

VARVELIKE BANDING OF POSSIBLE ANNUAL ORIGIN  
IN CELESTITE CRYSTALS FROM CLAY CENTER,  
OHIO, AND IN OTHER MINERALS<sup>1</sup>

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ABSTRACT

Some celestite shows a rhythmic, paired banding that may be of annual origin, visible with well-collimated transmitted light as straight, parallel, alternately darker and lighter bands, mainly parallel {210}. Although the thickness of the individual bands and of band pairs varies widely within a given crystal, these thicknesses are very uniform for sequences of hundreds of pairs. Individual pairs range from 3-70  $\mu\text{m}$  total width, and may be traced laterally without thickness change for 0.5 cm; some continue over former crystal terminations. They are visible owing to minute differences in index of refraction (proven with Nomarski interference contrast illumination) arising from variable substitution of barium for strontium (proven by electron microprobe). Somewhat similar banding is found in agate and "colloform" sphalerite from other localities.

Of eight mechanisms proposed, only one, annual seasonal variation, seems appropriate for these samples. It is hence concluded that the warm brine from which the celestite grew was diluted with surface water that varied in composition or amount over a yearly cycle, causing the compositional banding. If the band pairs are truly annual, i. e., if they are "varves", they yield valuable rate data on diagenetic processes and the hydrologic regimen, and should be searched for in other samples.

VARVELIKE BANDING IN CELESTITE

*Occurrence.* The large, pale-blue celestite crystals from vugs in dolomite in the vicinity of Clay Center, Ottawa County, Ohio, (lat. 41° 34'N.; long. 83° 22'W.) are found in many mineral collections. The celestite blades, some 10 cm or more in length, in part replace dolomite and also occur in vugs with somewhat later brown, fluorescent fluorite. Other associated minerals include calcite, aragonite, dolomite, strontianite, pyrite, marcasite, sphalerite, galena, barite, and gypsum (Strogonoff, 1966). Celestite crystals from similar occurrences to the north in Monroe County, Michigan, are associated with free sulfur and hydrogen sulfide-bearing water (Sherzer, 1895; Kraus, 1905; and Kraus and Hunt, 1906). These minerals are usually considered to have formed during a late stage of diagenesis. There is evidence that the enclosing Guelph faunal-zone-equivalent in the Cedarville Dolomite, of Silurian age, an evenly bedded, porous dolomite of shallow-water and possible coral-reef origin, was a solid, well-lithified rock at the time of vug formation (Morrison, 1935; Howard, 1959).

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

A suite of such specimens was examined for fluid-inclusion evidence of the conditions of origin. One blue, 10-cm celestite blade from the south-east wall of the Basic, Inc., quarry at Clay Center, about 15 m below top of bedrock (sample ER 65-72) was found to have a very regularly paired banding of microscopic dimensions. As these band pairs are believed to result from annual variations in the conditions of deposition, they are tentatively called "varves."

Many smaller celestite crystals from the vicinity of Clay Center were examined for similar varves, but although irregular and in part very visible striations parallel to crystal growth faces are present in all, only a few 6-8 cm crystals show regular varves (particularly ER 68-23). Well-developed varves were found in several celestite crystals from similar occurrences at Bascom, west of Tiffin, Ohio (lat. 41° 08'N.; long. 83° 17'W.; USNM<sup>1</sup> 94965), at the France Stone Co. quarry, Waterville, Ohio (lat. 41°30'N.; long. 83°45'W.; ER 68-24) at the Lime City quarry at Lime City, Ohio (lat. 41°02'N.; long. 83°33'W.; courtesy of Prof. L. Larsen), and in Michigan, including USNM R13950 (from Monroe County, Michigan, north of Clay Center, Ohio), Maybee quarry, Maybee, Michigan (lat. 42°01'N.; long. 83°30'W.; courtesy of Prof. L. Larson), and USNM 114789, 115954, 115958, 115959, and 115960 (all from Scofield, Michigan, lat. 42°02'N.; long. 83°28'W.), but not in celestite crystals from other occurrences in vugs in Paleozoic limestones and dolomites, such as Chittenango Falls, Madison County, New York (lat. 43°05'N.; long. 75°50'W.; courtesy of Miss Susan Marcus), from Mitchell, Indiana (lat. 38°43'W.; long. 86°29' W.; USNM 114193), and from Woodville, Ohio (lat. 41°27'N.; long. 82°23'W.; USNM R14979).

