The Noncolloidal Origin of "Colloform" Textures in Sphalerite Ores

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Abstract

"Colloform" ores have generally been considered to have been deposited as colloidal sulfide gels, and even transported as colloidal "sols." However, studies of doubly polished plates of "colloform" sphalerite-wurtzite assemblages from various deposits reveal crystal growth features that cannot have been formed by crystallization from gels, and indicate that most, and perhaps all, grew directly as minute druses of continuously euhedral crystals projecting into an ore fluid. Each of the many textural criteria proposed for recognizing colloidal deposition is shown to be invalid, ambiguous, or inapplicable to these samples, and perhaps also to most other "colloform" mineral samples.

Four conclusions pertinent to ore research are derived from this study: (1) Primary fluid inclusions in "colloform" samples are believed to represent the original ore fluid, not merely a residual fluid from the crystallization of a gel. (2) Although euhedral crystals may possibly grow directly from a sol, several features make a noncolloidal (true solution) ore fluid more probable. (3) Maintenance of the large number of crystal nuclei responsible for the "colloform" texture is attributed to relatively high supersaturation, and hence relatively high nucleation and growth rates, for the temperatures involved. (4) Remarkably uniform, regular compositional microbands, traversing many crystals in samples from the east Tennessee, Aachen, and particularly the Pine Point deposits, are tentatively interpreted as annual "varves." No actual growth rates have been determined, but each "varve" consists of a dark and a light band, outlining sharply euhedral former crystal growth patterns and suggesting an annual change in the ore fluid due to dilution with surface waters of varying volume or chemistry (e.g., oxygen or organic content).

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Introduction

Ever since Rogers (1917) proposed the term "colloform" fifty years ago to describe certain features that he thought were indicative of a colloidal, gel-like stage during ore formation, the term has become a shibboleth that many generations of students have learned. A review of the recent monographs, textbooks, and periodical literature on economic geology from the United States and abroad reveals that this concept is still accepted by many if not most economic geologists as a self-evident truth. Even worse, it is carried one step further by many to indicate colloidal transport of the ore elements in a colloidal solution or sol. Years ago, as a young mineral collector, I was often puzzled by the fact that a 10× or 20× hand lens revealed the botryoidal outer surfaces of some mineral specimens such as sphalerite, malachite, and the manganese oxides, which were described as "colloform" to be composed of bright euhedral crystal terminations. Thus they appeared to represent merely one size range in a continuum of multnucle.
ated, drusy, crystalline growth. If this is true, what textures are truly "colloform," in the original, genetic connotation of the term?

In a current study of fluid inclusions in "colloform" sphalerite-wurtzite assemblages from many localities. I found no evidence of colloidal deposition. Although these ores generally do not have plainly visible drusy outer surfaces, many internal structures, visible only in very thin, doubly polished plates, revealed that this material crystallized directly from the ore fluid, and not from a gel. Other than scale, there is no discernible difference between these textures, plainly visible only at magnifications of 100 to 1,000×, and ordinary coarse crustiform vein textures visible in hand specimen. The term "colloform" (but only with quotation marks) is perhaps an effective descriptor, in that it conveys to most geologists a clear picture of a common ore texture. The purpose of this iconoclastic report is to note, however, that the important parallels in colloform are not considered to be definitive of colloidal transport and deposition implicit in the derivation of the term is incorrect, at least for the material examined. It is probably incorrect also for many if not most other similar fine-grained, botryoidal, banded ores and minerals showing "colloform" textures, and generally should be replaced by other descriptive terms.

I am indebted to a number of colleagues and correspondents for many stimulating if not always conclusive discussions. A few of the samples were personally collected, but thanks are due for most of the other samples as follows: Prof. A. J. Sinclair, Univ. of British Columbia, Dr. Louis Mody, Natl. Museum of Canada, and Drs. Neil Campbell and F. S. Hultley, Jr.,—Cominco. (Pine Point deposit); Prof. H. Hüttenhain and H. Borchert, Tech. Hochschule Clausthal, and K. H. Wedepohl, Univ. Gottingen (various European deposits); Ecole des Mines, Paris (Silesian brunckite); Prof. A. Maucher, Univ. Munich (Bleiberg deposit); Prof. J. Kutina, Charles Univ., (Katovice deposit); Dr. R. Gussone and Prof. D. Schachner, Tech. Hochschule Aachen (Aachen deposits); and the following from the U. S. Geological Survey: Dr. A. V. Heyl, (Aachen); P. M. Bethke and P. B. Barton, Jr., (Upper Mississippi Valley) and Helmuth Wedow, Jr. (East Tennessee). USNM numbers refer to U. S. National Museum specimens. Special thanks are due to John P. Creel, who prepared the excellent very thin, doubly polished sections so necessary for this work. The manuscript profited greatly from the thoughtful reviews of John L. Haas, Jr., and E. W. Tooker.

Published Evidence and Criteria for Colloidal Deposition

In view of the long standing acceptance of "colloform" textures as the result of crystallization of colloidal gels, a review of the many criteria that have been proposed in the literature for colloidal deposition is appropriate. There are many minerals, not examined in this study, that also exhibit "colloform" textures and hence have been considered to have formed from gels. These include cassiterite or "wood tin" (Knöpf, 1916; Newhouse and Buenger, 1928; Lebedev, 1965); the cobalt nickel arsenides from Cobalt, Ontario (Lindgren, 1925b); pitchblende, coffinite, pyrite, chalcocite, aragonite (Lebedev, 1965, p. 29 and elsewhere), and even metallic copper (Carpenter and Fisher, 1930) and arsenic (Rozentsvit and Epshteyn, 1967). Let me hasten to add that most of the proposed criteria were considered by these and other authors to be only suggestive, or permissive, and not definitive of a colloidal origin, and many of the distinguishing features were assumed to have been lost during later crystallization to form "metacolloids" (Boydell, 1925; Laskey, 1930). For ease in reference to these criteria in later sections of this paper, they are presented in semibold outline format.

Several miscellaneous lines of evidence from the literature that are not particularly pertinent to the specimens at hand include: (1) Frambooidal textures, e.g., pyrite; (2) "Pellet" texture (Bastin, 1950); (3) "Frog-egg" texture (Rust, 1935); and (4) "Pulsed apart" sand or other mineral grains, "floating" in a mass of introduced material (Rust, 1935). There may well be other criteria presented in a large Russian book on the subject (Chukhrov, 1955) but unfortunately it has not been translated into English.

A. "Colloform" Texture (In The Restricted Sense)

Rogers (1917, p. 518) proposed this term "... for the rounded, more or less-spherical, forms assumed by colloidal and metacolloidal substances in open spaces." He included spherical, botryoidal, reniform, stalactitic, and mammillar forms, and later authors added rotund, scalloped, globular, olistic, pisolitic, and concretionary forms. The controlling property is considered to be surface tension, which acts to pull the viscous gel into spherical masses, and hence the value of any such form as a criterion varies with the degree of sphericity. Bastin (1950, p. 27) emphasizes the importance of a "... close approach—in cross section—to a circle or an arc thereof..." and Boydell (1925, p. 325) challenges a critic to propose a substitute for surface tension to develop such spherical forms. According to Lindgren (1925b; 1926, p. 140–141), Rust (1935), and others, gels formed as a result of replacement within a rock or mineral, without free surfaces, would also tend to...
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take on bulbous or spherical forms, presumably due to surface tension phenomena. On the other hand Lebedev (1965, p. 24 and elsewhere) considers flat faces between adjacent oolites, as in the Iokun'zh lead-zinc deposit, to be due to deformation of plastic materials, and impossible with a crystalline texture. An entirely different process for the formation of some spherical forms has frequently been proposed, based on radial diffusion through preexisting gels, from essentially point sources, and subsequent precipitation of substances in concentric (Liesegang) shells. It has also been invoked to explain spherical structures formed by replacement processes, as opposed to open space filling (Lindgren, 1926, p. 140; Bastin, 1950, p. 27).

B Shrinkage Or Syneresis Cracks

Syneresis cracks are a logical consequence of the loss of fluid during the formation of essentially anhydrous crystalline minerals from soft gels containing perhaps 50 percent or more water (or other fluids), and are frequently observed in dried synthetic gels such as varnish, glue, and gelatine. Several different types of cracks are observed in natural "colloform" minerals, each of which has been considered to be diagnostic of deposition as a gel. The most obvious type is the network of cracks or "cracked texture" dividing the mineral into more or less uniformly-sized polygons. This is observed in chryso-colla (e.g., Grigor'ev, 1961, p. 220), chalcedony and pitchblende (e.g.; Bastin, 1950, plate 6), bentonitic clay, opal, and various hydrated magnesium silicates. Where the mineral involved has concentric and radial structures, the cracks may occur between the concentric layers, yielding the "exfoliation spheroids" of Lebedev (1965), or may be parallel to the radial structures, and approximately perpendicular to the layers. One additional mode of occurrence is along the surfaces where individual botryoidal masses interact (the "interference surfaces" of Bastin, 1950, p. 31). Even cracks with a strong gridlike orientation imposed by the structure of the host mineral, e.g., in chalcopyrite, have been considered to be of shrinkage origin.

