6	Ord.	49.0	-45.3	-91.5	-16.6	
	Dark	70.5	-53.3	-26.8	3.5	
9	Ord.	36.75	-53	-54.25	26	
	Dark	64.25	-31	-64	69.5	
10	Ord.	-25.5	-55		11	
	Dark	3	-56.75		-10.75	
13	Ord.	-32	-44.75		10.5	<i>a</i>
	Dark	3.5	-30		<i>a</i>	18

samples were taken from selected polished and stained sections which exhibited relatively large and well-defined growth-zones and octahedral face-loci composed of dark-stained galena. Silver is uniformly present in significantly greater amounts in the dark galena, as is Si in the single determination made of this element. No systematic distribution is shown by the other elements reported. A ten-fold enrichment in Ag in the dark as compared to the ordinary galena was reported elsewhere (19) for another specimen, from Joplin, not included in this study. The amount of silver present in these galenas was estimated as never above 0.1 weight per cent, with the majority containing between 0.01 and 0.0001 per cent. The results of the analyses taken as a whole clearly indicate that the octahedral face-loci (to which the dark galena is relatively confined) are relatively rich in both Ag and Si. The Ag presumably is contained in isomorphous substitution for Pb. The manner in which the Si exists in the crystal, as discrete Si atoms, as SiO₄ groups or perhaps as colloidal particles of SiO₂, together with the housing mechanism itself, is entirely problematic. The mechanism by which the Ag and the Si were selectively distributed during the growth of the crystal between the octahedral and cubical face-loci constitutes a separate problem.

In connection with the enrichment of the octahedral face-loci in Ag and Si, it is interesting to note that octahedral crystals of galena long have been thought to be especially rich in Ag or to occur particularly with

silver ores. This correlation was first made by Werner in 1774, who stated (40) that

“Uebrigens scheint mir, so viel ich bemerkt habe, der mehrere oder wenigere Silbergehalt an der Verschiedenheit der Krystallisationen des Bleiglanz Ursach zu kenn, so, dass die Krystallisation desselben, wenn er mehr Silber halt, octahedrisch, und wenn er weniger halt, wurfelisch ist.”

Jameson in 1820 remarked (41) that octahedral crystals were typically associated with silver ores, and others have made similar observations. This correlation of octahedral habit with silver content may be well founded, inasmuch as an adsorption of a foreign material by particular faces of a growing crystal, as of Ag by the octahedral faces of galena, ordinarily results in the development of those faces as the dominant habit. Recent studies (42) of the crystal habit of galena in relation to the paragenesis of the mineral suggest that octahedral and cubo-octahedral crystals usually occur with tetrahedrite, sphalerite, calcite and cubical crystals with quartz. Much work remains to be done, however, before any generalities can be drawn in these regards.

TABLE 4. LOCALITY AND HABIT OF CALCITE CRYSTALS

Number	Locality	Habit
1a	Joplin, Missouri	Scaleno-hedral crystals. Violet zone.
1b		Yellow-brown zone.
2a	Loughborough township, Ontario	Deep violet zone parallel $\{10\bar{1}1\}$
2b		Almost colorless zone parallel $\{10\bar{1}1\}$
3a	Rossie, New York	Violet zone parallel $\{10\bar{1}1\}$
3b		Almost colorless zone parallel $\{10\bar{1}1\}$
4a	Andreasberg, Saxony	Crystal tabular $\{0001\}$. Face-locus of $\{0001\}$
4b		Face-loci of lateral steep rhombohedron
5a	Tsumeb	Colorless outer zone $\{21\bar{3}1\}$
5b		Pale yellow interior zone $\{21\bar{3}1\}$
6a	Galetta, Ontario	Violet zone parallel $\{10\bar{1}1\}$
6b		Colorless zone parallel $\{10\bar{1}1\}$
7a	Locality unknown	Zoned crystal with habit change.
		7a = inner colorless $\{10\bar{1}1\}$
7b		7b = outer pale brown $\{01\bar{1}2\}$
8a	Terlingua, Texas	Separate overgrown crystals.
		8a = early yellow crystals $\{02\bar{2}1\}$
8b		8b = late colorless crystals $\{01\bar{1}2\}$
9	Kelley's Island, N. Y.	Crystal pyramidal $\{8.8.\bar{1}\bar{6}.3\}$; bulk sample.
10a	Terlingua, Texas	Complex zoned crystal.
		10a = outer yellowish fluorescent zone
10b		10b = inner colorless non-fluorescent zone

SPATIAL DISTRIBUTION OF MINOR ELEMENTS IN
CALCITE SINGLE-CRYSTALS

Single-crystals of calcite were investigated along the same lines as was galena. Samples were taken symmetrically from different form-loci, and from growth-zones apparent within the crystal by reasons of color differ-