*Description.* The varves in the celestite are visible in some crystals under a binocular microscope, without polishing, but they are most readily seen in polished plates cut perpendicular to the plane of the varves and in well-collimated lighting. They may be plainly visible at one level of focus and invisible at others. Under the microscope the typical blue color of these celestite crystals is too pale to be visible, and the individual varves are seen as pairs of alternately lighter and darker bands that become more conspicuous as the substage diaphragm is closed down. Only parts of the crystals appear varved, but as the boundaries of the areas showing varves are in part gradational, varves may be present but invisible throughout. No differences in extinction position, index of refraction, or birefringence could be observed between the varved parts and the rest of the crystal, but differences up to 2° were noted in extinction positions for

<sup>1</sup> USNM refers to U. S. National Museum.

adjacent dark and light bands in grain mounts. The broken edges of some varved grains consist of a series of cusps that match the spacing of the varves, indicating a physical difference between adjacent bands. The more regularly varved parts of the crystals behave as diffraction gratings in parallel transmitted light and yield moderately pure spectra, as in "iris agate" (Jones, 1952).

Although the varves seem to be visible not due to coloring but only due to slight differences in index of refraction of the adjacent bands, no differences could be detected in grains mounted in index oils. In thick plates (1–2 mm), however, the varves are plainly visible by ordinary microscopy, and all four photomicrographs were taken with normal illumination. The index differences that make the varves visible were much more obvious using Nomarski interference contrast illumination; with this procedure the light and dark parts of each varve could be made to show as first order orange and blue, respectively, on grain mounts in oils. On the thick plates neither Nomarski interference contrast nor normal phase contrast microscopy was as effective as ordinary collimated lighting.

In orientation, the varves parallel common celestite crystal forms, and obviously represent stages in the growth of the crystal, as they parallel other evidences of growth such as zones of solid or liquid inclusions, gross color banding, and the present crystal faces. Varves parallel to  $\{210\}$  are most visible (Fig. 1) but plates cut in other directions show similar, although generally less regular banding parallel to other forms, particularly  $\{001\}$ .

*Thickness.* The thickness of individual varves or band pairs (one dark and one light) is mainly in the range of 6 to 20  $\mu\text{m}$ , but varies from a minimum of 3 to about 70  $\mu\text{m}$  in these specimens. In any given area, varve thickness is generally uniform. Thus one group of about 1000 varves has an average pair thickness that changes fairly uniformly over its length from 7.5  $\mu\text{m}$  to 10.6  $\mu\text{m}$ , but in other areas the thickness of adjacent varves may change abruptly, as seen in Figure 2A. With rare exceptions, no change in thickness or other irregularity was noted along the length of any given varve, but cracks and other crystal imperfections generally prevent tracing for more than about 0.5 cm. Many varves can be traced over the intersection of  $(210)$  with  $(\bar{2}10)$  along the centerline of some crystals, and irregularities in the varve sequence can be correlated between the two sides, but exact correlation is not possible with existing material (Fig. 1). The ratio of the thickness of the light to dark parts of any given varve varies from 1:1 to perhaps 4:1, but as seen in Figures 2A, 2B, and 2D, the edges of the individual bands are gradational and