Commonly these various cracks are filled with another mineral, particularly galena in "colloform" sphalerite (e.g., Kutina, 1952). Rust (1935) describes two additional textural features of shrinkage cracks filled with later minerals that he considers to be criteria for colloidal gels: (1) euhedral crystals of the early host mineral lining the walls of a fracture in it filled with a later mineral; and (2) segmented veinlets, with different minerals filling different parts.

C Concentric Banding And Radial Structures

Most "colloform" minerals exhibit a banding that parallels the curved external shape. At the center of each curved mass is an apparent nucleus that may be on the wall rock, an earlier layer, or a crystal of another substance. The scale of the banding varies over a wide range, from microscopic to macroscopic, and the individual bands differ in color, grain size, or mineral composition and sometimes alternate regularly between two types. Most "colloform" minerals also exhibit a radial structure, consisting of fibrous, acicular, or columnar crystals approximately perpendicular to the banding. The bands from adjacent radial botryoids intersect abruptly along "interference surfaces" that essentially bisect the angle of intersection.

Two entirely different and completely independent colloidal processes, primary depositional banding and secondary diffusional banding, each with a distinct set of physical and chemical requirements, and results, have been invoked to explain the bands. Unfortunately, the two processes are not always clearly distinguished, resulting in some confusion in the literature. The first process is that of primary deposition of a series of layers of gel, particularly in an open space, with the conditions of deposition changing from layer to layer so that the composition of the gel varies. This variation, caused, for example, by the selective adsorption of foreign materials by the charged surface layer of the original colloidal particles, may then yield crystalline bands of a given mineral such as sphalerite of various colors, or a variable assemblage of minerals. Also, solid crystals of other minerals may be enclosed by the accreting gel, thus marking the layers. Crystallization of a layer may occur even before the next layer is deposited.

The second process is that of secondary diffusion banding or "Liesegang rings." These may be formed whenever any diffusion of substances, for example through a preexisting mass of gel, causes a build up and eventual precipitation of a new solid phase at the front; further diffusion yields a series of such precipitations as a series of bands or "Liesegang rings." Park and MacDiarmid (1964) give the banding in agate nodules as an example. If the source of the diffusing materials is effectively a point in an isotropic gel, the bands will be concentric about the point, and if several sources are involved, the bands might be expected to intersect with reentrant angles as are commonly seen in agate as well as "colloform" sphalerite. This compositionally banded but amorphous structure may then crystallize.

A variety of concentric and radial textural features, some mutually exclusive, have been used as criteria for a colloidal origin. Some of the most commonly used textural criteria are as follows:

1. Ill-defined or gradational margins to the bands. Edwards (1954, p. 27-28) states that "Gel origin is assured, however, by textures like those of 'schalen-
blende,’ where the zoning arises from a rhythmic distribution of iron through the zinc-sulfide, in zones which have ill-defined or gradational margins, and must be regarded as Liesegang rings formed by a rhythmic diffusion of the iron ions through a zinc sulfide gel.”

(2) Fibrous, radial crystallization, particularly of hydrous minerals (Boydell, 1925, p. 198).

(3) Thin, delicate, smooth concentric layers (emphasized by Lindgren, 1925a), or even just the presence of “colloform” banding, as opposed to crustification banding which is “… generally attributed to repeated opening and filling of the vein structure…” (Edwards, 1954, p. 19).

(4) Banding, presumably Liesegang, with a regular progressive spacing, becoming progressively ill-defined and wider away from the center. However, Stansfield (1917) showed that under some conditions Liesegang bands could become closer in spacing away from the center.

(5) Interference surfaces. Bastin (1950, p. 31) states that these “… suggest interference in a yielding medium growing from many centers.” Lebedev (1965, p. 48) states, “Thus, the formation of flat contact surfaces between spherulites is almost impossible during joint crystallization of spherulites from true solutions.” He believes that reniform surfaces can form from crystallization rather than surface tension, but that the contact surfaces (i.e., interference surfaces) will then consist of interpenetrating crystals, rather than essentially planar surfaces.

(6) Individual crystals “… extend through more than one zone without interruption” (Edwards, 1954, p. 28). Several authors emphasize this as an important criterion which proves that the crystallization occurred later than and independent of the formation of the Liesegang rings. Edwards (1954, p. 21 and elsewhere) indicates that the fibrous or columnar crystals from “crustification,” as opposed to colloidal processes, “… do not extend across more than one band.”

(7) Crystal size increases toward periphery.

(8) Very fine grain size, or possibly noncrystalline.

(9) Mineral intergrowths of widely variable compositional ratios, particularly minute inclusions of ore minerals in “colloform” gangue.

(10) Complexity of the banded structures.

(11) Nonparallelism of the banding with the walls of the vein.

(12) Different parts of the sample have different banding patterns.

(13) Banding envelops preexisting crystals, as opposed to merely being “deflected” by them. This is emphasized as a valid criterion by Knopf (1916, p. 657).

(14) Bending of bands around embedded, younger, coarse crystals that have grown in the material, indicating a plastic nature. (Edwards, 1954, p. 23; Kutina, 1952; and several other authors.)

(15) Broken fragments of banded material, indicating deformation of the material while still plastic, presumably by the “bursting of colloidal membranes by osmotic forces” (Knopf, 1916, p. 658).

(16) Curvature always convex toward younger, free surface (emphasized by Schwartz, 1951).

(17) High gloss to outer surface.

(18) Small size of the spheroidal structures.

(19) Rhythmic compositional banding, particularly in minor element content.

(20) Widely variable degrees of crystallinity of different minerals, and diversity of textures for a given mineral (Lebedev, 1965, p. 124).

(21) Agreement of the apparent order of aggregation of sulfides in the samples with the known order of flocculation of sulfide sols (Rust, 1935).

D. The Colloidal State as A Necessary Intermediary During Condensation

This argument is based on the requirement that since every substance may occur in all degrees of aggregation, all must go through a colloidal stage on condensing from an ionic, molecular, or atomic solution to form crystals (Boydell, 1925; Doelter, 1931).

Evidence for Direct Crystallization

The lead-zinc ores from the Pine Point deposits described in the preceding paper in this journal (Roedder, 1968a) provide the main evidence presented here for the genesis of “colloform” textures, but are supplemented by additional samples from a series of classic localities in Europe and America. Only the more significant features exhibited by sections from the other localities will be described, as they are all rather similar. Except for Gilman and Creede, Colorado, these are all stratiform lead-zinc deposits (Brown, 1967).

Pine Point, Northwest Territories, Canada

General Features.—The lead-zinc ores of Pine Point (lat. 60°52’N; long. 114°27’W) have been described by Campbell (1966, 1967) and others as having “colloform” textures, and many of the available samples do indeed exhibit the standard features normally included in that term. Although some of the sphalerite occurs as discrete crystals, much occurs as finely banded, botryoidal crusts several centimeters thick, coating breccia fragments and lining vugs. In hand specimen the bands coat over and around small irregularities in the substrate, whether
they be in previous bands or wallrock. Individual bands vary in color in reflected light from almost white through yellowish-brown to very dark reddish-brown, and closer examination generally reveals additional, still finer banding. With a hand lens the white bands appear almost porcellaneous on broken surfaces, but all colored bands show evidence of crystals of sphalerite, visible as cleavage reflections. These crystals are greatly elongated perpendicular to the bands, and individual crystals may cross many thin bands. The subparallel arrangement of such crystals yields a radial-columar or almost fibrous appearance. Thin, doubly polished plates (≈ 0.5 mm thick) reveal even more details of banded, radial textures, as seen in Figures 1 and 2.

Galena.—Three distinct textural varieties of galena in these ores (Fig. 1) are pertinent to discussions of the origin of the "colloform" textures. Type I consists of large skeletal crystals, mainly in the centers of the botryoids of banded sphalerite, where they appear to cut across the bands. Type II consists of equant to elongated, single crystal blebs, generally arranged radially in the sphalerite botryoids. The ends of the crystals are generally blunt, and sometimes even faceted toward the outside. Type III consists of coarsely crystalline veinlets that cross the samples in part randomly, but which are frequently found along the "interference surfaces" between botryoids. Campbell (1966, p. 958) indicates that type I is presumably formed by replacement of sphalerite, and that type II "... suggest the filling of cracks caused by drying and shrinking in such deposits." Kutina (1952) illustrates veinlets of type III (from Moresnet, Belgium), which are assumed to be due to shrinking.

There is little doubt that some galena has replaced sphalerite, as seen, for example, in Figure 3, where one of the concentric bands of a sphalerite botryoid has apparently been completely replaced by a single galena crystal. It is also obvious that the ore has been brecciated (Fig. 2), and that type III galena fills some of these cracks. The fact that the cracks may be radial and/or concentric does not necessarily indicate colloidal deposition, however, as any radially fibered, concentrically banded crystalline mass would also be expected to fracture this way, and does so (Fig. 3). Similarly, the occurrence of cracks, now filled with galena, following interference surfaces, does not require shrinkage to have occurred, as these surfaces are weakly cemented and are frequently opened during brecciation.