TABLE 5. RESULTS OF SPECTROGRAPHIC ANALYSES OF CALCITE

Number	Mg	Cu	Al	Fe	Mn	Sr
1a	.23	-.12	-.39	-1.07	-.13	-.42
1b	.23	-.60	-.21	-1.04	.44	.28
2a	.49	.02	-.18	-.42	.60	.21
2b	.23	-.79	-.35	-.93	1.00	.30
3a	.12	-.20	-.06	-.98	.51	.02
3b	-.49	.26	-.18	-1.17	-.29	.10
4a	-.03	-.34	-.24	-.95	.28	.01
4b	-.18	-.47	-.10	-1.00	.28	.18
5a	.12	-.70	-.03	-1.24	-1.01	-1.14
5b	.07	-.65	-.20	-1.26	-1.07	.26
6a	-.32	-.53	-.38	-.98	-.19	.03
6b	.14	-.35	-.38	-.56	.66	.24
7a	.04	-.51	-.38	-.33	1.06	.90
7b	.09	-.29	-.08	-.28	.61	.40
8a	.16	-.66	-.09	.28	.03	.70
8b	.16	-.61	-.06	.45	-.14	.48
9	.14	-.40	-.25	-.99	-.48	-.05
10a	.10	-.74	.58	-.50	-.33	.36
10b	.10	-.79	-.10	-.83	.00	.43

ences. The transparency of the mineral is a valuable aid in controlling the sampling. Descriptions of the specimens examined are given in Table 4. The results of the spectrographic analyses are listed in Table 5. The limits of error are ± 0.05 for Mg, ± 0.10 for Sr and ± 0.15 for Al, Fe, Mn and Cu. The results of the analyses clearly show that the minor elements are not uniformly distributed within the host crystal. This is true both for different form-loci and growth-zones in the same crystal and for separate generations of calcite crystals present on the same specimen. Due to

the simple habit and limited number of specimens examined it is not possible to trace any special connection between a minor element and particular form-loci, such as was found with galena. Such a relation may well exist, however, and is in fact to be inferred from observations such as the differential luminescence phenomena previously remarked and the known responsiveness of the habit of artificial calcite crystals to particular impurities in the crystallizing solution. Examples also are known of the selective coloration of form-loci in both calcite and aragonite.

There appears to be no definite correlation between the color of successive growth zones in the crystals and the content of minor elements. The violet and lilac colors of many calcites are known, however, to be due to the presence of rare-earths, and in some instances (23) the percentage and kind of rare-earths in successive growth zones has been shown to be different.

REFERENCES

1. PHEMISTER, J.: *Mineral. Mag.*, **23**, 541 (1934).
2. NOTHAFT, J., AND STEINMETZ, H.: *Chemie der Erde*, **5**, 225 (1930).
3. HABERLANDT, H., AND SCHIENER, A.: *Zeits. Krist.*, **90**, 193 (1935); STEINMETZ, H.: *Zeits. Krist.*, **61**, 380 (1925); DRUGMAN, J.: *Mineral. Mag.*, **23**, 139 (1932); KENNGOTT, G. A.: *Akad. Wiss. Wien, Sitzber.*, **11**, 605 (1853), *ibid.*, **13**, 481 (1854).
4. ITO T.: *Beitr. Min. Japan, n.s.*, **2**, 124, Pl. 8 (1937); ARDAGH, E. G. R., *et al.*: *J. Chem. Soc. London*, "Chem. & Indust.", **53**, 1035 (1934); SWEET, J. M.: *Mineral. Mag.*, **22**, 257 (1930); PELIKAN, A.: *Min. Mitth.*, **16**, 1 (1897).
5. FRONDEL, C.: *Am. Mineral.*, **25**, 91 (1940); BUCKLEY, H. E.: *Zeits. Krist.*, **88**, 381 (1934), *ibid.*, **91**, 375 (1935); BUCKLEY, H. E., AND COCKER, W.: *Zeits. Krist.*, **85**, 58 (1933); FRANCE, W. G., AND RIGTERINK, M. D.: *Jour. Phys. Chem.*, **42**, 1079 (1938).
6. HAHN, O., KÄDING, H., AND MUMBRAUER, R.: *Zeits. Krist.*, **87**, 387 (1934).
7. JOSTEN, A.: *Cbl. Min.* (1930), 432. Figs. 1, 2.
8. GAUBERT, P.: *C. R.*, **182**, 143 (1926); HAWKINS, A. C.: *Am. Mineral.*, **11**, 164 (1927).
9. SCHNEIDERHÖHN, H., AND RAMDOHR, P.: *Lehrb. der Erzminer.*, Berlin, **2**, Figs. 82, 91, 92, 101, 102, 112 (1931).
10. VAN DER VEEN, R. W.: *Mineragr. and Ore Dep.*, The Hague, **1**, Figs. 24, 25, 26, 56, 57, 57a, 100, 123 (1925).
11. BUNN, C. W.: *Proc. Royal Soc. London*, **141A**, 567 (1933).
12. GOSSNER, B., AND BÄUERLEIN, T.: *Jb. Min., Beil.-Bd.* **66**, 1 (1932).
13. SHANNON, E. V.: *Proc. U. S. Nat. Mus.*, **66**, 57, Fig. 7 (1924).
14. HOLZNER, J.: *Zeits. Krist.*, **87**, 1 (1934); PELIKAN, A.: *Min. Mitth.*, **16**, 1 (1897).
15. CORNU, F.: *Jb. Min.*, **1**, 22 (1908).
16. TERTSCH, H.: *Cbl. Min.*, 273 (1917).
17. STEINMETZ, H.: *Zeits. Krist.*, **61**, 380 (1925); HABERLANDT, H., AND SCHIENER, A.: *Zeits. Krist.*, **90**, 193 (1935).
18. SCHWAB, G. M., AND PIETSCH, E.: *Zeits. phys. Chem.*, **2B**, 262 (1929).
19. NEWHOUSE, W. H.: *Econ. Geol.*, **36**, 622 (1941).
20. HESS, F. L., AND SCHALLER, W. T.: *U. S. Geol. Survey, Bull.* **583**, 30, Pl. XIII (1914).
21. WILD, G. O., AND LIESEGANG, R. E.: *Cbl. Min.*, 737 (1923); BREWSTER, D.: *Trans. Royal Soc. Edinburgh*, **9**, 139 (1823).