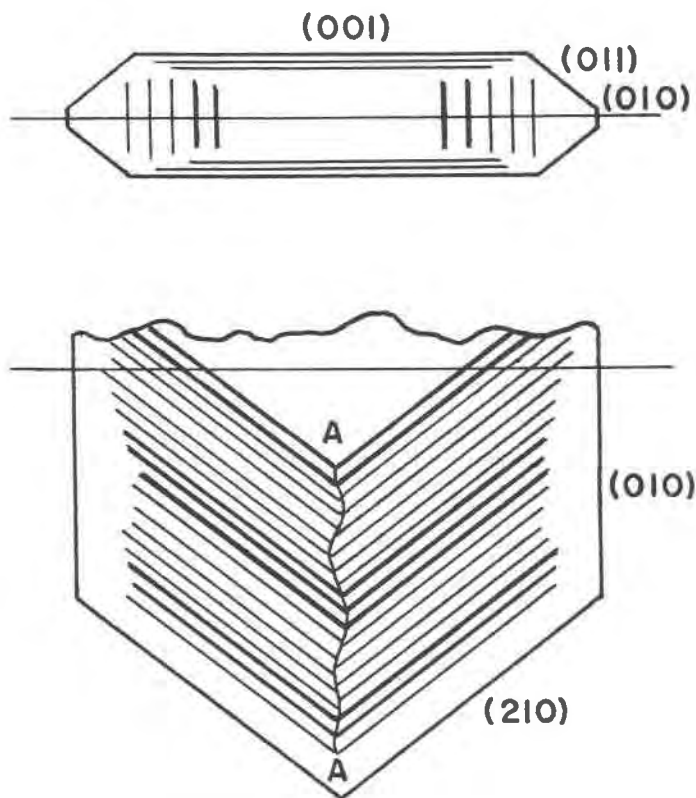


FIG. 1. Sketch showing orientation of varves in two sections cut from the same celestite crystal (diagrammatic). In each the plane of the other (perpendicular) section is shown by a line. The most prominent varves are parallel to  $\{210\}$ , viewed along  $c$  in sections cut perpendicular to  $c$  (lower fig.); in sections cut perpendicular to  $a$  (upper fig.) these varves are not perpendicular and hence visible only with difficulty. Some regular varves occur near and parallel to  $\{001\}$  (upper fig.). Viewing difficulties along the centerline (A-A) make exact correlation between the two sides difficult, and hence the total number of varves is not *known* to be identical, but irregularities in varve spacing or apparent darkness do correlate.

cannot be measured with precision. This ratio also appears to be nearly constant for large numbers of adjacent varves.

*Impurity content.* Variation in the number of submicroscopic inclusions of organic matter might be proposed to explain the apparent color of the darker bands, as considerable amounts of brown organic matter, including liquid hydrocarbon fluid inclusions, are found in the associated vug minerals at Clay Center, and as occasional inclusions in the celestite from

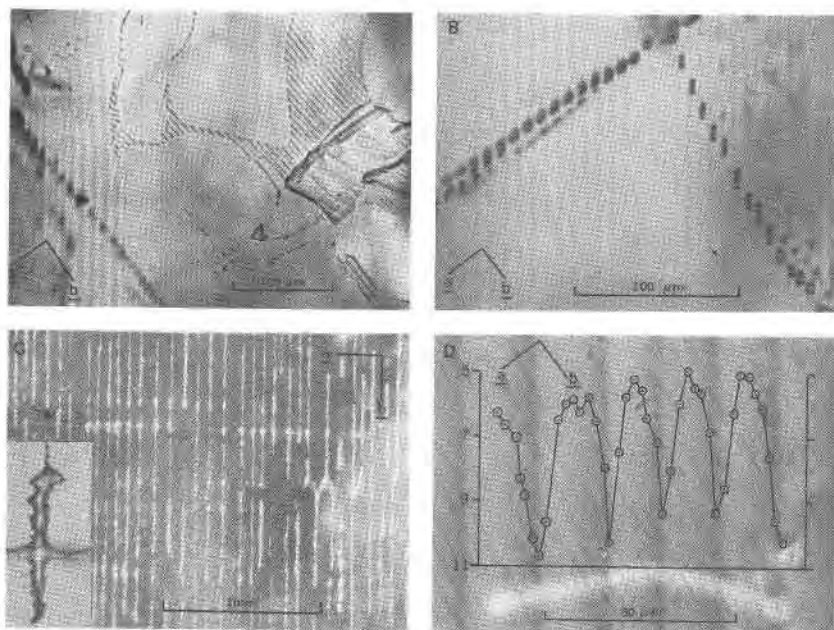


FIG. 2. Varved celestite crystals, viewed looking along  $c$ . Figures A, B, and D are of sample ER 65-72 from Clay Center, Ohio, are taken in transmitted, strongly collimated light, and are oriented so that varves parallel to  $\{210\}$  appear N-S, but C, of sample USNM R13950 from Monroe County, Michigan, has the  $b$  axis N-S (see indicated positions of crystal axes).