Origin by replacement or by crack filling does not seem adequate to explain the features shown by most of the galena. The evidence seems to point to type II, and possibly even type I galena being formed mainly, if not completely, by simultaneous growth of coarse, relatively large galena crystals and a druse of much smaller sphalerite crystals. Many of the type I galena crystals consist of skeletal but sharply euhedral cube corners, projecting out from the center. This corresponds to what is commonly seen to be the fastest growth direction of galena, perpendicular to the form (111). Cross cutting relations, in which the elongated, carrotlike galena crystals of both types I and II appear to "interrupt" bands of sphalerite, would be expectable under these conditions; exact counterparts are found in more coarsely crystalline hand specimens of crustified ores wherever a large crystal of one phase has grown simultaneously with a druse of another. Additional evidence is seen in the fact that the innermost parts of some groups of galena crystals all start at one band (Fig. 1, center left), indicating a burst of nucleation of galena. Similar carrotlike structures are also formed when small crystals of one phase are embedded in a single crystal of the same or another mineral, for example, chalcopyrite in fluorite (Roedder, 1960, Fig. 1), and have grown in competition with it for access to the nutrient solution.

The curvature of later bands of sphalerite over the top of euhedral galena crystals, which is evident in samples from Pine Point and most other similar deposits, has been used to signify growth of the galena in a soft, banded, plastic gel (criterion C-14), but is better explained by a simple retardation or cessation in the growth of the galena, permitting it to be engulfed by the growing sphalerite druse. If no new nucleation of sphalerite takes place, this engulfment occurs by radial enlargement of the preexisting sphalerite fibers past the lip of the galena crystal (Fig. 23, I). Similar phenomena are illustrated by Grigor'ev (1961, p. 212), and were recognized by Kutina (1952) as suggestive of noncolloidal growth, but have been proposed by others as criteria for colloidal deposition (C-13). If, instead of growth of pre-existing sphalerite crystals, a new burst of nucleation of sphalerite occurs, the surface of the galena would be covered with a band of sphalerite that appears to grow out from it. This later type of engulfment (Fig. 23, II) has also been considered to be a valid criterion for colloidal deposition (C-14). Both types are seen in "colloform" samples from Pine Point and other localities, and identical but coarser counterparts can be found in crustified mineral samples in almost any museum.

Sphalerite.—At magnifications under about 20×, the banding in the sphalerite appears to be smoothly botryoidal (Fig. 1) or subparallel and slightly crenulated (Fig. 2). When the pure white zones of Figure 1 are examined at high magnification in transmitted light, they are seen to consist of translucent granular masses of very tiny pale yellow sphalerite crystals,
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and contain no plainly evident additional structural detail except for a variation in grain size of individual bands, which causes the variation in reflectivity. Such textures cannot be considered proof of either colloidal or direct crystalization, although they are suggestive of the latter.

When the coarser grained, darker, more translucent portions of sphalerite shown in Figure 1, or almost any part of the plate shown in Figure 2 are similarly examined in transmitted light, even at only 130×, the bands are seen to be made up of a series of sharp crystal facets outlining individual color zones (Figs. 4, 5). These indicate that these "colloform" crusts grew as fine-grained polycrystalline druses, with euhedral crystal facets at the outside growing surface at all times. The present surface of such crusts, where they line cavities, now consists in part of such druses. Although plainly visible at high magnification, by adjusting the level of focus and lighting to reveal the third dimension, these crystal features are not particularly photogenic in these relatively thick plates. They would probably be more apparent in a very thin section (5 μm thick), if such could be made. Only a few of these flat crystal facets are seen in Figure 4, as straight color bands that outline sharp crystal terminations. Each "point" represents a view, in section, of a single color band following over the sharp edge where two former crystal termination faces met. Cleavage surfaces and etching of the polished surface reveal that the individual sphalerite crystals grew approximately perpendicular to and across many color bands. A sequence of such sharp termination points with flat crystal faces on either side, representing the same single crystal edge at various stages in its growth, can be traced through hundreds of bands. The light used in Figure 4 reveals only the color bands, but with strongly collimated lighting and higher magnification, many fine lines, indicating microscopic zones of slightly different index of refraction paralleling the color bands, can also be found in any one of the coarser color bands; these also repeat the sharp crystal-termination angles. As there were many crystals growing side by side, when a change in the growth conditions resulted in the precipitation of a different color of sphalerite, each growing crystal received a layer of the new composition, yielding the distinct color bands. These minute crystals are thus the exact counterparts of the large (1–10 cm) similarly color-zoned sphalerite crystals from Creede, Colorado (Barton, Bethke, and Toulmin, 1963). Relatively uniform maximum growth rates in certain directions for large numbers of such optimally oriented crystals, growing on irregular surfaces, resulted in a growing front that was always smoothly curved, when viewed at low magnification.

Another feature that is indicative of direct crystallization is shown in Figure 5. Here a color photograph would be advantageous, as different parts of this single sphalerite crystal are different colors, even though the banding is essentially perpendicular to the section throughout the area shown. By photographing in deep blue-green light (second order blue-green interference filter), that part of the crystal that grew as the flat facet across the blunt tip (X, Fig. 5), which is striated in oranges and yellows in the mineral, is registered in low contrast dark gray tones. The two adjacent sloping faces (Y), which are minutely banded in shades of grayish purple and yellow in the mineral plate, are rendered in more contrasting tones. Similar crystal growth phenomena are common in these "colloform" sphalerites, but are

**Figs. 1-7, Pine Point, NWT, Canada.**

**Fig. 1.** Doubly polished plate of botryoidal sphalerite (ER 65–101) in diagonal incident light. Three types of galena (black) are indicated by Roman numerals (see text). White bands are fine-grained, almost opaque sphalerite; dark- and light-gray bands are transparent to translucent sphalerite, yellow in plate 0.10 mm thick.

**Fig. 2.** Doubly polished plate from specimen ER 65–99 in transmitted light showing brecciated crust of "colloform" sphalerite that grew from left to right. Color is pale yellow to almost opaque reddish brown in plate 0.09 mm thick. Figs. 4–7 are magnified views in transmitted plain light of areas A, B, and C.

**Fig. 3.** Broken surface of ore specimen ER 65–101 showing a concentric mass of "colloform" sphalerite (s) partly replaced by galena (g). One band near the center (arrow) has been completely replaced with galena, all of which is part of the single crystal, as indicated by the bright coherent cleavage reflection. This was photographed in reflected light, using the method described by Schaller (1953). A later unfractured wedge across the whole specimen follows the galena cleavage and the radial and concentric planes of weakness of the "colloform" sphalerite.

**Fig. 4.** Magnified view of area at "A" in Figure 2, in same orientation, exhibiting various crystal growth details on the left (see text), and a minutely banded or "varved" layer at the right. Nearby parts of this same "varved" layer, area "C" of Fig. 2, are also enlarged in Figs. 6 and 7.

**Fig. 5.** Magnified view of area at "B" in Figure 2, in same orientation, showing a single crystal of sphalerite with different colors in material grown on the different faces, X and Y (see text).

**Fig. 6.** Magnified view of area at "C" in Fig. 2 in same orientation, showing textural detail of a regularly "varved" band. The finer "varves" (band pairs) are 7 μm thick. The wrinkles in the bands represent the intersections of adjacent pointed subparallel crystal terminations that grew from left to right.

**Fig. 7.** Magnified view of a small area from upper center of Figure 6 in the same orientation, but at a slightly different level of focus. One single sphalerite crystal, occupying the center of the photograph, between the two lines, grew from left to right. Each color band follows over the pointed termination, but only one, at F, is in focus at this level.

**Fig. 8.** Left—Upper Mississippi Valley lead-zinc district, sample PMB 62–131. Photographed in transmitted light; oriented with the direction of growth from bottom to top. It consists of sphalerite crusts ranging from yellow to dark reddish brown to almost opaque in doubly polished plate 0.45 mm thick. The many regular alternations (coarse "varves") of yellow and dark-red sphalerite are continuous from one crystal to the next, but do not always appear so colored through yellow and red to dark brown in this doubly polished plate 0.15 mm thick.
usually less photogenic in that they are all in shades of red and yellowish brown.

The general explanation of the color variations in such crystals is simple, but the specific mechanism and coloring agents for these crystals are unknown (Roedder and Dwornik, 1968). It is well known that many (if not all) crystals take up different amounts of trace constituents on different crystal faces. This is apparently the result of surface equilibria, wherein for any one of a variety of possible crystal-chemical reasons, one face accepts a trace constituent more readily than another. Thus the differences in aluminum contents of individual parts of single synthetic quartz crystals grown on various crystal faces may be as large as several orders of magnitude. Once completely enclosed in a more or less perfect crystal of effectively infinite extent, these portions of different composition are not at equilibrium with each other, and self-diffusion should eventually level out the differences. But in sphalerite, at the temperatures at which these deposits formed, such diffusion is much too slow.