22. CHESLEY, F.: *Am. Mineral.*, **27**, 20 (1942).
23. HEADDEN, W. P.: *Am. Jour. Sci.*, **5**, 314 (1923), *ibid.*, **21**, 301 (1906); see also BROWN, W. L., ref. 24.
24. BROWN, W. L.: *Univ. Toronto Stud., Geol. Ser.*, no. **35**, 21, Pl. III, Figs. 3, 5 (1933).
25. DOELTER, C.: *Handb. der Mineralch.*, Leipzig **4** [3], 228 (1930).
26. SMITH, F. G.: *Am. Mineral.*, **27**, 1 (1942).
27. SCHNEIDERHÖHN, H., AND RAMDOHR, P., ref. 9, Fig. 225, among many other descriptions.
28. LUEDEKING, C., AND WHEELER, H. A.: *Am. Jour. Sci.*, **42**, 495 (1891).
29. NICOLSON, A. McL.: *Trans. Amer. Inst. Elect. Eng.*, 1315, Fig. 7 (1919).
30. OCHSENIUS, C.: *Zeits. Krist.*, **28**, 305 (1897).
31. STÜTZEL, H.: *Cbl. Min.*, **65**, (1937).
32. SCHOUTEN, C.: *Econ. Geol.*, **29**, 611, Figs. 1, 5, 6, 11, 26 (1934).
33. BRAMMALL, A., cited in GROVE, A. W., AND MOURANT, A. E.: *Mineral. Mag.*, **22**, 92 (1929).
34. LIESEGANG, R. E.: *Naturwiss.*, **3**, 500 (1915).
35. FRONDEL, C.: *Am. Mineral.*, **19**, 316 (1934); FRONDEL, C.: *Am. Mus. Nat. Hist., Novit.*, no. **759**, 11 pp. (1934), *ibid.*, no. **695**, 6 pp. (1934), *ibid.*, no. **918**, 4 pp. (1937).
36. HARKER, A.: *Metamorphism*, London, 44 (1939).
37. BECKE, F.: *Min. Mitth.*, **6**, 237 (1884).
38. FACKERT, H. W.: Inaug. Diss. Albert-Ludwig. Univ., Freiburg, 55 pp., Figs. 20, 22, 29 to 39 (1929).
39. STROCK, L. W.: *Spectrum Anal. with the Carbon Arc Cathode Layer*, Adam Hilger, London (1936).
40. WERNER, A. G.: *Abhandlung von der äusserlichen Kennzeichen der Fossilien*, Leipzig, 187 (1774).
41. JAMESON, R.: *System of Mineralogy*, Edinburgh, **3**, 355 (1820).
42. OBENAUER, K.: *Jb. Min., Beil.-Bd.* **65**, 87 (1932); KALB, G., AND KOCH, L.: *Cbl. Min.* **308** (1929).
43. GAUBERT, P.: *Bull. Soc. Min.*, **25**, 232 (1902).
44. COLOMBA, L.: *Acc. Lincei Roma, Rend.* **18**, 530 (1909).