- A. Regular varves parallel to  $\{210\}$ , with intermediate, wide, and narrow spacings visible in sequence from left to right. In the upper right a thin flat fluid inclusion has fluted walls, which appear offset by a step near the top of the photograph.
- B. Two planes of secondary inclusions, formed by healing of fractures crossing the varves, reveal differences in solubility of the different parts of the individual varve.
- C. Recrystallization of a large fluid inclusion flattened parallel to  $\{001\}$  to yield regularly spaced jagged tubular inclusions elongated in the  $b$  direction, viewed here in diagonally incident light. These tubes are believed to be parallel to coarse, poorly-visible varves. The inset shows a magnified view of the area indicated by the arrow, taken in transmitted light.
- D. Plot of the count ratio  $\text{Sr } L\alpha/\text{Ba } L\alpha$  (raw data, uncorrected) made by electron microprobe at 39 spots arranged in  $2\text{-}\mu\text{m}$  steps along a curving traverse across four and a fraction varves, superimposed in correct register on a photomicrograph of the area analyzed. The traverse of the electron beam is shown by the light streak burned into the gray transparent carbon film at the bottom. The diagonal lines are polishing scratches. The crystal grew from left to right.

Scofield, Michigan. The uniformity of the "coloring" and the complete lack of any visible finely divided material in the celestite, even at high magnification, makes this explanation of the varves rather unlikely.

Most celestite crystals and, for that matter, many other minerals show striae parallel to crystal growth faces when viewed in well-collimated light, presumably due to differences in composition causing differences in the indices of refraction. The varves described here seem to be a result of the same phenomenon, but on a regular basis. The substitution of barium for as much as one-third of the strontium represents the major chemical variation found in natural celestite<sup>1</sup>, and should raise the indices of refraction appreciably (approximately 0.001 for each 7 mole percent BaSO<sub>4</sub>). To determine if barium might cause the observed varves, part of sample ER 65-72 was cut so that the polished surface actually intersected conspicuous varves spaced at about 17  $\mu\text{m}$ . Electron beam scanning images in Ba L $\alpha$  radiation were obtained from several parts of this sample through the courtesy of Edward J. Dwornik of the U. S. Geological Survey. These verified that the distribution of barium correlated perfectly with the varving. The broad lighter bands have perhaps twice as much barium as the intervening darker bands. As the boundaries between bands are gradational, the resultant index gradients cause the apparent brightening of the higher-barium, higher-index parts, just as in normal schlieren photography.

Electron microprobe analyses for strontium and barium were also made by Dwornik, with a 1 to 2- $\mu\text{m}$  spot at a series of 39, 2- $\mu\text{m}$  steps, on a traverse approximately perpendicular to the varves. These were made with an accelerating voltage of 20 kV., and a specimen current of 0.025  $\mu\text{A}$ , with 20 seconds counting at each step. A plot of the ratio of the simultaneous counts for Sr and Ba, which is a function of the Sr/Ba ratio, is superimposed on the photomicrograph of the analyzed varves in Figure 2D. The actual counts obtained were approximately 7000 for Sr and 1000 for Ba at each step. Similar results were obtained on a second traverse across other varves. Both the scanning images and the microprobe analyses show a tendency toward asymmetry in the varves in that the changes from earlier light (high-barium) bands to later dark (low-barium) bands tend to be less abrupt than the reverse. This correlates with a similar apparent asymmetry under the microscope (Fig. 2D).

For various reasons, any attempt to convert these raw count data directly to quantitative Ba analyses on such small features would be hazardous at best. An average Ba analysis across several varves was obtained, however, on an area centered on the microprobe traverse shown in Figure 2D. This value, using two different methods and including areas ranging from  $8 \times 10^3$  to  $9 \times 10^4 (\mu\text{m})^2$ , was  $1.3 \pm 0.2$  weight percent Ba, cor-

<sup>1</sup> These tubes act as a diffraction grating and produce a readily apparent but spurious finer "banding" from light interference at higher levels of focus that should not be confused with the actual varves.