Barton, Bethke, and Toulin (1963) discuss the problem of surface equilibrium, with particular reference to growth bands in sphalerite crystals as follows (modified). If time and temperature are adequate for complete self-diffusion throughout the solid crystal, the entire crystal will maintain a uniform, nonbanded condition, at all times, even with different compositions being deposited on different crystal faces, at the same or at different times. If relatively less time (or temperature) is available during growth, surface diffusion may still be adequately rapid to permit the newly deposited, near-surface layers to equalize their originally different compositions continuously from face to face, but without equilibration with the inside layers. This yields a zone of uniform color, the thickness of which is a measure of how much material was deposited under essentially uniform conditions. I believe that this is a reasonable explanation for the normal, relatively uniform color of individual bands, as in Figure 4, which may be traced over many different sphalerite crystal faces without any visible change in color. If even less diffusion occurs during growth, each portion of the crystal will maintain the trace constituent concentration (and hence color) characteristic of the crystal face by which it grew, as shown in Figure 5.

*Varve-like, Possibly Annual Banding.—Some of the color bands shown in Figures 4, 6, and 7 are very unusual, in that they are surprisingly uniform in thickness and alternate regularly between two com-
positions. The measured thickness of each pair of bands, light plus dark, is about 7 \( \mu \)m in this zone, and individual bands can be traced for many micrometers in the section. As these bands also show crystal facet outlines in detail (Fig. 7), they cannot be Liesegang diffusion bands. Similar rhythmic banding, although not as photogenic, was found throughout this sample and in several other Pine Point samples.

A series of electron microprobe traverses were made by Harry Rose, Jr., of the U. S. Geological Survey, across the area shown in Figure 6, with a spot of 1–2 \( \mu \)m diameter. Unfortunately little or no variation in iron content was detected, and hence the actual cause of the color banding is unknown. An analysis of the general area of Figure 6, averaging many bands, yielded 2.4 percent Fe (Roedder and Dwornik, 1968).

Although many mechanisms may be proposed to explain such a regular, periodic change in composition, it is tempting to consider the possibility that these are annual "varves," resulting from an annual change in the composition of the depositing solution and hence a change in the trace constituents (and color) of the sphalerite. These changes might be expected if percolating meteoric water were involved in the process, as many changes in the chemistry of meteoric water would occur with the change of seasons. The two most obvious possibilities for annual variation would be organic content (from biologic activity in the soil) and dissolved oxygen content. The latter would vary with the temperature at which the water was equilibrated with air, and would persist during percolation even though the temperature variations would be eliminated rapidly.

"Varves" of similar appearance have also been found in celestite crystals from another area, and may be due to similar processes (Roedder, 1968b). In both cases, the depths at which crystallization occurred are believed to be great enough to smooth out all diurnal variations, and probably even annual variations in temperature of the percolating surface waters. It is possible, though rather improbable, that such "varves" could be biannual, arising from deep seated hydrologic changes brought about by the "kneading" effect of earth tides. P. M. Bethke (oral communication, 1967) has suggested convective overturn as an alternate periodic mechanism. As the ore fluids were hot, this is a distinct possibility, but rather special conditions are needed to achieve periodic overturn rather than continuous convection.

Regardless of the mechanism chosen to explain these "varves" it must, of course, be compatible with the mode of origin of the ores. Similar "varves" have been found in samples from several other zinc deposits, as shown below. In each of these deposits,
there has been an opportunity for mixing of the ore-bearing brine (as determined by fluid inclusion studies) with surface water, thus verifying at least the feasibility of the hypothesis of annual periodicity. One presently unexplained feature of the contacts between adjoining bands needs to be noted, as it may eventually be of use in understanding the environment of formation of these “varved” sphalerites. Although many of these contacts are irregularly or smoothly gradational, there are some abrupt changes, where the line of contact between lighter and darker layers appears as a knife edge, even at 1,250× magnification. The nature of the process that caused the color changes was such, however, that most of the more abrupt transitions are from an early dark zone to a later light zone. The reverse case is considerably rarer.

Another unexplained feature of the “varves” in Pine Point sample ER 65–99, as well as samples from several other deposits, particularly Aachen and Silesia, is the occurrence of an additional color periodicity, superimposed on the “varves,” evident as alternating groups of “varves” with an overall darker or lighter color (Figs. 6, 13). It is most readily recognized where the “varves” are most uniform in spacing and visible, and hence might well be present but unrecognized in many of the less uniformly “varved” samples. The number of “varves” per “cycle” for this larger periodicity is irregular from four to about ten, but the occurrence leaves no doubt that this feature is the result of some real periodicity in the conditions of deposition and not merely a statistical accident in a random variation of “varve” color.

European Deposits

*Moresnet, Belgium.*—This district, which lies about 10 km southwest of Aachen, Germany, is represented by three samples, USNM 73659 and ER 67–64 from the Eschbroich mine, near Moresnet (lat. 50°43'N; long. 5°59'E), and USNM R 549, from Welkenraedt, which is about 5 km south of Moresnet (lat. 50°39'N; long. 5°58'E). Sample 73659 contains dendritic galena crystals as the cores for the botryoids. The banding varies from yellow to red (and opaque) in a plate 0.070 mm thick, and “varves,” mostly in the range of 4–16 μm, are common. Sample ER 67–64 shows “varves” very similar to those from Pine Point. Sample R 549 is similar. The nearly opaque (white) portions show fine banding in strong transmitted light. The transparent bands consist of plumose, highly birefringent wurtzite (?) crystals that crosscut the color bands and cause angular deflections in them (Figs. 19 and 20). Several of the white, opaque bands (as at “A,” Fig. 17) show an irregular series of minute dark cracks. Most of their apparent width is due to staining. The measured total amount of true opening indicated by these cracks corresponds to shrinkage of less than 0.2 volume percent.

*Aachen District, W. Germany.*—Specimen ER 67–35, from the dump of the Breineberger mine, in the Stolberg area (lat. 50°46'N; long. 6°14'E), is an exceedingly fine grained, banded, botryoidal, typically “colloform” sphalerite; individual bands vary from almost white to very dark red brown in a doubly polished plate only 0.10 mm thick (Fig. 9). The coarser individual bands (as at A, Fig. 9) consist of individually color-banded crystals up to 50 μm wide; thin, fine-grained, inclusion-rich layers have been deposited on top of these, conforming to the crystal facets (Fig. 10). Some coarser crystals of galena have formed during the deposition of the banded material (as at B, Fig. 9, and enlarged in Fig. 11). These crystals do not disturb the layers below, but concentrically layered masses of sphalerite above them appear to originate at points of nucleation on the galena surfaces (see Fig. 12). Some of this sphalerite shows a minute but rather regular variation in color and index of refraction, visible as pairs of dark and light layers (Fig. 12). These minute bands or “varves” still show sharp crystal terminations, faithfully repeated in each band, as single crystals of wurtzite (?) grew out radially from the point of nucleation. As the individual layers are much thinner (less than 2 μm per pair) than the plate itself, they are difficult to photograph. Figure 12 shows one fairly sharp string of crystal terminations at the arrow; numerous other similar strings are slightly out of focus.

Another sample (USNM 80659, from “near Aachen, Germany”) is the specimen illustrated by Bastin (1950, pl. 4; Fig. 1) as an example of “delicate cockade structure” rather than colloform deposition, presumably on the basis of grain size, although it shows most of the features usually considered to be “colloform.” The dark portions in reflected light are dark red to yellow in transmitted light at a thickness of 0.18 mm, and show color bands following crystal forms across plumose wurtzite (?) crystals. The white portions are fine grained and almost opaque, but do show some banding and radial fibrous structure. Some transparent yellow to dark red bands are partly changed to opaque white material, particularly adjacent to cracks (Fig. 14). This is a common occurrence in these ores. Partial conversion of wurtzite to sphalerite was considered as an explanation, but X-ray powder diffraction patterns of converted and unchanged material from the same band showed only minor differences. “Varves,” approximately 2 μm thick, were found in some bands. Rows of galena crystals up to several millimeters in
Figs. 9-17, Aachen-Moresnet district, West Germany-Belgium.

Fig. 9. A doubly polished plate, 0.10 mm thick, photographed in plain transmitted light. Sample ER 67-35, from Aachen. Typical "colloform" textures, consisting of opaque and dark-reddish-brown to pale-yellow layers. Areas "A" and "B" are enlarged in Figs. 10-12.

Fig. 10. Magnified view of small area in vicinity of "A" on Figure 9, rotated 90° clockwise to put youngest layer at the top. Note that the banding in the fine-grained, inclusion-laden part conforms to the euhedral crystal shape of the sphalerite (s).

Fig. 11. Magnified view of galena crystal at "B" in Figure 9, embedded in sphalerite and covered by growth of a layer starting from several new nuclei on the surface of the galena (g). Very closely spaced "varves" are visible (arrows).

Fig. 12. Magnified view of upper surface of galena crystal (g) of Figure 11, showing centers of two microbotryoids, very thin "varves" (each less than 2 µm), and some larger radial crystals that appear as abrupt changes in direction in the "varves" (arrow).

Fig. 13. Sample ER 67-20, from Vieille Montagne, in the Aachen area, in transmitted light, oriented with the direction of growth from bottom to top. The curving patterns that appear to reflect the individual 4 µm "varves" are highly birefringent, single, plumeose wurtzite crystals. An additional color banding is superimposed on the "varves," yielding...
diameter grew at each of several stages and were then covered by nucleation and growth of sphalerite as in Fig. 23, II. Several of the white, opaque bands show a few minute cracks (Fig. 14).

Samples ER 67–49, ER 67–62, –63, and –65 through –70, also from the Aachen district, including Vieille Montagne, showed good “varves” mainly in the range of 2 to 4 \( \mu \text{m} \), (Fig. 13) but some as much as 12 \( \mu \text{m} \). In other respects they were very similar to the other samples from Aachen. Sample ER 68–16, from Altenberg, in the vicinity of Aachen (lat. 50°38’N; long. 6°29’E) shows large galena crystals in fine-grained banded sphalerite. Etching reveals growth patterns in these galena crystals that prove them to have grown contemporaneously with the sphalerite (Figs. 15, 16).

Wiesloch, Baden, W. Germany.—This district lies 18 km south of Heidelberg, at lat. 49°17’N; long. 8°42’E about 250 km southeast of the Aachen-Moresnet district. A specimen from “Grube Segen Gottes” (USNM 106766) consists of a polycrystalline mass of galena with a smoothly botryoidal layer of banded sphalerite and later barite crystals. The sphalerite is colored in dark reds and yellows at 0.5 mm thickness, and brown to pale yellow in 0.080 mm. Crystal-growth features in the bands are similar to those at Pine Point except for small sunbursts of light-colored, highly birefringent needles (wurtzite?) at the base of the sphalerite crusts (Fig. 18). “Varves” from 4 \( \mu \text{m} \) to < 1 \( \mu \text{m} \) are common, but regular for only a few cycles in any given zone. Samples ER 67–50 and ER 68–15, also from Wiesloch, are similar.

Blieberg, Austria.—(lat. 46°38’N; long. 13°42’E). A single specimen, ER 66–5, consists of botryoidal crusts of sphalerite several centimeters thick, with individual layers colorless, through yellow and orange to dark reddish brown in plates 0.20 mm thick. Birefringence is moderate, and appears fibrous to bladed. Individual color bands, both in fine- and coarse-grained parts, follow former crystal terminations, and “varves” are present but poorly developed.

Lafatsch Mine, Tirol.—(lat. 47°20’N; long. 11°20’E). This mine lies a few kilometers south of Lafatsch Pass in the Northern Alps, about 15 km east of Scharnitz. A single specimen, ER 67–48, of coarse-grained botryoidal yellow to white sphalerite reveals poorly developed “varves.”

Fig. 18. Wiesloch, Baden, West-Germany; USNM 106766. A mass of galena (g) is covered with a crust of sphalerite and presumably wurtzite that is pale yellow to dark reddish brown in a plate 0.080 mm thick. A composite photograph—lower right half taken in plain transmitted light, and upper left with crossed polarizers. Each curving segment of band “A” has its own radial array of fibers and extinction positions. Many minor color bands and “varves,” 2–4 \( \mu \text{m} \) thick, which zigzag across highly birefringent crystals in bands “B” and “C,” outline the crystals seen under crossed polarizers.

Fig. 19. Polished plate from same sample as Fig. 18. Sphalerite, pale yellow to dark red in a plate 0.040 mm thick, in the form of botryoids nucleated on the surfaces of dendritic galena (black), in plain transmitted light. Coarse curved wurtzite (?) crystals (arrows) cross many bands (see Fig. 20). Where the bands are not nested in the plane of the section, they appear very diffuse, as at “A.” “Varves,” less than 4 \( \mu \text{m} \) thick, are visible in other parts of this section.

Fig. 20. Identical area as in Figure 19, under crossed polarizers, showing wurtzite (?) crystals.

Fig. 21. Sample ER 67–39, from Orel Bialy, near Katowice, Poland, in transmitted light. This minutely banded sphalerite is pale yellow-brown in a section 0.13 mm thick. Long fine fibrous birefringent crystals, which grew from left to right, are arranged perpendicular to the layers. At “A,” a new nucleus (of unknown origin) formed. Initial radial growth from “A” was faster than that from the adjoining areas, thus forming a bump and a cone-shaped interference surface, which is intersected by the plane of the section as a curved line. The birefringent wurtzite (?) needles within the cone are arranged radially, approximately perpendicular to the color bands. Fairly long “varves,” about 20 \( \mu \text{m} \) thick, are evident in several parts of the section.

Fig. 22. Same sample as Fig. 21, showing a growth stage in a single, relatively large (0.15 mm wide), yellow sphalerite crystal that is outlined by rounded droplets, presumably of oil, that stuck to the growing crystal termination and were covered over by continued growth of the same crystal. Similar features are visible in some of the smaller crystals from the finer, fibrous bands, but are much less photogenic.
Raibl, Italy.—This deposit lies 8 km south of Tarvisio, Italy, at lat. 46°30'N; long. 13°35'E, near the village of Cavle del Predil. A single specimen, ER 67-52, of yellow to reddish-brown botryoidal sphalerite shows rather irregular "varves" with a thickness of approximately 2 μm. Some are outlined by specks of unidentified opaque matter.

Silesia, Poland.—The specimens are from four of the mining areas in the vicinity of Krakow, Poland. ER 67-46 and -47 consist of pulverulent white ZnS ("brunckite") from Olkuszy (lat. 50°16'N; long. 19°35'E) and from Boleslaw (6 km west of Olkuszy); they have banded spherical textures, with individual bands varying from transparent to opaque. ER 67-51, from Bytom ("Beuthen"). lat. 50°22'N; long. 18°53'E., consists of yellow botryoidal sphalerite, in part with strongly birefringent plumose crystals and faint but definite "varves." Samples ER 67-58 through -61 are from Orzel Bialy, near Katowice (lat. 50°15'N; long. 19°01'E). All consists of yellow to brown, botryoidal sphalerite, with some bands of strongly birefringent, plumose crystals similar to Figures 13, 19 and 20. Oil (?) inclusions outline some crystal growth bands in sample ER 67-59 (Fig. 22), and similar inclusions are present in sample ER 67-51 from Bytom. Bleaching and conversion to an opaque mass along very thin fractures are very similar to Figure 14. Haranycz (1962) presents photomicrographs of the Silesian ores, including many "colloform" textures similar to these samples. "Varves," mainly 2-8 μm thick, are visible in most sections. Some "varves" show an additional, superimposed color periodicity. approximately every 10 "varves," similar to Figures 6 and 13. Samples ER 68-17 and -18 from "Scharley, Oberschlesien" are similar.

United States Deposits

Gilman, Colorado.—A mass of very smoothly botryoidal sphalerite from the Eagle mine (USNM R16531) about 20 miles north of Leadville, Colorado (lat. 39°14'N; long. 106°18'W) appears as brown to white bands in reflected light; in transmitted light these bands are yellow and opaque, respectively, at 0.30 mm thickness, and have a moderate birefringence and fibrous extinction. This type of material was found below the main magmatic-hydrothermal ore body at depths of perhaps 3,000 feet below the surface (Ogden Tweto, oral communication, 1967). The features visible under the microscope are similar to those in the Pine Point samples. "Varves" are about 4 μm thick, but are not regular for more than 5 cycles in any zone.

Creede, Colorado.—Sample ER 65A-104 from the Bulldog vein, Creede, Colorado (lat. 37°52'N; long. 106°56'W) contains a few multiply banded almost spherical botryoidal crusts of sphalerite up to 1 mm diameter embedded in barite in a barite-silver vein. This vein is believed to have formed rather near the surface, and is part of a group of hydrothermal veins obviously related to volcanism. The sphalerite bands vary from pale orange to deep reddish brown in a section 0.45 mm thick. The individual crystals are color banded, with multiple termination patterns visible. No regular "varves" were seen.

Upper Mississippi Valley Lead-zinc District.—Examination of a number of samples of banded sulfides from this district that have typical "colloform" textures in hand specimen and at low magnifications revealed that in each, the individual bands outline euheral crystal growth surfaces and have many of the features described above for the Pine Point samples, except that the crystals are larger. The best examples of such "colloform" textures were PMB 62-131, from the Blackstone mine, Lafayette County, 18 miles southeast of Plateville, Wisconsin (lat. 42°44'N; long. 90°29'W) (Fig. 8, left). PMB 62-106, from the Thompson mine (lat. 42°36'N; long. 90°26'W), and PBB 116-62, from the Piquette No. 2 mine (lat. 42°42'N; long. 90°42'W), Grant County, Wisconsin. Although many samples from the district have alternating dark and light bands, very few had regular "varve" alternations for more than 5 "cycles." A few samples show exceedingly fine-grained to almost opaque bands, particularly at the start of sphalerite precipitation. Although these appear structureless at first glance, they commonly have a slight radial structure. The ores from this district have generally been considered to have formed as colloidal precipitates, but Bailey and Cameron (1951, p. 631-632) present several lines of evidence for direct crystallization.