responding to 2.2 percent  $\text{BaSO}_4$  or 0.0175 mole fraction  $\text{BaSO}_4$ . As the actual counts for Ba on the electron probe scan across individual varves shown on Figure 2D varied from about 700 to 1200 with position in the traverse, these maxima and minima probably correspond to approximately 0.013 to 0.022 mole fraction  $\text{BaSO}_4$ . A range of composition this small would be expected to change the index of refraction only about 0.0001, thus explaining the lack of measurable differences using ordinary immersion methods. Celestite crystals from similar localities in Maybee, Michigan (immediately north of Clay Center) show approximately 0.017 mole fraction  $\text{BaSO}_4$  on gross chemical analysis (Kraus and Hunt, 1906).

*Fluid inclusions.* One interesting aspect of the varves is the manner in which they affect the form taken by secondary fluid inclusions outlining healed fractures across the crystals. Quite obviously there are differences in the solubility of the celestite in this fluid, between the dark and light bands, as recrystallization along such fractures commonly has resulted in the trapping of a regular series of fluid inclusions, one (or a linear group) for each varve (Figures 2A and 2B). Observational problems make exact correlation difficult, but generally the inclusions seem to be located in and elongated parallel to the light (high-barium) bands. Thus they are elongated parallel to the intersection of (210) and (001).  $\text{BaSO}_4$  is far less soluble than  $\text{SrSO}_4$  in pure water, but the behavior on recrystallization would indicate that the solubility of the intermediate solid solution is higher than that of the purer celestite. Relatively large, very thin, flat inclusions commonly occur in celestite parallel to {001}. Where these occur in a varved area, the walls of the inclusions are frequently fluted with ridges that parallel the varves. Some such inclusions have changed shape through recrystallization to yield a regular series of tubular inclusions parallel to the varves (Fig. 2C)<sup>1</sup>. A few inclusions flattened parallel to {001} show a parallel ridging or fluting at about the same spacing as the varves in the surrounding crystal but strongly inclined to them (Fig. 2A). As the varves in the host crystal here are vertical, parallel to {210}, and as the fluted inclusion walls are nearly perpendicular to them, the inclination of the fluting is real and not just apparent. Presumably these fluid inclusions are in a thin part of crystal at a slightly different level, which grew on a crystal form other than {210}.

#### OTHER EXAMPLES OF REGULAR BANDING IN CRYSTALS

Many examples of regular banding have been reported in natural minerals, both in single crystals and aggregates, and it seems probable

<sup>1</sup> Miropolsky (1941) has shown that many relatively pure celestites contain more calcium than barium, but no analysis was made for calcium on the present samples.

that others will be found (e.g., Grigor'ev, 1965). Mackin and Coombs (1945) found that about 30 layers of carbonate were deposited on "cave pearls" formed in a mine opening in about 30 years, Mathews (1930) described lamina in carbonate oolites from Great Salt Lake, and there have been numerous studies of banding in the calcite crystals of stalactites (e.g., Fisher, 1934). A regular alternation of dark and light color bands has been found in "colloform" sphalerite from the near-surface portions of many zinc deposits (Roedder, 1968). Deicha (1966) has reported a similar banding, with lamina about  $10\mu\text{m}$  thick, in gypsum crystals from the Paris basin, and Poty (1968) described somewhat irregular "bandes de croissance" in quartz that are much thicker (about one millimeter per pair). A series of inclusion-rich zones have been reported in Permian salt by Dubinina (as quoted by Grigor'ev, 1965, p. 66).

Although the fluorite, calcite, and sphalerite crystals associated with celestite at Clay Center are obviously zoned, most showed no regular banding. Several fluorite crystals, however, from the Basic, Inc., quarry at Clay Center, (samples ER 65-69 and ER 68-20) showed faint traces of regular banding with a spacing of 8-30  $\mu\text{m}$ .

A regular banding very similar in scale and appearance to that in the celestite was reported in synthetic crystals of ADP (ammonium dihydrogen phosphate) containing significant amounts of arsenate substituting for the phosphate ion (Zapffe and Worden, 1949). Regular bands form during spherulitic crystallization of some substances under the microscope, and during the growth of many synthetic crystals, particularly metals (Laudise, 1967; Utech and Flemings, 1967).