East Tennessee-Zinc District.—A large number of finely banded, very dark "colloform" sphalerite samples from various mines in this district show features similar to those of the Pine Point samples. Many exhibit moderately regular "varves," as shown in Figure 8, right, of sample ER 65-44 from the Flat Gap mine, near Treadway, 25 miles northeast of Jefferson City, Tennessee (lat. 36°07'N; long. 83°30'W). When examined in detail, these "varves" are seen to consist of zigzag color bands outlining former crystal terminations, similar to Figure 4. Many of these banded samples show the asymmetric (light color changing to dark gradationally with growth, then abruptly changing to light again). Much coarser crystals of galena, embedded in this banded sphalerite, have grown simultaneously with it. Some of these, that happened to be oriented with (100) parallel to the bands, grew as skeletal, cuplike forms (from predominately edge growth). These
of one liquid in another, as oil in water, the interfacial (surface) tension causes the oil to flow into the spherical, minimum energy configuration. As there is no threshold on the flowage of a liquid under stress, even these very tiny surface forces are adequate to yield the same result eventually. If we assume an irregular mass of soft sulfide gel, however, the problem is different. Many, and perhaps all soft gels are thixotropic to some degree, and in fact this physical property is responsible for their gel-like consistency. The most characteristic feature of thixotropic behavior is the existence of a threshold on the stress vs strain curve. Below a certain magnitude of stress, these gels behave as an elastic solid, rebounding when the stress is relieved, i.e., no permanent shear or flowage occurs; above this magnitude, they flow as liquids. As the magnitude of the surface tension forces tending to round all nonspherical surfaces varies inversely with their radius of curvature, small irregularities are smoothed out most readily. Thus if an irregular mass of gel-like material responded to surface tension forces at all, the smallest projections, with very small radii, should smooth out first, and if the material is thixotropic, there should be a radius above which surface tension cannot overcome the strength of the gel. However, the curved mammillary or reniform surfaces of "colloform" minerals exhibit a very wide range of radii, even for the same layer. On the other hand, the radius of curvature of a multinucleated (drusy) crystallization front is basically a function of the amount of growth since the last nucleation occurred, and the spacing of those nuclei. An approach to sphericity is merely an indication of a large number of nuclei and spatially uniform growth conditions.

An additional serious difficulty with the colloidal theory lies in the nature of the interference surfaces between individual botryoids, as seen in Figures 1, 9, 14, 15, 19 and 21 (criterion C-5). If two spherical globules of oil in water come in contact, surface energy is minimized by their coalescing into a single globule with less total surface. If any given band in a "colloform" mineral is assumed to have been a continuous layer of gel, and to have coalesced into subspherical forms as a result of surface tension, sharp reentrant angles between adjacent, contacting spheroids in the outermost surface of this gel should be eliminated rapidly by flowage. Yet such reentrants are characteristic of these minerals. On the other hand, multinucleated radial crystallization from sep-

Evidence Against Colloidal Deposition

A "Colloform" Textures (in the restricted sense)

Surface tension is commonly invoked to explain the spherical shapes of "colloform" minerals, but there are several problems involved, even if a colloidal gel stage occurs. In order for surface tension to reshape a nonspherical mass of gel into a spherical form, it must overcome frictional forces. In a mass

For convenience this is discussed in terms of the published criteria given earlier. Most of the additional lines of evidence mentioned in the previous sections and in the photomicrograph captions are not duplicated here.

6 Park and MacDiarmid (1964, p. 128) state that "... care must be taken to distinguish colloidal deposition from precipitation around corners," but no distinguishing criteria are given. Similarly, Bastin (1959, p. 27, and plate 4, Fig. 1) states that the textures of schalenblende from Aachen, Germany, which would generally be called typically "colloform," are actually delicate cockade structure, but he presumably bases this on grain size.
"COLLOFORM" TEXTURES IN SPHALERITE ORES

...are centers must lead to such sharp reentrants, unless special care is taken, as in some metallurgical casting practices.

The odd oolitic textures displayed by some sphalerite from the Iokun'zh deposits are considered by Lebedev (1965) to be a result of colloidal processes. In particular, the apparent flattening of oolites (or pisoliths) wherein mutual contact is taken as evidence for the deformation of soft masses of gel by gravity. It is well known, however, that similar flattened interfaces can and do develop from direct crystallization processes.

B Shrinkage or Syneresis Cracks

Several problems are involved in the application of this criterion. Perhaps the most serious is that of the volume percent shrinkage to be expected. Most gels (even hydrophobic types) contain 50 to 90 or even more weight percent water (or other dispersant), and hence can be expected either to shrink 50 to more than 90 percent by volume on crystallization to form dense solids, or to form highly porous solids. Weiser (1935, p. 8) mentions sulfur gels that shrink 99.8 percent in volume. The evidence from the sphalerite samples examined, however, is that although there might have been a minute amount of shrinkage in a few layers...as much as 0.2 percent by volume (Fig. 17), generally there was no shrinkage at all and the resultant minerals are dense. This lack of good evidence for shrinkage cracks is common and has been recognized as a weakness in the colloidal theory, but Park and Cannon (1943, p. 45; also Park and MacDiarmid, 1964) explain it on the basis of the "Wiegen effect" (quoting Liesegang (1931)). Liesegang (p. 253 and 255) defines the effect by reporting that unrefined work of Wiegn and Galecki indicates that, "...when a polydispersoid sol coagulates, submicro will act as coagulation nuclei for amicrons..." (i.e., the larger particles act as nuclei for the smaller). How such a mutual coagulation process would eliminate the shrinkage to be expected on crystallization of the resulting coagulating gel is not made clear.

Some have assumed that individual thin layers of gel are deposited one at a time, and each shrinks in one direction only (perpendicular to the surface) to form a hard layer before the next layer is deposited. This oft-quoted explanation raises several new problems, however, the first of which is residual shrinkage. In the drying of paint films a gelatinous stage is followed by considerable shrinkage in one direction to form a much thinner layer of hard paint. A small amount of residual shrinkage parallel to the surface occurs over a period of years, however, yielding the cracked, checkerboard surface so characteristic of old, multiply painted surfaces. The analogy may not be strictly parallel, but the lack of cracks and the low elastic limit of minerals in tension requires almost perfectly complete shrinkage of each layer before further deposition. Second, if the individual layers are so thin that they do not shrink parallel to their surface, it seems difficult to attain large, smoothly botryoidal surfaces by surface tension. Lastly, there should be gross shrinkage on crystallization, if, as is commonly assumed, the crosscutting radial crystals formed after the "hardening" of the bands (or at least very considerable porosity should form). Thus Lebedev (1965, p. 217) reports as much as 18 percent H₂O in synthetic ZnS "gels" air dried for 24 years.

There is little doubt that fracturing of crystalline "colloform" sphalerite does occur, and that these cracks are frequently filled with later galena. This cracking may be expected to follow weakness in the crystalline sphalerite, yielding radial and concentric cracks within the botryoids, and along the interference surfaces between groups of elongate crystals. This latter is a common source of weakness in metallurgical castings, where special techniques must be used to avoid interference surfaces. In addition, partial replacement could yield some of these same patterns. Similar fracturing can be expected if a phase transition results in a volume change, as in chalcocite-digenite-djupelite (Roseboom, 1966, p. 670), or if a slightly porous finely divided crystalline substance recrystallizes even slightly. This latter may well be the explanation of the small amount of shrinkage cracking apparently present in some very fine grained sphalerite bands (Fig. 17). It is important to note that even this small amount of shrinkage is evident only in the porous, finest grained portions, and not in the coarser bands that should have shrunk even more if they had crystallized from a gel.

Not infrequently veinedets of one mineral found crosscutting a single or polycrystalline mass of another mineral are considered to be evidence of the filling of shrinkage cracks. Almost identical features can form, however, by simple mechanical fracturing of the original crystal, followed by replacement along each fracture. The serpentine veinedets crossing crystals of olivine present a good example.

C Concentric Banding and Radial Structures

As mentioned earlier, two separate and distinct processes have been proposed to yield the banding of "colloform" minerals: (1) varying conditions of deposition of the gel, yielding layers of varying composition, and (2) later diffusion banding or "Liesegang rings" formed in a preexisting mass of gel.

† Two "criteria" given by Rust (1933), based on the nature of the crystals filling these cracks, do not seem to require colloidal conditions.
However, neither process, nor a combination, seems adequate to explain the features shown.

Although varying conditions of deposition of gels could, in theory, yield curving bands of varying composition, thickness, and grain size (all “C” criteria except C-4, -11, -12, and -19), these features can also be expected to occur as a result of normal direct crystallization. Grigor’ev (1961) gives examples of some of these, although mainly in reference to macroscopic textures. In addition, several of these criteria are ambiguous. It has been suggested that the “wrapping” of the “colloform” bands over embedded crystals, criterion C-14, is caused by the embedded crystals forming later than the bands, and lifting the soft plastic layers as they grew. This, however, presents a paradox. As the underlying bands show absolutely no effects of the presence of the crystals (Figs. 11, 14), they must be assumed to have been firm at the time of nucleation and growth of the crystals. Many younger bands do reflect the presence of the crystals, yet new, and otherwise very similar nucleation and growth of crystals has occurred at higher levels in these “deformed” bands, and each of these crystals in turn shows no effects on the earlier bands (Fig. 14).

The possibility of “lifting” of bands of gel by crystal growth is important in another respect. If it could be proven to occur, it might explain the zigzag outline of the color bands simply as a later “crystallization texture” superimposed on the previously smooth concentric colloidal banding (Lebedev, 1965). I find it impossible to visualize a process whereby later crystallization could deform a smoothly curving banded gel into the zigzag crystal patterns (Figs. 4-6, 12, 13, 19, 21) because such a process would require that each euhedral crystal termination, as it grew, caused a displacement of the material in the bands above it in exact duplication of its shape. However, these bands are not inert sheets of elastic material, yielding in front of a rigid crystal point—they are presumably the material from which the crystal is forming, with almost no change in volume.

All criteria based on Liesegang phenomena, such as C-1, -4, -7, -11, -12, and -19, are subject to severe limitations. First and most important, a zigzag crystal-controlled outline for any given compositional band (see Figs. 4, 6, 12, 13) precludes any diffusion process; Second, it would be completely fortuitous to find any spatial parallelism of compositional banding from conditions of deposition, such as adsorption of foreign materials on the surfaces of the colloidal particles before or immediately after deposition, with the banding from later Liesegang diffusion through the gel. A crosscutting of two sets of bands might be evidence for a superposition of Liesegang bands on some previous banding, but this textural feature has not been observed. Third, if the Liesegang banding process alone was assumed to have occurred, the shape of the actual banding, and particularly of the interference surfaces, cannot be explained by diffusion of material from the outside surfaces inward as the cause; the diffusing materials would have to have moved outward from the apparent centers of the botryoids, and each time new botryoidal “centers” appear, as in Figures 1, 11, and 21, some mechanism must be invoked for introduction of the diffusing materials into the gel at these new “point” sources. Fourth, an important, seldom mentioned feature of Liesegang banding (Schade, 1928) is that by the very nature of the process, both the composition and the spacing of the alternate bands must be uniform and consistent. Not only are the bands in “colloform” sphalerite usually far from rhythmic in spacing, but their composition varies widely; occasional layers may consist of pure pyrite, or contain crystals of galena, dolomite, or other minerals that would be impossible by this process. Fifth, banding that is rhythmic in composition and spacing does not constitute proof of Liesegang diffusion. Sixth, Liesegang banding itself does not require colloidal gels—it occurs in aqueous solutions (Morse, 1930) and even in gases (Lloyd and Moravek, 1931)—and one of the most commonly quoted (although not proven) geological examples involves diffusion in the water in the pores of crystalline rocks, forming the iron oxide bands in many sandstones.

An additional problem stems from the obvious relationship between the pattern of crystallization and the compositional banding of the botryoids. Many gels crystallize from a very large number of nuclei scattered throughout the mass, yielding an exceedingly fine grained product. Regardless of whether the compositional banding in the assumed mass of hardened gel was caused by differential adsorption of materials during the various stages of deposition, or from later Liesegang diffusion banding, it is an impossible coincidence that the nucleation of this crystal growth occurred not just commonly but always at the very center of each botryoid. Similar reasoning applies in the case of interruptions in growth such as Figure 21 or the crystal in Figure 11, where nucleation would have to occur at the center of each subsidiary microbotryoid beyond the crystal. There is no necessary spatial connection between the two processes, yet the structure of the resultant

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* Some replacement ore bodies do have large masses of regularly alternating sulfide mineral bands; such material is coarse-grained and far from “colloform,” and was not examined in this study.
crystalline masses shows that crystal growth must have been radial outward from these many centers, and essentially perpendicular to the layers. The reverse direction of crystallization, from the outside in, has been suggested in the literature (for example, Edwards, 1954, p. 20), but the evidence seems to be overwhelmingly against it.

Criterion C-6, concerning the extension of a given crystal across several bands, which has been used frequently, is based on two premises: (1) the crystals must be later than the bands; and (2) since the crystals are later, the bands must be of colloidal origin. The writer believes that neither of these premises are valid. Crystals can and do grow with color bands. Only if the color bands curved smoothly through the crystal might this criterion be valid, and even then it might be a result of coarse recrystallization of a formerly concentrically banded fibrous botryoid. Examples of such coarse crystals with an inherited finely banded structure are seen in native copper samples that have been recrystallized (Carpenter and Fisher, 1930).

Criteria C-11 and C-12 should be valid, and these features should occur commonly in diffusely banded material, but I have found only evidence to the contrary in the published photomicrographs and my own samples. Criterion C-17, a high gloss to the outer surface, might also be valid. Thus the last very thin layer of deposited material on certain "colloform" minerals, particularly iridescent goethite and some manganese oxides, might have been colloidal; all that can be said with certainty is that this surface material is obviously very fine grained, if not amorphous. Similarly, criterion C-8 would be an excellent one if the material is proven to be actually amorphous. Thus Lebedev (1965, p. 29, p. 143, and elsewhere) reports amorphous aragonite and casserite in some "colloform" minerals, apparently on the basis of optical isotropy. Even with the high birefringence of these minerals, however, crystals less than one micron in thickness will appear isotropic.

The degree of smoothness of the individual bands (C-3) is obviously a function of the size of the crystals and the scale at which the sample is examined. Examined in sufficient detail, most such surfaces appear to consist of zig-zag crystal terminations.

D The Colloidal State as a Necessary Intermediary During Condensation

It is true that many ionic solutions go through a colloidal stage on precipitation, so it may be argued that throughout the sphalerite growth process a thin layer of gel formed first and then immediately crystallized to form the crystalline crusts we see (criterion D). Several lines of evidence may invalidate this "criterion." First, it seems impossible to achieve the gross differences in trace constituent composition of the material forming on different faces (e.g., Fig. 5) of a given crystal, if these had formed by the crystallization of a series of thin layers of gel added sequentially. Second it is difficult to imagine a process that would permit a new layer of colorant-rich gel deposited on a druse to be used up completely to form a uniform layer of colored crystal terminations on the druse, each sharply euhedral. Third, the colloidal state is a necessary intermediary only during the original condensation of an ionic, atomic, or molecular solution to form nuclei of precipitate; subsequently these crystals may grow directly from the fluid without the intervention of a colloidal stage. As long as the rate of precipitation of particles is lower than the rate at which these particles are able to arrange themselves into crystals, no colloidal stage will be involved, and in fact, the great majority of crystallization occurs in this direct manner. Kohman (1965) has suggested that crystals might grow from colloidal dispersed systems, and some experiments by Kanin (1936) showed growth of chalcopyrite crystals from sulfide sols, but do not preclude a true solution as an intermediate stage.

An additional problem should be mentioned here. Although there is an extensive older literature on laboratory studies of colloidal sulfide sols (Weiser, 1938), there is no verification of the existence of any truly amorphous zinc sulfide gels. When metal sulfide sols were caused to congregate to form "gels." X-ray studies showed that the precipitates were crystalline SnS₂, PbS, ZnS, or FeS, even immediately after precipitation. However, Lebedev (1965, p. 211) reports some 3-year-old precipitated ZnS "gels" which are stated to be amorphous to X-rays. He does not indicate why he got different results than the earlier work. Frondel (1967) reports co-precipitation of an organometallic zinc compound with zinc sulfide to form a "gel" which dried to a "hornlike mass," but the presumed equivalent natural mineral, voltzite, is rare.

10 One process that is perhaps possible in theory would entail a continuously replaced layer of sulfide gel through which diffusion of trace constituents was fast but from which crystallization was slow. In this case, the growing crystal terminations within the gel would have, in effect, "see" the changes in composition of the fluid outside and hence would develop all the features we now see. Since this is not known to occur in synthetic systems, nor would it generally be expected to leave any evidence of its existence in either synthetic or natural systems, it cannot be considered further.

11 Amorphous lead-arsenic sulfide glasses are made in the laboratory for optical uses, but not from gels. An amorphous material of similar composition ("revoride," Milton and Ingram, 1959) occurs naturally and may represent a dried colloidal gel.
A Proposed Model for the Formation of "Colloform" Textures

From an examination of the growth of crystals in laboratory and industrial processes, and published studies of the theory of crystal nucleation and growth, it is apparent that the dominant parameter controlling the formation of "colloform" textures is a relatively high degree of supersaturation, resulting in relatively high rates of nucleation and crystallization. All crystallization from solutions indicates some degree of supersaturation. If the degree of supersaturation is low, crystal growth rates will also be low, but as spontaneous nucleation is then insignificant or completely absent, all precipitated material may collect on the one or several nuclei present. These are the conditions used in the synthesis of all large crystals in the laboratory, and presumably also in nature. Substances that crystallize readily from solutions of high concentration (the limit is pure melt) can undergo higher amounts of supersaturation (weight percent in solution) without spontaneous nucleation than can diffusively soluble materials, but in either case, as the degree of supersaturation increases, the rates of nucleation and growth increase.