Regular banding is common in agate, many samples of which have regularly alternating bands differing in color or grain size. Under the microscope many others show a very fine banding, presumably due to variations in index of refraction along the length of the individual crystals. More rarely this fine banding is so regular that it acts as a diffraction grating in transmitted light; this constitutes the "iris agate" studied by Brewster (1843) and more recently redescribed by Jones (1952). Brewster reported as many as 17,000 darker bands per inch ( $1.5\mu\text{m}$  per band) and a specimen in the author's collection (locality unknown) has regular dark bands at a spacing of about  $0.9\mu\text{m}$  per pair (28,000 pairs per inch). Similar banding at  $2.24\mu\text{m}$  per pair has been reported in irisopal (Sinkankas, 1966). Actually "iris agate" may have three different types of banding superimposed. In addition to the regular, fine banding, many samples have a parallel and plainly evident, regular banding at a spacing that is larger by one or two orders of magnitude. And between crossed polarizers, these agates may show a very jagged series of extinction bands of irregular width that follow the other bands in a crude way, but do not match either in spacing.



## PROPOSED MECHANISMS FOR ORIGIN OF BANDING IN CRYSTALS

Many different mechanisms have been proposed to explain regular banding in crystals and crystal aggregates, and although any given mechanism might be shown to be the cause in a specific example, other mechanisms may well be responsible elsewhere. Some of the more explicitly-stated mechanisms are as follows:

*Periodic convection currents.* A large body of literature on crystal growth reveals that many synthetic crystals are compositionally striated (*e.g.*, Laudise, 1967). Wilcox and Fulmer (1965) show that these striae are caused by fluctuations in temperature at the growing face, from irregular convective flow. In general, the appearance of striae correlates with high growth rates, whether they be from large concentration gradients or large temperature gradients (Brice, 1965; Utech and Flemings, 1967). Hurle (1967) has shown that regular temperature oscillations with a period of several seconds can occur in liquid metals when there is a coupling of conducted and convected heat flow, yielding compositionally striated crystals; strong magnetic fields during crystallization can eliminate the striae by increasing the viscosity.

The convection mechanism is thought to be inapplicable to the natural mineral banding because of the difficulty in setting up a geologically reasonable model that will yield the high heat flow necessary to maintain the rapid convection. A hydrologic system in which a continuous supply of low density liquid is maintained under a higher density liquid theoretically could provide such a model, but the temperatures and salinities of the fluids responsible for depositing the celestite and sphalerite are believed to have been such that the depositing fluid density would have been greater than that of the overlying (fresh) groundwater.

*Spontaneous rhythmic crystallization.* In this there is a buildup of impurities and/or heat at the interface of the rapidly-growing crystal and fluid. This causes a change in the growth rate and the nature of the material precipitated. Diffusion carries away the heat or impurities and permits renewed nucleation and/or fast growth to repeat the cycle. When diffusion to the crystal interface is from a supercooled fluid, instability can develop and yield a striated crystal (Jackson, 1967). Here also it is difficult to construct a geologically valid model, as the mechanism requires growth rates of the same order as diffusion rates. Combined with the low solubility of  $\text{SrSO}_4$  (Blount and Dickson (1968), this would require unreasonably large flow rates through the vugs.

“*Micelle layer*” *crystal growth.* Zapffe and Worden (1949) attribute the

the banding in their ADP crystal to the entry of different amounts of arsenate into the interior and exterior parts of the "micelles" or "micelle layers" by which they assume this crystal grew (Zapffe, 1950). Growth of reasonably perfect crystals of pure compounds requires very uniform conditions, as even slight irregularities in conditions may cause a veil or cause growth irregularity for each such change. It is even more difficult to grow uniform crystals of solid solutions, as the composition of the material being deposited changes, in general, with the conditions of deposition, and in particular with the temperature. No statements are made by Zapffe and Worden as to the growth rates or techniques used for the solid solution crystals they studied. However, if it is assumed that the growth rates were on the order of 3 mm/day, as is commonly used for growth of ADP crystals, the widths of the bands they illustrate would correspond to depositional periodicities of a few minutes duration and hence could possibly result simply from laboratory thermal regulator action during growth. In fact it would be difficult to prevent such effects.