Relatively high degrees of supersaturation are easy to achieve in solutions of materials of low solubility. Thus if the solubility product of a given metallic sulfide is $10^{-8}$, the addition of sulfide ion to even a relatively dilute solution, such as $10^{-4}$ molar in the metal ion, may yield a 10-fold supersaturation. Such a fluid would probably spontaneously nucleate large numbers of sulfide crystals and each would grow until the supersaturation was eliminated, yielding a very small amount of a fine-grained precipitate. If, however, the fluid became supersaturated while moving through a chamber lined with a previously formed precipitate of crystals of the same substance, each of these crystals would tend to grow. As growth rates vary widely on different crystal faces, only the "fittest" crystals, oriented with a fast-growing direction facing the fluid, would survive (with apologies to Charles Darwin). The average size of the individual crystals should vary with the rates of precipitation; if the rate becomes low, the few most optimally oriented crystals should grow at the expense of the rest, overriding them and perhaps eventually yielding a vug with a few museum-sized crystals. If the rate is high, there is inadequate time for the necessary diffusion, and the nearest crystals receive the precipitated material. New nuclei may form in the fluid and settle on crystal surfaces to compete with the others. If a radial group forms around a projection on the substrate, as soon as the individual fast-growing points become separated too far by their radial growth, such new nuclei will have a good chance of surviving and adding to the total number of growing crystals. These areas between crystal terminations can also be filled in by divergent sub-parallel splinter growth as in stilbite.

A flat growing front, consisting of a large number of crystal terminations lying in a plane (for example, Grigor'ev's Fig. 192, p. 216, 1965) is basically unstable, as any minute projection in it will be reinforced or enlarged by easier accretion of new material onto it, as opposed to adjacent areas. Thus the flat front will soon develop a series of arcuate botryoidal projections, and individual polycrystalline projections will overgrow adjacent ones, eliminating them by a process of "natural selection" almost identical to that occurring between individual adjacent crystals. All these individual segments of the surface would be convex outward. If, however, the original substrate were strongly concave, the resultant growth layers will be concave inward, at least for part of the sequence. Thus concave curvature is commonly exhibited by some "colloform" minerals such as certain agates (e.g., Frondel, 1962, p. 211) as well as by the banded, acicular calcium sulfate deposits which may block some hot water pipes.

If the crystallization conditions change, for example if the fugacity of sulfur changes during the growth of sphalerite, each and every growing sphalerite crystal, whether 1 cm or 1 μm in size, will reflect the change by the iron content of the layers deposited on it, just as a vug of quartz crystals frequently will be given a capping layer of milky or amethystine quartz as a result of some change in the conditions of crystallization.

Although analogies may be considered to constitute only permissive evidence, similar-appearing fine-grained, banded, radial crusts are commonly formed by direct, relatively rapid crystallization from liquids or gases in many high temperature industrial processes where no gelatinous colloidal intermediate stage exists between the depositing fluid and the crystalline crust. This includes graphite (e.g., Ramdohr, 1955, p. 299), as well as various metals and oxides. Similar fine-grained banded crusts may be found in the ice on cooling coils of household freezers and refrigerators, and in rapidly deposited, electroplated metals. The crystallization times required to obtain such structures vary with the system involved over many orders of magnitude, e.g., from a few seconds in some metal systems to many years for the fibrous calcium sulfate scale blocking a hot water pipe. Beautiful examples of almost identical textures can be seen to form by spherulitic crystallization of various organic and inorganic preparations under the microscope.

One may also ask whether any natural sphalerite
"COLLOFORM" TEXTURES IN SPHALERITE ORES

has been deposited as a gel. The most suspect candidates are those bands that are so fine grained that they are opaque and white, even in very thin sections. When these portions are examined at high magnification, however, a faint radial structure is seen in some, as well as a banding that is essentially a function of variation in grain size. Although inadequate in themselves, these features are taken to be indicative of noncolloidal origin. Even when structureless, these bands show sharp reentrant angles where they bridge from one botryoidal cusp to another (Figs. 1, 9, 15), precluding at least a surface tension origin for the botryoidal shape. 

Certainly some minerals such as opal, deweylite, and possibly some limonite and bauxite do form as gels but a cursory examination of a number of samples of banded, reniform, botryoidal or stalactitic limonite and agate, as well as malachite, manganese oxides, and "gel pyrite" generally revealed similar banding paralleling the terminations of radiating fibrous crystals, indicating origin by direct crystallization. "Colloform" textures are frequently found in many limestone cave formations, but these also show evidence of direct crystallization, and Edwards (1934) specifically points out that colloform-appearing "cave pearls" form by direct precipitation.

Significance of Noncolloidal Origin of "Colloform" Textures to Ore Deposition Research

If a mineral forms initially as a gelatinous colloidal precipitate, and at some later time changes into a crystalline crust, fluid inclusions in the resulting crystals represent fluids present during the recrystallization, and might bear little or no relation to the fluids from which the gel precipitated. This concept has been used to denigrate the significance of inclusion data to studies of ore formation. However, if the crystals in "colloform" minerals have grown directly, inclusions in them represent an original ore fluid, and are not merely the residue of a later fluid. Although this is most pertinent for studies of fluid inclusions in obviously "colloform" ores, such as those from Pine Point, some geologists suggest that many of the coarser, high temperature assemblages may also have been recrystallized from gelatinous progenitors. There is abundant evidence, however, that all colloidal solutions are basically unstable and very heat sensitive. Therefore, if those ores that are the most likely candidates for a colloidal origin, the low temperature "colloform" ores, are accepted as noncolloidal in origin the possibilities of similar colloidal processes being involved in the higher temperature deposits are that much less likely. Also, there is extensive experimental evidence that much higher crystallization rates are possible at these higher temperatures, making direct crystallization without the intervention of even a transient colloidal stage seem more probable.

As many combinations and concentrations of various ore-forming constituents are possible in colloidal solutions that cannot be achieved with true solutions at equilibrium, it might be tempting to invoke colloidal solutions for the transport of the ore minerals, as opposed to colloidal deposition. Thus it might be proposed that the crystals in the "colloform" aggregates grew as euhedral entities, as proposed here, but from a colloidal solution or "solv." The mechanisms by which crystals may grow from colloidal sols are not known. But it is difficult to visualize a process wherein the composition of the individual colloidal particles adhering to the faces of a crystal, each particle consisting of thousands (or millions) of zinc and sulfur atoms plus trace constituents, could be sufficiently biased to yield the compositional differences between faces seen in Figure 5. Also, entirely apart from the fact that colloidal solutions are unstable and from the fact that such a growth-mechanism does not explain the "colloform" textures, it seems unlikely in view of the apparent evidence of "leach zones" in some of these individual crystals. Although these "leach zones" are far too small to be as readily evident as those described by Barton, Bethke, and Toulmin (1963) in single large sphalerite crystals from Creede, Colorado, they do seem to be present. As colloidal solutions cannot dissolve a crystal of the same material as the dispersed solid phase, such evidence of leaching is critical and should be looked for and examined carefully. Figure 15 shows an apparently similar leach zone, but here an entire polycrystalline band has been partly removed before deposition of the next band.

As the large number of crystal nuclei characteristic of a "colloform" texture is attributed to relatively high supersaturation, this evidence concerning the nature of the ore-forming fluid may eventually be of significance in considerations of the chemistry of ore mineral transport and deposition. If it can eventually be proven that the "varves" in the sphalerite are truly annual features it would be particularly significant, as the combination of data on concentration, degree of supersaturation, and crystal growth rates will, in effect, define the hydrologic regimen at the time of deposition, including both rates and volumes of flow.

It seems reasonable to infer, both from the evidence of relatively high supersaturation implicit in the "colloform" textures and the presumption of mixing with
surface waters proposed to explain the “varves,” that ore deposits showing these features are more likely to have formed near the surface of the earth. This is true because it is here that relatively rapid changes in ore-fluid conditions are most expectable. The occurrence of “colloform” textures and “varves” in a variety of strata-bound lead-zinc deposits, presumably formed under shallow conditions, supports this, but the occurrence of similar textures in sphalerite at Gilman, Colorado, which presumably was formed at depths of perhaps 5,000 feet below the surface, shows that they should not be considered as a proof of shallow origin. Even more significant, perhaps, are the indications that “colloform” textures tend to disappear with depth in some of these deposits, for example in Silesia (Haranucz, 1962), in Pine Point (p. 68 in Campbell, 1967), and perhaps in all of them.

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