*Twisted crystal fibers.* Frondel (1962, p. 203) indicates that the extinction bands in agate may be the result of periodic group extinction of the parallel helically twisted quartz crystal fibers composing it, and suggests that this twisting may be involved in causing the fine, light-diffracting banding. However, it should be noted that the extinction banding is not only much more irregular, but occurs at a spacing that is generally one or two orders of magnitude larger than the fine banding.

*Liesegang rhythmic precipitation (Hedges, 1932).* This mechanism involves diffusion plus periodic supersaturation and precipitation in gels, and can produce exceedingly regular patterns, although not in single crystals. It has frequently been proposed to explain color banding in natural sphalerites and agate, but many of the features exhibited by such materials, particularly in thin doubly-polished plates under the microscope, preclude its operation in these examples (Roedder, 1968, p. 466).

*Crystal spiral dislocation growth steps.* The very uniform spacing of the varves and their obvious relationship to the crystal growth habit might suggest formation by some sort of spiral (and hence repetitive) crystal growth mechanism. The thickness of the varves is so much greater, however, than the step height of even the large steps from spiral growth, as occur in SiC and CdI, (Gilman, 1963), that such a mechanism appears unlikely. In addition, such an origin would not ordinarily lead to bands that cross over one crystal face to another.

*Earth tides.* The kneading action of earth tides is known to cause periodic movements of the water level in wells on a 12-hour cycle (White, 1968), and hence should cause a reciprocating movement of the water flowing through porous rock systems, but it is difficult to visualize a mechanism whereby this reciprocating motion could result in the deposition of celestite having uniformly varying barium contents. Furthermore, if two varves form each day by this mechanism, extrapolation from the thickness of the individual varves would indicate deposition of the largest celestite crystal in about 13 years. Although this is not impossible, it does not agree with normal (uniformitarian) geological prejudices about the slow processes of diagenesis.

*Annual periodicity in crystallization conditions.* Many long-continuing geological processes occurring near the surface of the earth are influenced by the changing seasons, and in fact it is difficult to propose a model for any near-surface hydrologic process that would not reflect periodic annual changes, if continuous monitoring were possible. Fortunately, slow-growing crystals such as celestite, sphalerite, and possibly even agate, provide such continuous monitors. In view of the apparent inadequacy of all other mechanisms to explain the periodicity in these crystals, and the ease with which annual periodicity seems to fit the various facts, as detailed beyond, it is accepted by the writer as the best explanation.

#### POSSIBLE GEOLOGIC SIGNIFICANCE OF ANNUAL PERIODICITY

The Paleozoic dolomites and limestones in which the celestite crystals occur have probably never been deeply buried. It is not known at what stage or stages in their history the vugs were formed and the celestite grew. As the enclosing strata are relatively flat-lying and the region involved has been of low relief topographically since the Paleozoic, the former circulation patterns for interstratal brines and meteoric waters can only be guessed. The region is on the Findlay arch, and Howard (1959) suggests that extensive leaching occurred during emergence at the close of the Niagaran epoch.

Although the celestite crystals probably formed at some depth in an otherwise very static environment, a rather obvious source of periodicity in conditions would entail variations in the composition of the depositing fluid from mixing with surface water. Even under the laminar flow conditions expected with these slow movements, considerable mixing can occur and will be followed by further mixing through diffusion. It is not unlikely that mixing of waters itself could cause the precipitation, if oxidized, sulfate-bearing surface water mixed with strontium- and bar-

ium-bearing interstratal chloride brines. Such brines are rather common (White, 1965). The thickness of the overlying beds was probably more than adequate to level out all annual temperature differences, but seasonal variations in composition or amount at the point of inflow can be expected to cause periodic changes in the water that could persist even at depth. Freezing data on fluid inclusions in specimen 94965 from Bascom, Ohio, indicate the liquid to be approximately 2-molar in NaCl equivalent, and homogenization temperatures for the relatively few inclusions that did not leak were in the range 68–114°C. Similar studies of fluid inclusions in fluorite from Clay Center reveal that it also formed from moderately hot fluids, but with considerably higher salinities (approximately 4–5 molar NaCl equivalent concentration). These data would require that only moderate to small amounts of diluting surface water were involved.

The specific mechanism for such periodicity to cause banding in the celestite is obscure. Although the solubility of celestite in water increases greatly with decreasing temperature (Strübel, 1962, as quoted by Holland, 1967), making precipitation on mixing with presumably cooler surface water unlikely, there is a much larger and opposite effect with decreasing salinity. Lucchesi and Whitney (1962) show a sevenfold decrease in isothermal solubility of celestite from that in 3 *N* NaCl solution to that in pure water, and Strübel (1966) shows a tenfold decrease from that in 2 *N* NaCl solution to that in pure water. Templeton (1960) reports a thirteenfold decrease in solubility for BaSO<sub>4</sub> under a similar change in conditions, so it is possible that the degree of dilution alone could cause significant variations in the Sr/Ba ratio of the deposited material. It is hazardous to extrapolate from simple systems into complex natural brines, particularly with strongly non-ideal solid solutions, but extensive studies on the distribution coefficient for Sr between solution and precipitated BaSO<sub>4</sub> (Gordon and others, 1954; Cohen and Gordon, 1961; Starke, 1964; Hanor, 1968) have shown that although the coefficient varies little with Ba/Sr ratio, it does vary with temperature and other factors.

If it is assumed that the celestite banding is annual and is representative of the growth rate for the whole crystal, approximately 10,000 years would be required for the growth of the 10-cm crystal from Clay Center. Only very low flow rates are required for such growth rates. The SrSO<sub>4</sub> solubility data of Blount and Dickson (1968) would indicate that as little as one liter of fluid per year moving through the vug could have formed this one crystal. An additional factor in favor of growth rates in this range, as opposed to the much faster growth rates described for the mechanisms involving periodic convection currents or rhythmic crystal-

lization (approximately  $10^7$  times faster), is the large size and high degree of perfection of crystals of a relatively insoluble material such as celestite.

A similar mixing of brines and fresh surface waters has been proposed as the cause of the varves in sphalerite (Roedder, 1968), although there the actual chemical nature of the very prominent color variations that constitute the varves is uncertain (Roedder and Dwornik, 1968). As the layers in ordinary agate seem to vary in crystal size and water content, and as there is no evidence of saline brines being involved, this banding may be merely a reflection of a periodically varying rate of deposition, presumably also related to annual variations in surface water flow. Whether the same explanation also holds for the much finer and more regular bands in "iris agate" is not at all certain at this time.

The present examples of varving in celestite and sphalerite are too isolated in occurrence to be of much direct use, and are presented here mainly to encourage further studies. Attempts should be made to correlate irregularities in varve sequence from one crystal to another of the same or different size in a given vug, and from one vug to another (Poty, 1968). Such correlations were not possible with the available material. The lack of evidence of varves in most of the codeposited, smaller celestite and other crystals examined here may be merely a result of their equivalent varves being too thin to be visible with the light microscope.

Similar growth banding in response to annual changes in conditions should occur in many minerals formed near the surface of the earth, but will be most obvious in those that form slowly, so that many varves are present in a single sample. Thus varves might be expected in sedimentary hopper halite crystals, and these do have alternately inclusion-rich and inclusion-free growth bands, but most individual hopper halite crystals have only a few bands and hence may have formed in a short time. Such inclusion zones in Permian salt have been attributed to seasonal changes (Dubinina, as quoted by Grigor'ev, 1965, p. 66). A very low rate of self-diffusion is also necessary to preserve such fine structures; Hanor (1968) has shown from precipitation kinetics that this is true for the celestite-barite series. Varves also should be most readily detected in minerals such as celestite that commonly have a variable composition and hence variable index of refraction, but the use of phase contrast or Nomarski interference contrast microscopy may detect much smaller changes in index of other minerals. In addition laboratory etching studies (possibly combined with electron microscopy) might reveal varves in minerals that have negligible variation in index or that have grown even more slowly.

If similar growth features can be found at more localities, particularly in minerals more common than celestite and sphalerite, and their annual

nature can be verified, they will prove to be of considerable use in the solution of geologic problems such as the hydraulic regimen during diagenesis and the rates of such processes in nature.

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